

A Novel Carbon Nanotube Structure Formed in Ultra-Long Nanochannels of Anodic Aluminum Oxide Templates

J. Y. Miao, Y. Cai, Y. F. Chan, P. Sheng, and N. Wang*

Department of Physics and Institute of Nano Science and Technology, Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China

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We report the fabrication of a novel carbon structure consisting of uniform carbon nanotubes formed in the nanochannels of anodic aluminum oxide (AAO) templates, with the surface side open and connected by a uniform carbon sheet. The uniformity of the fabricated CNT arrays, plus the carbon film on the AAO surface interconnecting the open ends of all CNTs, constitute the major characteristics unique to our carbon structures. Some potential applications of such structures are noted.

Introduction

Carbon nanotubes (CNTs)¹ with controlled diameters and alignment are generally fabricated using mesoporous templates by chemical vapor deposition (CVD).^{2–4} The importance of CNTs' alignment and size distribution in various potential applications has propelled extensive research on CNT synthesis via different techniques.^{5–9} Anodic porous aluminum oxide (AAO) films (also known as anodic alumina membranes) are ideal templates for the synthesis of highly ordered nanostructures because they are thermally and chemically stable, with fully controllable pore sizes (hence the diameter of the nanostructures formed in the pores).^{5–11} It has been reported that, without using metal catalysts, uniform CNTs were formed in the AAO channels under certain experimental conditions of CVD.^{8,9,11} CNTs have also been synthesized through the carbonization of organic polymers¹⁰ filled in the AAO channels. The carbonization temperature is about 600–900 °C, and the nanotube quality was found to be sensitive to the polymer-filling process. In our previous paper,¹¹ we reported an effective method of preparing CNT arrays in AAO templates by bias-enhanced microwave plasma CVD (MWCVD) at a low temperature. The resultant CNTs were highly pure. However, the diameters of the CNTs grown in ultra-long nanochannels with close ends were generally not uniform, owing to fast carbon deposition near to the open ends of the nanochannels, leading to less carbon material reaching the close ends of the AAO channels.

In this work, we report a new approach to the preparation of uniform carbon nanotubes in AAO nanochannels at low temperatures. The CNTs are observed to have very uniform tube wall thickness along the entire length of the CNTs, up to 150 μm long and 20 nm in diameter. In addition, on the surface side the nanotubes are always open and connected by a surface carbon sheet, which grows on the surface of AAO closely. These properties of the as-synthesized CNTs are distinct from those grown in AAO by other CVD processes using ethylene, with or without metal catalysts.^{8,9,12} In particular, the deposition process of carbon source, e.g., ethylene (directly decomposed on the channel surfaces of AAO) is different from that used in the present work. According to our investigation, the vapor phase

of ethylene is unable to fully reach the close ends of the AAO channels if the channels have only one end open. Hence CNTs would not grow along the whole ultralong and ultrasmall AAO channels with close ends. Our method consists of two steps, in which the vapor of poly(ethylene glycol) is first diffused into the AAO nanochannels. Because of their affinity to the AAO surface, the poly(ethylene glycol) molecules are uniformly deposited on the inner walls of the nanochannels (as a wetting film). The molecules are subsequently molded through thermal annealing. Carbon nanotube structures containing the “Y” geometry were also observed. This rather unique feature of the connected CNTs is shown to offer advantages in applications.

Experimental Section

AAO templates containing large channels (about 60 nm in diameter) were prepared by anodic oxidation of pure aluminum plates in a 0.3 M oxalic acid electrolyte under a constant direct current (DC) voltage of 40 V at 17 °C. Smaller channels with diameters of about 20 nm were produced in a 1.2 M sulfuric acid under 15 V at 2 °C. The anodization period was 8–20 h, and the thickness of the resultant AAO templates was approximately 40–150 μm . Figure 1 schematically shows the experimental setup for CNT synthesis. The AAO–Al template (AAO on Al substrate) was placed face down in a quartz tube heated by a tube furnace. Poly(ethylene glycol) 200 (or 4000, resulting the same CNTs) in a vessel beneath the AAO–Al plate provides the main carbon source. Ar flowed through the quartz tube at 500 sccm during the preheating stage. When the temperature of the furnace reached 600 °C, the flow rate of Ar was decreased to 100 sccm and maintained for 30 min. The as-synthesized CNTs/AAO–Al plate was dipped into the solution of CuCl_2/HCl to remove the Al substrate. For visualization, the AAO template was then dissolved in the solution of H_3PO_4 (6%) at 60 °C for 12 h. Black flakes of pure carbon nanotube structures were obtained. Structural characterization was carried out in a Philips XL30 scanning electron microscope (SEM) and a JEOL 2011 transmission electron microscope (TEM) operating at 200 kV. The analysis of thermally evolved gases from poly(ethylene glycol) was carried out using a Hewlett Packard pyrolysis-mass spectrometry (PYRO-MS) and a Netzsch thermogravimetric analyzer (TG-209) coupled with a Bruker VICTOR-22 Fourier transform infrared spectrometer.

* To whom correspondence should be addressed. Fax: 852-23587489. Email: phwang@ust.hk.

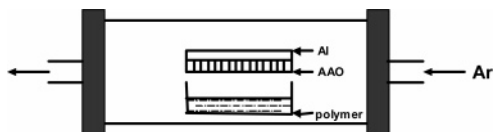


Figure 1. Experimental setup for the synthesis of CNTs in the nanochannels of AAO templates.

Results and Discussion

Figure 2a is a SEM image (topview) showing the interconnected open ends of CNTs protruding from the surface of the AAO template partially dissolved by an acid. The insert is the typical morphology of the CNT arrays viewed along the sideways (the AAO template has been dissolved). The CNTs consist of pure carbon as determined by X-ray energy dispersive spectroscopy (EDS). Parts b and c of Figure 2 are TEM images showing the open and close ends of the CNTs, respectively. The close ends of the CNTs and their uniform wall thicknesses are evident. It is clear that the CNT arrays grew only in the template and that the length of the CNTs are limited by the thickness of the template. Figure 2d (a TEM image) shows an enlarged section of the open ends of the carbon structure. A rather remarkable feature—a thin carbon film linking the open ends of the CNTs—is clearly evident. The thickness of this film is equal to the CNT walls. We have examined a number of CNTs from one end to the other and found that the thickness of the tube walls was extremely uniform. This can be clearly seen at the close ends of the CNTs shown in Figure 2c, in which all CNTs have caps (close ends). The thickness of the tube walls at the caps is almost identical to that at the open ends. The formation of the caps was due to the blocked ends of the nanochannels formed at the final stage of anodization at the interface between AAO and Al substrate.

The CNTs fabricated at 600 °C contained a high density of defects. However, the defect density was largely reduced after annealing the CNTs at 1300 °C as shown in the high-resolution TEM (HRTEM) image (inset to Figure 2c). The electron diffraction pattern taken from the CNT indicated that the fringes in this image were from graphite-layered structure with an interplane spacing of 0.34 nm.

We have systematically investigated the interface structure between the CNTs and the AAO template by cross sectioning the CNTs/AAO film. We found that the CNTs simply replicated the nanochannel shapes even when the channels have a complicated morphology, such as “Y”-shaped nanochannels¹³ made in the AAO template. The “Y”-shaped channels were produced by first synthesizing 60-nm channels and then changing the experimental condition to that used for synthesizing 20-nm channels. By use of the same thermal evaporation process, CNTs with “Y” structure were obtained. Figure 2e shows a typical “Y” shaped CNT, in which both the thick tubes (about 60 nm) and thin tubes (about 20 nm) have a similar thickness of tube walls. Obviously, the deposition of carbon layer in the nanochannels with different diameters was uniform. In all the figures the uniformity in size and wall thickness is clear. The formation of uniform carbon wall thickness in the present approach is highly unusual, in contrast to conventional techniques such as CVD or thermal pyrolysis of hydrocarbons or other polymers in references. Usually it is difficult to obtain CNTs with a uniform thickness of tube walls in the ultra-long nanochannels (with close ends) in AAO templates.^{10,11} For the present experiment, the wall thickness of the CNTs formed in AAO can be controlled by changing the quantity of the polymer carbon source and the heating rate of carbonization ap-

propriately. In our previous studies,¹¹ we have shown that carbon atoms in the form of graphite deposited layer-by-layer on the inner walls of AAO nanochannels by MWCVD. We believe that the microwave plasma and the special surface state of AAO enhance the graphite deposition in the channels. Since the temperature generated by plasma on the top surface was higher than that at the inside of the channels, simultaneous with the high concentration of highly reactive hydrogen atoms (generated by the plasma), the deposition of carbon at the top surface was highly retarded. This enabled the channels to stay open and the carbon deposition in the deep channels to continue. However, when the CNT walls became thick, abnormal growth of tube walls was initiated in the channels near the top surface, where the inner diameter of CNT became small. This resulted in the blocking of the channels. When the CNTs were blocked at the top ends, further growth of CNT walls in the channels was limited. Therefore, the thickness of the CNT walls was not uniform along the length of CNTs. Similar CNT growth phenomenon has also been observed in AAO channels (30–40 nm in diameter).¹⁰ For thermal CVD, carbon sources such as CH₄ or C₂H₂ can deposit in the nanochannels of AAO. However, the channels have to be opened on both sides of the AAO template in order to obtain continuous CNTs.

The evaporation process of poly(ethylene glycol) (the carbon source for the CNT growth) was analyzed using the TG-FTIR and PYRO-MS methods. Poly(ethylene glycol) (12.56 mg) was heated in nitrogen at 10 °C/min in the temperature range of 23–723 °C. We observed weight loss starting from 160 to 320 °C. FTIR spectra showed the peaks of hydroxyl group in this temperature range. The mass spectra of the pyrolyzed poly(ethylene glycol) were obtained at 170, 220, and 315 °C by gas chromatography combined with mass spectrometry (GC/MS) in nitrogen. The results are graphed in Figure 3, in which the various molecules (such as 1,2-ethanediol, diethylene glycol, triethylene glycol, ethanol, 2,2'-[oxybis(2,1-ethanediol)]bis-) were shown to successively evolve from the poly(ethylene glycol) in the order of their respective molecular weights. The peak from the biggest molecule (3,6,9,12-tetraoxahexadecan-1-ol) appeared only when the pyrolysis temperature was higher than 315 °C.

On the basis of our results, we propose a plausible model (shown schematically in Figure 4) for the formation of CNTs in the ultra-long AAO nanochannels, as well as the surface carbon sheet linking the open ends of the CNTs. The formation process may consist of the following steps. Low-temperature evaporation of poly(ethylene glycol) starting at 160 °C is the initial stage, by which the evaporated molecules penetrate the channels and deposit on all exposed AAO surfaces, forming the initial polymer layer. The thickness of this polymer layer may not be uniform initially since there should be more materials deposited near the open ends of the channels. In the medium-temperature annealing range of 320–500 °C, the enhanced diffusion (wetting of the AAO surface by the polymer film) homogenizes the deposited film. The reason the poly(ethylene glycol) molecules adhere to the AAO surface, and do not desorb from AAO even when the temperature was higher than 315 °C, is not precisely known at present. However, it is noted that the AAO surfaces are known to be charged,¹⁴ caused by the large numbers of oxygen vacancies. Most of the evaporated molecules from poly(ethylene glycol) are of the polar type. Hence, they should have a special affinity to the charged AAO surfaces, leading to the formation of uniform (wetting) polymer layer on the inner walls of the nanochannels, as well as on the top surface of the AAO template. The subsequent high-temperature car-

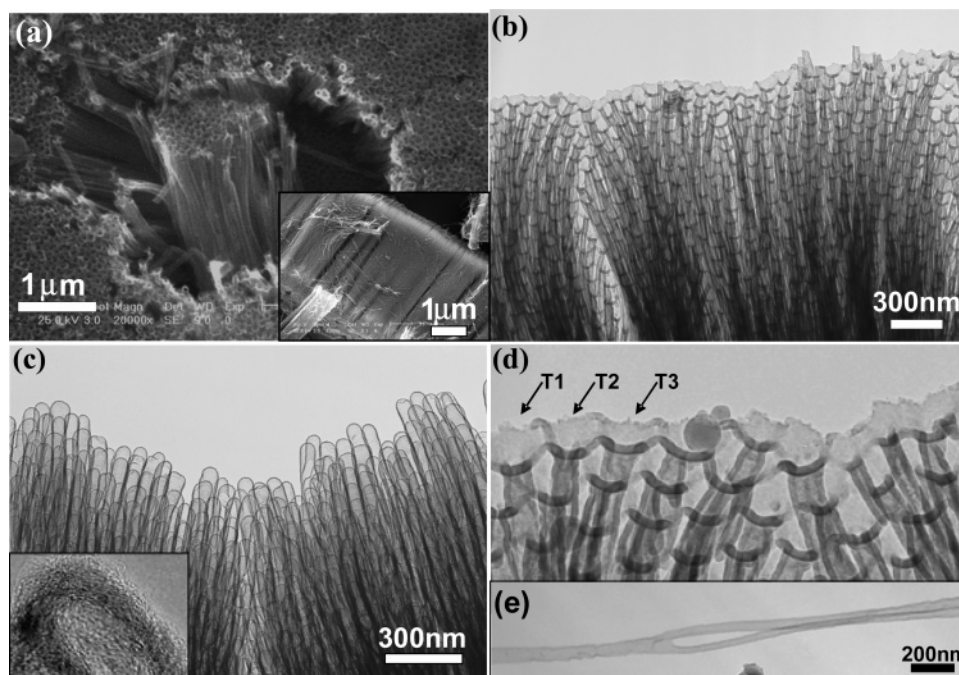


Figure 2. (a) SEM image (topview) showing the interconnected open ends of CNTs. The insert is a SEM micrograph (sideview) taken from CNT bundles extracted from the AAO template by chemical etching. (b) TEM image of the open (surface) side of the CNT bundle. (c) TEM image of the close (capped) side of the CNT bundle. The insert is a HRTEM image taken along the axis of the CNT. (d) The enlarged picture of the open side of the CNT array. The CNTs marked by T1, T2, and T3 are linked by the carbon film. (e) TEM image showing the Y structure formed by templating the AAO structure. Uniform thickness of the tube walls in all the images is to be noted.

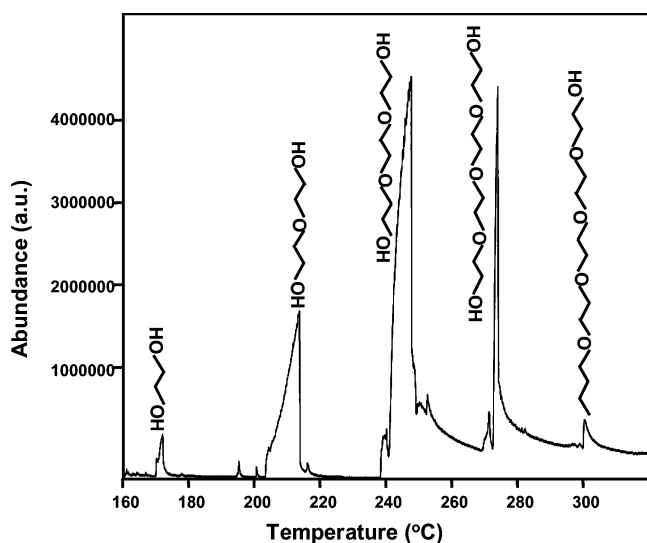


Figure 3. The molecular evolution of poly(ethylene glycol) plotted as a function of temperature.

bonization (above 500 °C) of the polymer layers leads to the formation of CNTs with uniform walls, with a surface carbon layer linking them together. Under our experimental condition, the AAO surfaces should be easily wetted by the molecules from poly(ethylene glycol). However, we have found that the AAO templates annealed at a high temperature (e.g., 1000 °C) in air became much more difficult to catalyze CNT growth using poly(ethylene glycol), presumably because they contain much less oxygen vacancies. This evidence provides additional support to our explanation.

Our method provides an effective way for growing or molding uniform carbon nanostructures using AAO templates. These CNT arrays are expected to exhibit properties that offer exciting possibilities for technological applications. For example, by removing the Al substrate of the AAO film and making the

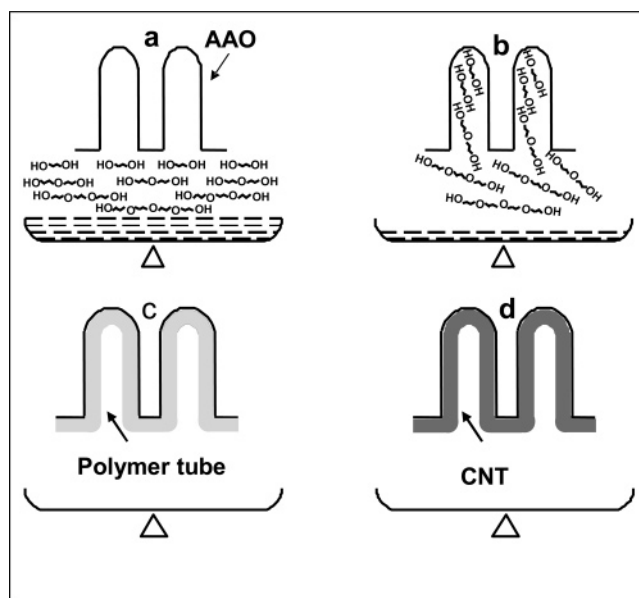


Figure 4. Schematic diagrams showing the formation process of CNTs in the AAO channels and a carbon sheet on the surface. (a) The initial evaporation of poly(ethylene glycol). The vapor lines the inner walls of the channels as well as the surface of the AAO. (b) Diffusion of the poly(ethylene glycol) molecules on AAO surfaces leads to the formation of polymer tubes with uniform tube thickness, as well as a thin polymer film on the AAO surface, shown in (c). (d) High-temperature carbonization leads to the formation of CNTs in the channels and a carbon sheet on the surface.

AAO nanochannels open on both surfaces, we have fabricated carbon structures that are open and connected on both ends, by using the same process as described above. For such a novel structure, air or solution can readily flow through the CNTs from one side of the CNT/AAO structure to the other. Such CNT arrays can be easily made into a device because all CNTs are already interconnected, and the resistance of the CNT array

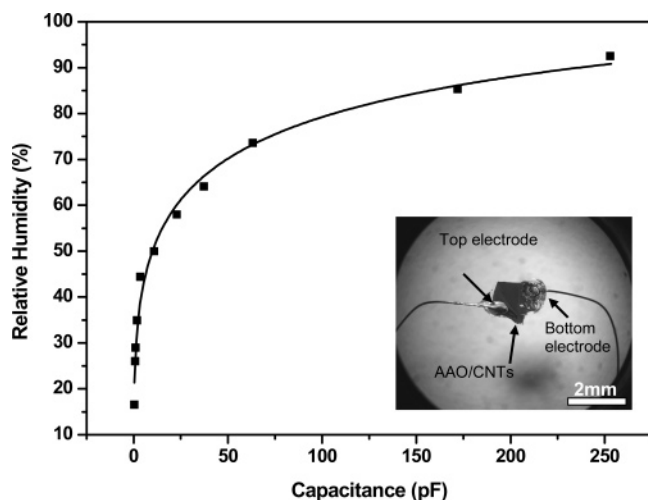


Figure 5. The relationship of the ambient relative humidity and the capacitance of the CNTs/AAO humidity sensor. (■) The experimental data were measured and calibrated independently by using different saturated aqueous salt baths. The solid line is the fitting curve described by eq 1. The inset shows a picture of the humidity sensor.

can be simply measured using the carbon films on the AAO surfaces as the electrodes.

We have verified that such simple devices display excellent electrical sensitivity to humidity or CO gas (depending on the concentration of carbon deposited) as well as to the pH values of solutions. As shown in Figure 5, the humidity sensor made from the interconnected CNTs/AAO exhibits the relationship between the ambient relative humidity and the capacitance of the sensor given by

$$H = P_1 + P_2 \exp\left(-\frac{C^{0.3}}{P_3}\right) \quad (1)$$

where H is the relative humidity expressed in percentage, C the capacitance in pF, and P_1 , P_2 , and P_3 are constants. The resistance of the sensor also displayed a similar behavior to the humidity. However, we found that the stability of the DC resistance was dependent on the concentration of carbon in the AAO channels. The capacitance of the sensor has a much more robust response vs a change in the humidity. This sensor can work at high ambient temperatures and demonstrates fast response to the humidity compared to the commercial ones made from porous Pt. Other than the humidity sensor, details on the fabrication of the AAO/CNT arrays for application as carbon monoxide sensors can be found elsewhere.¹⁵ It is also reasonable to conjecture that such CNT arrays may offer excellent

thermal conductivity (due to the strong carbon–carbon bonds and the surface carbon film linking the tubes), equal to or even better than that of the metal conductors. Work in this direction is actively being pursued at present.

In summary, we report the fabrication of a novel carbon structure consisting of uniform carbon nanotubes (up to 150 μm in length and 20 nm in diameter with one side close) formed in the nanochannels of AAO templates with the surface side open and connected by a uniform carbon sheet. These structures were prepared using the vapor phase of poly(ethylene glycol), in which the thermally evolved molecules were first uniformly deposited on the inner walls of the nanochannels due to their affinity with the AAO surface, and multiwalled CNTs with uniform tube wall thicknesses were subsequently molded during the carbonization process. The conductive and uniform surface carbon sheet linking the CNTs and the uniformity of the fabricated CNT arrays constitute major advantages for technological applications in comparison to other competing CNT fabrication methods involving the AAO templates.

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References and Notes

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