1036 *Chem. Mater.* **2006,** *18,* 1036−1040

Template Synthesis of Water-Dispersible Carbon Nano "Test Tubes" without Any Post-treatment

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Received September 22, 2005. Revised Manuscript Received December 5, 2005

Water-dispersible and uniform tubular nanocarbons with a diameter of about 10 nm were synthesized by the template method without any additional treatment after the synthesis. Since one end of each tubular nanocarbon is always open but another end is closed, the nanocarbons look like a "test tube". It was found that the present test tubes with a length not exceeding 5 μm were dispersible in water, but the 20 μm long tubes were precipitated. The origin of such water dispersibility was investigated by the detailed analyses of their structure and the dispersion state in water. It was concluded that the observed dispersibility was caused by the presence of an electric double layer around the wall of each nano test tube in water.

Introduction

Carbon nanotubes (CNTs) hold great potential for a variety of industrial applications, but the lack of size uniformity and the difficulty in size controllability, especially in their length, narrow the range of their application fields. In addition to these problems, the extremely poor dispersibility of CNTs in solvents hampers their practical use in several applications. To illustrate, the application of CNTs in the field of biotechnology, which has recently started to emerge with great hopes, is based on the premise that CNTs are dispersible in water.[1,2] A large number of studies have thus been conducted to disperse CNTs in solvents. The most typical way is to produce carboxyl groups on the surface of CNTs by strong acid treatment and then to functionalize the CNTs with large molecules through the resulting carboxyl groups.[3,4] Alternatively, some dispersing agents such as polymer[5] and DNA[6] have been utilized as additives. In any case, additional treatments are always necessary to disperse CNTs after they are synthesized.

Some researchers have investigated the possibilities for protein,[3] peptides,[7] and plasmid DNA[8] delivery system using CNTs functionalized by these biomacromolecules and found that the CNTs become soluble in normal saline solution and penetrate cells. However, a delivery system using the inner voids of CNTs has never been reported so far since both ends of CNTs are usually closed and the size of the CNT cavity, especially in the case of single-walled CNTs, is too small for the usual biomacromolecules.

The template method using straight nanochannels of an anodic aluminum oxide (AAO) film is known as a useful technique to obtain uniform tubular nanocarbons. In this technique, both the tube diameter and the tubes length are controllable.[9−10] Furthermore, one can obtain the tubular nanocarbons with both ends open, or with one end open but another end closed (the latter type of carbon can be termed as a carbon nano "test tube"). Therefore, the carbon nano test tube synthesized by this method, if they are dispersible in water, would be best suited for the applications of biotechnology, especially as a capsule for a drug delivery system. Here we report the template synthesis of water-dispersible and uniform carbon nano test tubes without any post-modification.

Experimental Section

Preparation of Carbon Nano Test Tubes. An overview of the synthesis process of the carbon nano test tubes is shown in Figure 1. First, one side of an aluminum plate (purity 99.99%) with a thickness of 0.5 mm was anodically oxidized with a constant voltage of 10 V in sulfuric acid (20 wt %) at 293 K until the depth of straight nanochannels reaches a desired length in the range of 0.5−20 μm. After the anodic oxidation, the aluminum plate with a thin AAO layer was washed with deionized water and dried at 343 K. Then it was placed in a horizontal quartz reactor (i.d. 40 mm). The reactor temperature was increased to 873 K under a flow of N_2

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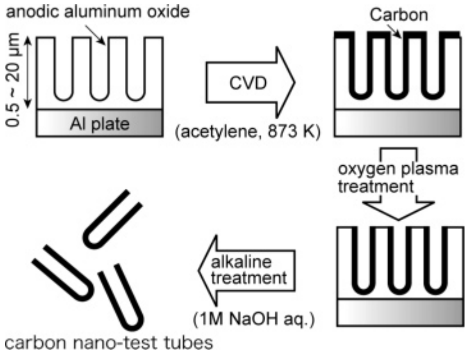

Figure 1. Synthesis process of carbon nano "test tubes" by the template method.

and acetylene gas (20 vol % in N_2) was passed through the reactor at a total flow of 500 cm^3 (STP) min^{-1} for 2 h. During this chemical vapor deposition (CVD) process, pyrolytic carbon deposition took place not only on the external flat surface of the AAO layer but also on the inner wall of the AAO nanochannels. The resulting carbon-coated sample was subjected to oxygen plasma treatment to remove only the carbon layer deposited on the outer surface of the AAO film. This treatment was conducted by using a plasma reactor (Yamato Scientific, PR-301) under an O_2 flow of 30 cm^3 (STP) min^{-1} for 1.5 min. For some of the samples, instead of the plasma treatment, Ar ion beam sputtering over the external carbon layer was performed for 80 min in a vacuum chamber equipped with an ion gun (Ulvac-phi, USG-3) under an acceleration voltage of 1 kV and an emission current of 30 mA.

After the plasma or sputtering treatment, the template was dissolved by immersing it in 1 M NaOH aqueous solution, and as a result, the tubes were liberated from the template. Al ions in the resulting suspension were completely removed by several cycles of centrifugation, decantation, and rewashing with 1 M NaOH aqueous solution that prevents the precipitation of Al ions. To neutralize the alkaline suspension, it was thoroughly washed with 1.8 wt % NaCl solution in a similar manner. Finally, the test tubes that were salted out by the NaCl solution were filtrated by using a membrane filter (Whatman, Anodisc; pore diameter 0.02 μm) and washed by deionized water. As illustrated in Figure 1, each nanochannel of the template is always closed at their bottom. Thus, it is easily understood that one end of each tube is always open, but another end is always closed.

Characterizations. To examine the dispersibility of the present test tubes in various solvents, the test tubes having a length of 1 μm (about 0.1 mg) were mixed with 7 mL of each solvent. Four kinds of solvents (water, ethanol, chloroform, and toluene) were used and the resulting suspensions were ultrasonicated for several tens of seconds. In addition to this experiment, the effect of the tube length on water dispersibility was examined as follows; the test tubes with a length of 0.5, 1, 5, and 20 μm were prepared using the AAO films with the corresponding lengths, respectively, and each type of the test tubes (0.07 mg) was mixed with 2 mL of deionized water.

Transmission electron microscope (TEM; JEOL, JEM-2010) observation was conducted under an acceleration voltage at 200 kV. Its sampling was done simply by drying a copper grid immersed in a water suspension of the tubes. ζ-Potential analysis was performed at 298 K with an electrophoretic light scattering spectrophotometer (Photal, ELS-8000) equipped with a He−Ne laser. A measurement cell was filled by a diluted water suspension of the test tubes and the pH of the suspension was controlled by adding a small amount of HCl solution. The measurement was made at least two times at the same pH. The surface of the test tubes was analyzed by using X-ray photoelectron spectroscopy (XPS; Perkin-Elmer, PHI-5600-ESCA) with a radiation source of Mg Kα (8 kV, 30 mA) under a pressure of less than 10^{-6} Pa. A powdery sample was placed on an indium sample holder to cover the whole top surface of the holder. Binding energy correction was made to account for sample charging based on a peak top of C 1s profile at 284.6 eV. A Fourier transform infrared spectrometry (FTIR) measurement was performed for the test tubes by an attenuated total reflectance (ATR) method. A sufficient amount of dried sample was placed on a Ge prism of an ATR attachment (Pike technology, MIRacleA) installed to a spectrometer (Shimadzu, FT-IR 8900). The spectrum was taken by adding 100 scans at a resolution of 1 cm^{-1}.

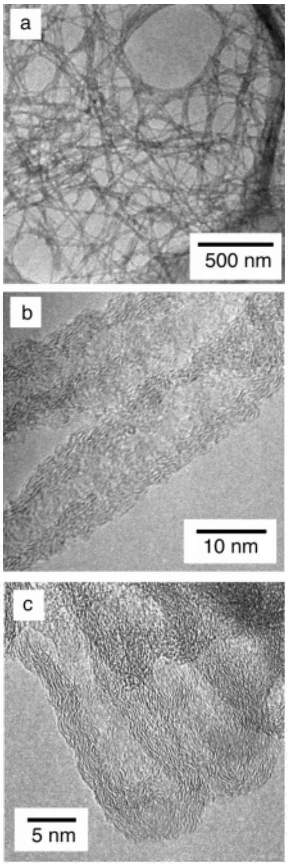

Figure 2. TEM images of uniform carbon nano "test tubes" having a length of 1 μm. (a) A low-magnification image and (b and c) high-resolution images.

Results and Discussion

Shape and Structure of Test Tubes. Figure 2 shows TEM images of the tubes prepared using the AAO film with a thickness of 1 μm (unless otherwise noted, the external carbon layer was removed by the plasma treatment). In a low-magnification TEM image (Figure 2a), many tubes are observed on a TEM sample grid without any impurity. It should be noted that the tubes overlap to a great extent but they are not obtained as a bundle form but as individual ones. High-resolution TEM images of the test tubes are shown in Figure 2b,c. From two tubes in Figure 2b, the tube diameter and the wall thickness are found to be around 10 and 3 nm, respectively. In the walls of the two tubes, many short and wrinkled lines that correspond to graphene layers are observed, indicating the ill-crystallized nature of the present tubes. This is probably due to both the low CVD temperature

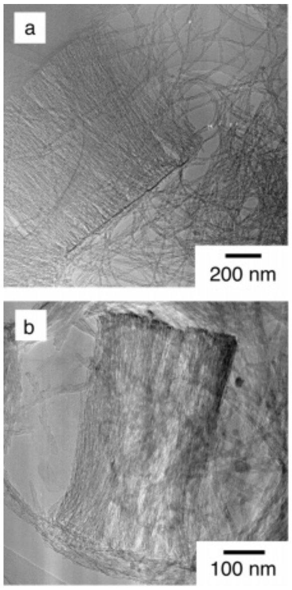

Figure 3. TEM images of bundled carbon tubes prepared using AAO layers with a thickness of 1 μm (a) and 0.5 μm (b).

(873 K) and the absence of metal catalyst. Because of such low crystallinity, the surface of the tubes must be more reactive than the conventional CNTs synthesized by the arc discharge and the catalytic CVD methods. In Figure 2c, although several tubes overlap in this image, it is evident that the bottoms of the tubes are closed and this is direct evidence for the synthesis of carbon nano "test tubes".

If the removal of the carbon layer deposited on the AAO outer flat surface is not sufficient, some bundled test tubes remain as observed in Figure 3 because many of the test tubes are still connected at one of the ends with the outer carbon layer. The formation of such bundles should be avoided for the purpose of this study (the plasma treatment for longer than 60 s reduces the fraction of bundles significantly), but TEM images of the bundles help to know the length of the test tubes. The bundles in Figure 3a reveal that the length of the test tubes is around 1 μm, which is the same as the thickness of the parent AAO film. When an AAO film with a thickness of 500 nm was used, bundled test tubes with a length of about 500 nm are formed (Figure 3b). There results demonstrate that the length of the test tubes is controllable by changing the thickness of the parent AAO film.

Dispersion State of Test Tubes in Solvents. Figure 4a shows the dispersion state of the 1 μm long test tubes in the various solvents (2 weeks after the preparation of these suspensions). Surprisingly, the color of both deionized water and ethanol suspensions is dense black and this state has been kept for several months ever since the suspensions were prepared. On the other hand, in both toluene and chloroform, the test tubes were agglomerated and precipitated in several minutes. This finding clearly indicates the hydrophilic nature of the present test tubes, even though carbon is hydrophobic by nature. Since the length of the present test tubes is fully controllable as demonstrated in Figure 3, we can examine the effect of the tube length on their dispersibility in water. As can be seen in Figure 4b, the test tubes with a length of 0.5, 1, and 5 μm are dispersed in deionized water, but the longest ones (20 μm) are not dispersed (they were precipitated just in 3 days). However, we could not find any essential difference between the 20 μm test tubes and the others both in microscopic morphology (from TEM observation) and in surface composition (from XPS analysis). Thus, the reason only the 20 μm test tubes were not dispersible is unclear at present, but there is no doubt that the dispersibility in water depends only on the geometrical length of the carbon test tubes.

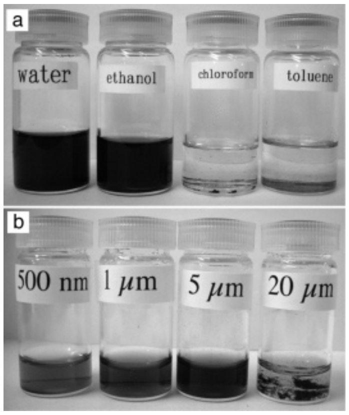

Figure 4. Dispersion state of the carbon nano "test tubes" in solvents. (a) Mixtures of the 1 μm long tubes with four types of solvents (water, ethanol, chloroform, and toluene) and (b) water mixtures of the tubes with different lengths of 0.5, 1, 5, and 20 μm.

The most remarkable finding of the present study is that the test tubes with a length of not more than 5 μm are dispersible in water without any post-treatment. To know the stability of the water suspension, we added stepwise some amount of KCl to the suspension of the 1 μm test tubes (0.02 mg) in deionized water (2 mL). The test tubes kept their dispersed state until the ionic strength became 0.015 M, but they were precipitated when the strength was higher than this value. The presence of such salting-out effect suggests that an electric double layer (EDL) was formed near the surface of each tube. Since the presence of EDL indicates that each tube is repulsive, the test tubes cannot be agglomerated and they are dispersible in water. When the electrolyte (KCl) was added to the suspension, the EDL of each tube was compressed and the tubes were agglomerated and precipitated, as a result. Sano et al. reported that the critical coagulation concentration of single-walled CNTs oxidized by inorganic acids was 0.026 M in the presence of potassium ions.[11] This value is not far from our case (0.015 M), suggesting that the surface chemistry of the present test tube is similar to that of the oxidized single-walled CNTs.

For further understanding of the water solubility, we measured the ζ-potential of the 1 μm test tubes in aqueous solutions with various pH values (Figure 5). From the plots in this figure, we can confirm that the test tubes are negatively charged in deionized water (pH ~ 7) and this indicates the presence of an EDL around each tube. The isoelectric point of the tubes is roughly estimated to be around 4 from the plot, which is close to the values reported for oxidized carbon materials such as steam-activated coal chars (3.4−5)[12] and activated carbons oxidized by nitric acid

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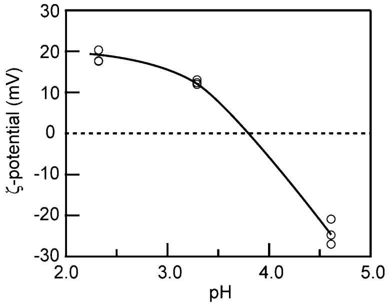

Figure 5. Values of ζ-potential for the water suspension of the carbon nano "test tubes" (1 μm long) at different pH values.

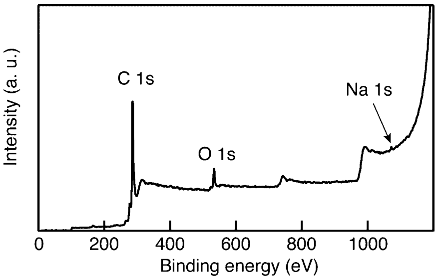

Figure 6. XPS wide-range scan spectrum of the carbon nano "test tubes" with a length of 1 μm.

(1.4−4.9).[13] It is well-known that acidic oxygen-containing surface groups can be formed on the carbon surface in such oxidation processes and these groups give rise to the negative charge on the surface. This implies the presence of acidic oxygen-containing functional groups on the surface of the present test tubes, although they were not subjected to any post-oxidation treatment.

Surface Analyses of Test Tubes. To ascertain the presence of oxygen atoms on the tube surface, the 1 μm and 5 μm long test tubes were analyzed with XPS. A wide-range XPS profile of the shorter tubes (1 μm) was shown in Figure 6, which clearly indicates the presence of oxygen (8.0 at. %) as well as carbon. The oxygen would present as surface functional groups such as ester, carbonyl, and carboxyl groups. For the longer tubes (5 μm), a similar XPS profile (not shown here) was obtained and their oxygen content was determined from the profile to be 7.7 at. %, which is very close to that of the shorter ones. Noteworthy is the presence of a small XPS peak from Na 1s in Figure 6. Sodium (0.7 at. %) may come from NaOH remaining even after the washing and/or may exist as the form of phenoxide and/or carboxylate salts. A Fourier transform infrared (FT-IR) spectroscopy measurement was conducted for the 5 μm test tubes and the resulting spectrum is shown in Figure 7. Two peaks appear at 1580 and 1680 cm^{-1}. The band at 1680 cm^{-1} can be assigned to a C═O stretching vibration of carboxyl acid groups.[14] The assignment of the band at around 1580 cm^{-1} is not completely settled.[15] Many researchers had been assigned this band to carbonyl-like species, but the assignment to "aromatic ring stretching coupled to highly conjugated carbonyl groups" seems to be most popular these days.[14,15] In any case, the band at 1580 cm^{-1} supports the presence of oxygen-containing functional groups on the tube surface.

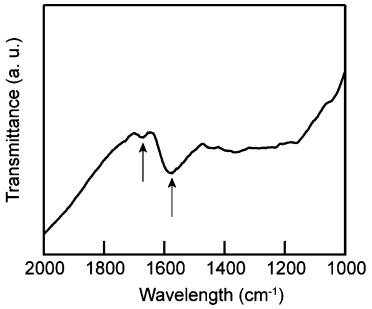

Figure 7. IR spectrum of the carbon nano "test tubes" with a length of 5 μm. The two arrows in the figure indicate two IR peaks at 1580 and 1680 cm^{-1}, respectively.

Both the results from the XPS and the FT-IR confirm the presence of oxygen-containing functional groups in the test tubes and such presence is responsible for the hydrophilicity of the present test tubes. Probably, ionized functional groups such as carboxylate ions play an essential role in the formation of EDL in water and consequently this leads to the water dispersibility.

Origin of Surface Functional Groups on Test Tubes. Since any post-oxidation treatment was not conducted for the present test tubes, oxygen atoms must be introduced during one of the steps in the synthesis (Figure 1). The most probable one is the oxygen plasma treatment. To check the effect of the treatment on the water solubility, Ar ion beam sputtering, instead of the plasma treatment, was performed under high vacuum to remove the external carbon deposit on the AAO film with a thickness of 1 μm. It was found that the sputtering method could not completely remove the carbon deposit but the liberated 1 μm long tubes were dispersible in water as shown in Figure S1 in the Supporting Information, indicating that the plasma treatment is not essential for preparing the water-soluble test tubes. This is probably because the oxygen plasma irradiation onto the test tubes embedded in the template resulted in the formation of oxygen functional groups only at the open ends of the test tubes, and the amount of the groups would be therefore negligibly small in comparison with those formed by the process that will be discussed in the following paragraph.

Another chance for the test tubes to contact oxygen atoms is when the test tubes were exposed to the alkaline solution during the template removal process. Taking the less-crystallized nature of the test tubes into consideration, we can judge that there may be many defects such as dangling bonds on the outer surface that were completely protected by the template. When these reactive sites are exposed to the NaOH solution, these would easily be reacted to form surface oxygen functional groups on the whole outer surface of the test tubes and an EDL would immediately be formed around the wall of each test tube, as a result. This idea is supported by the XPS results that the oxygen content of the

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1 μm long tubes was almost the same as that of the 5 μm long tubes since the oxygen content of the longer tubes would have become smaller if the majority of oxygen atoms have been introduced around the open edge of the test tubes during the plasma treatment.

Conclusions

The water-dispersible carbon nano “test tubes” with a diameter of about 10 nm were successfully synthesized by the template method without any post-treatment. The length of the tubes can easily be controlled by changing the thickness of the parent template and this particular feature makes it possible to investigate the effect of the tube length on the water dispersibility. In the present case, the test tubes with a length of not more than 5 μm were found to be soluble in water. The test tubes thus prepared are poorly crystallized so that oxygen atoms would easily react with the outer surface of the test tubes when they were exposed to the alkaline solution during the template removal process. Such formation of oxygen-containing functional groups, especially ionized functional groups, on the outer surface resulted in the formation of an EDL around each test tube and this is the primary origin of the water dispersibility.

Acknowledgment. We would like to express our appreciation to Dr. Carlos Leon y Leon of Hexcel Corporation for his helpful discussion. This research was partially supported by the Ministry of Education, Science, Sports and Culture, Grant-in-Aid for young scientists (B), 17710085. This work was performed as one of the research studies in the Materials Science & Technology Research Center for Industrial Creation at the Institute of Multidisciplinary Research for Advanced Materials of Tohoku University.

Supporting Information Available: A photograph of water suspension of carbon nano “test tubes” liberated from the template after Ar ion beam sputtering (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

CM0521368