VERTICALLY ALIGNED CARBON NANOTUBE ARRAYS ASSEMBLED ON GLASSY CARBON ELECTRODE

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ABSTRACT: Carbon nanotubes have been widely utilized in electrode modification for their fascinating electrochemical catalytic properties. Given that the tube ends are the reactive sites of carbon nanotubes, modifying electrode with up-right carbon nanotubes is particularly desired. However so far, the well-organized standing carbon nanotubes on carbon electrode can only be realized by in situ nanotube growth which is very complicated and hard to manage. Herein, we present a new strategy to modify carbon electrode surface with vertically aligned carbon nanotubes. The single –walled carbon nanotubes were first chemically oxidized and carboxyl-derivatized at the open ends. The underlying glassy carbon electrode was introduced with nitrophenyl group via the chemical reduction of the corresponding nitrobenzenediazonium tetrafluoroborate salt.Then aminophenyl groups on electrode were obtained by reduction of nitrophenyl group in alkaline iron ammonium sulfate solution. Finally the nanotubes were attached through acylation-amidation. X-ray photoelectron spectroscopy and cyclic voltammetry were employed to characterize the two reduction reactions. Tapping mode atomic force microscopy (AFM) images clearly show that nanotubes have been successfully vertically organized on the glassy carbon electrode surface. Electrochemical behavior of glucose oxidase on the assembled electrode was measured to test the electrode performance.

INTRODUCTION

Bioelectrochemistry is a new interdisciplinary field, which combines biotechnology with electrochemical science and focuses on the structural organization and the electron transfer functions of biointerfaces (Chen, Wang et al. 2007). Among the bioelectrochemical systems, biofuel cells are gaining more and more attention. The bioelectrochemical systems such as microbial fuel cell (MFC) and microbial electrolysis cell (Mele, Cardos et al. 1979; Murphy 2006) are of fundamental interest in view of their potentials in energy generation. To scale up the devices towards actual industrial application, particular emphasis is directed to the exploration of bioelectrochemical design of electrode interface, especially to those where direct electron transfer can be obtained on electrode surface, this is rather critical for the performance of entire system(Sun, Zhao et al. 2010).

In this respect, carbon nanotubes (CNTs) have came into spotlight, because CNTs have the characteristics of high surface-to-volume ratio, high mechanical strength, ultra-light weight, rich electronic properties, and excellent chemical and thermal stability. Recent studies demonstrated that CNTs can enhance the electrochemical reactivity and the electron transfer rates of biomolecules, accumulate important biomolecules, and alleviate surface fouling effects (Guiseppi-Elie, Lei et al. 2002; Lim, Cirigliano et al. 2007; Rivas, Rubianes et al. 2007). To take advantage of these remarkable properties of CNTs in bioelectrochemical applications, the CNTs need to be properly functionalized and immobilized.

In addition, Studies have demonstrated that the vertical alignment of CNTs on electrode surface is in favor of the direct electron transfer between enzyme/bacteria and electrode(Liu, Chou et al. 2005; Gooding, Chou et al. 2007). However, how to stably manufacture CNT based nanostructures with appropriate volume and orientation control to realize efficient transport of electrons, and to successfully apply them to practical application are still deemed of critical importance.

Given that the tube ends are the reactive sites of carbon nanotubes, and taking into consideration of the extraordinary electrical conductivity in the direction along the tube axis, modifying electrode

with up-right carbon nanotubes is particularly desired. So far, the well-organized standing carbon nanotube on carbon electrode has only been realized by in situ nanotube growth which is very complicated and hard to manage. Several other methods for general vertical alignment of CNTs were also used, for example, by using magnetic fields (Tian, Park et al. 2009), but the strict manufactural conditions have confined their applications and made them not suitable for large quantity production or modification.

Except in-situ growth, another way to control orientation of CNTs is mostly conducted by Au-S bond on gold electrode surface (Gooding, Wibowo et al. 2003), which restrict the rang of underlying electrode material. Carbon is an attractive bio-benign electrode material and would be an suitable choice for undelying electrode. Modifying carbon electrode surface in a way that allows efficient electron transfer between the electrode and the redox protein or bacteria is of great importance in the development of enzyme biofuel and microbial fuel cell. So we present another free-radical reaction based modification strategy, which can be also applied to carbon electrode surface and will support large quantities of manufacture.

MATERIALS AND METHODS

Chemicals. SWCNTs (Shenzhen Nanotech Port Co. Ltd., China) were purified and functionalized through a well-established way with slight modification. It is worth noting that the SWCNTs thus prepared were functionalized with carboxyl groups and could be dispersed in both water and dimethylformamide(DMF). 4-nitrobenzenediazonium tetrafluoroborate and N,N'-dicyclohexylcarbodiimide (DCC) were from J&K，All other reagents were purchased from Sinopharm Chemical Reagent, Beijing Co. Ltd. (Beijing, China), and were of highest grade available and used without further purification.

Instruments. X-ray photoelectron spectroscopy (XPS) measurements were performed on an AXIS-Ultra electron spectrometer from Kratos Analytical. The data were taken using monochromatic Al Ka radiation (225W, 15 Ma, 15 kV) and to compensate for surface charge effects, binding energies were calibrated using C 1s hydrocarbon peak at 284.80 eV. The film topography was observed by tapping mode atomic force microscopy (AFM) imaging in respect to CNT structure and orientation.

Oxidation of Carbon Nanotube. Following a reported procedure (Sun, Zhao et al. 2010), the as-received SWCNTs (95%, 10–20nmdiameters) were purified and oxidized prior to use. Firstly the SWCNT oxidation procedure was as follows. First, the SWCNTs were sonicated in a mixture of H2SO4–HNO3 (volume ratio: 3:1) for 4 h, neutralized with a large amount of ultrapure water, filtered with a Millipore membrane (pore size 0.22 lm), and finally dried at 60 oC overnight. The ultrapure water was obtained from a Millipore-MilliQ system with a resistivity of 18M cm. The carboxylated and shortened SWCNTs were prepared and could be well-dispersed in water after ultrasonication for extended periods of time.

Introduction of amino groups onto electrode surface. Glassy carbon (GC) plates were used as substrate electrode. Prior to surface modification, the GC electrode was polished carefully to a mirror with alumina slurries and then washed ultrasonically in distilled water and ethanol for a few minutes, respectively. The 4-nitrophenyl groups were introduced by using the chemically activated one-electron reduction of the corresponding 4-nitrobenzenediazonium salt. The hypophosphorous acid (50% v/v aqueous solution). First, the GC plates were immersed into 10ml 50 mM aqueous solution of 4-nitrobenzenediazonium tetrafluoroborate at 5 ^{o}C, 20 ^{o}C and heated to 40 ^{o}C; then 20ml of hypophosphorous acid was slowly added and stayed for 60min. The resulting 4-nitrophenyl modified carbon electrode was washed with acetonitrile, acetone and water to remove any unreacted species. Next, the GC electrode with 4-nitrophenyl group was reduced in 25ml of 10 mM aqueous ferrous ammonium sulfate solution, and 20ml of 2N alcoholic sodium hydroxide solution was added. The resulting 4-aminophenyl GC electrode was then immersed in hydrochloric acid (37%) to remove any Fe(III) precipitates.

The vertical alignment of CNTs on GC

electrode. The shortened SWNT was dispersed in dimethylformamide (DMF) to form a well dispersed solution of 0.1mg/ml SWNTs, together with 0.5 mg/ml dicyclohexyl carbodiimide (DCC) to convert the carboxyl groups at the ends of the shortened SWNT into active carbodiimide esters. The 4-aminophenyl group modified GC electrode was placed in the nanotube solution for 24 hours to allow the amines at the electrode surface formed amide bonds with the end of the CNT tubes.

RESULTS AND DISCUSSION

It is known that the poor solubility of CNTs in most solvents has been standing in the way of facile fabrication of homogeneous and stable CNTs film or composite layer. Versatile modification approaches have been employed for this issue; including most commonly used the covalent attachment of chemical groups through reactions onto the Π-conjugated skeleton of CNT, and the non-covalent adsorption or wrapping of various functional molecules like cationic /anionic surfactant attachment. Here, in order to protect the electron structure of CNTs to the utmost extent, the concentrated acid oxidation procedure has been taken to add the negative charge carboxylic groups to CNTs to make them disperse stably and homogeneously in solution, and simultaneously remove metal catalyst and amorphous carbon left from synthesis process.

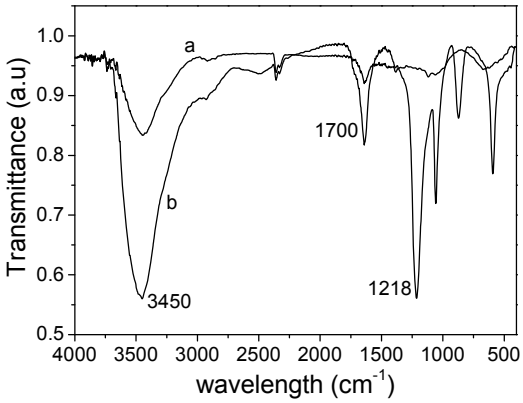

Figure 1. the Mid-IR spectrum of CNTs before and after oxidation.

CNTs were pretreated with mixed acid following the described procedure. After the oxidation process the CNTs were slightly shortened, which makes it easier for the abundantly negative charged CNTs to stay uniformly dispersed in aqueous suspension for a long period of time (more than 2 weeks). The mid-IR spectrum of primary SWCNTs and oxidized SWCNTs are displayed in Fig. 2. For the concentrated acid-treated CNTs, an absorption peak at 1218 cm^{-1} is observed and can be ascribed to the stretching vibration of C-OH. In addition, two drastically enhanced absorption peaks at 3454 cm^{-1} and 1708 cm^{-1} are clearly displayed, which are typically attributed to the O-H stretching vibration and C=O carbonyl vibrations of carboxylic and carboxylate groups respectively, indicating a successful introduction of –COOH to the end or sidewalls of the SWCNTs.

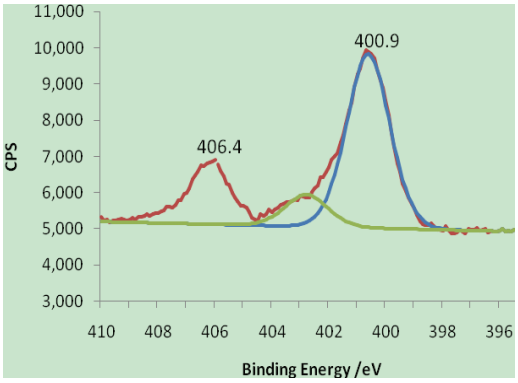

Figure 2. the N1s region of XPS results for 4-aminophenyl group modified GC electrode surface.

To confirm the introduction of amino groups onto GC surface and successful reduction of nitrophenyl groups, XPS was performed on the 4-aminophenyl group modified GC electrode surface. As shown in Figure 3, the major peak exhibited at 400.9 eV was ascribed to aniline (398.3–403.5 eV) which demonstrated the presence of amino group. However the peak is observed at 406.4eV corresponding to a nitrogen atom in an aromatic nitro group (N1s emission for nitrobenzene itself is 405.9 eV)(Masheter, Wildgoose et al. 2007), implying a not complete reduction of nitro groups. The ratio of peak areas indicates that the conversion of nitro to amino groups using ferrous hydroxide is ca. 64%.

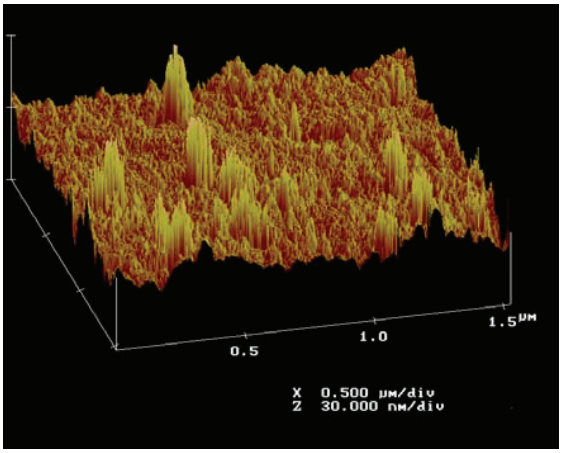

Figure 3. the AFM images of vertically aligned SWCNTs on GC electrode surface.

The result of shortened SWNT aligned normal to the electrode surface was shown in Figure 4. The AFM image clearly shows that the tubes assemble on the surface were in bundles and with different length, which is in accord to other research result(Gooding, Wibowo et al. 2003), and may be caused by the aggregation tendency of SWCNT and would be alleviated by shortening the reaction time.

CONCLUSIONS

In summary, with the proposed process, we have shown that shortened SWNTs can be aligned normal to carbon electrode by self-assembly.

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