Nanotube Synthesis

Carbonization of Disclike Molecules in Porous Alumina Membranes: Toward Carbon Nanotubes with Controlled Graphene-Layer Orientation**

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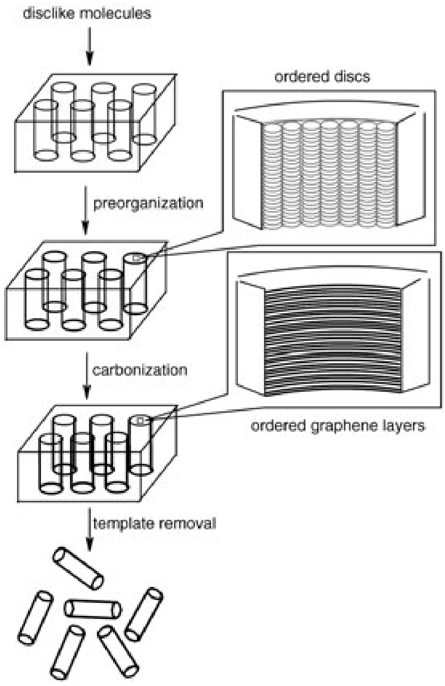
Graphitic carbon nanotubes have attracted great attention since their discovery[1] because of their unique electronic properties and many potential applications.[2] Pyrolysis of organic precursors is a commonly used chemical method for carbon-nanotube preparation[3] in which metal catalysts are believed to play a key role in the incorporation of carbon atoms into graphitic (not amorphous) carbon structures at high temperatures.[2a,4] One serious problem is the separation of catalysts from the nanotube products, as typically most of the catalyst particles are encapsulated into the nanotubes.[2i,4c,5] Template methods have also been used to conduct the formation of carbon tubes.[3c,h,6] However, without metal catalysts, even with the help of templates, it is difficult to form graphite-structured carbon nanotubes.[3c,6b,6e,7] This graphitic structure yields materials with excellent properties for which many potential applications have been proposed.

To form ordered graphite structures without metal catalysts, one possible approach is carbonization within a liquid-crystalline mesophase. By this method, large aromatic molecules preorganize into ordered columnar superstructures before carbonization and maintain this architecture during carbonization under a controlled heating process. Experiments showed that disclike polycyclic aromatic hydrocarbons (PAHs) in pitch can be preorganized on many kinds of substrates such as glass, quartz, polytetrafluoroethene (PTFE), aluminum, and alumina by an edge-on orientation, with the main axis of the discs approximately parallel to the substrate surface.[8a] Recently, carbon nanofibers with ordered graphene architectures have been fabricated by carbonization of pitch in a mesophase by using an alumina template method.[8b] However, to create a well-defined supramolecular order of the graphene sheets, especially for nanoscale carbon tubes, is still a challenge. It is well known that disclike PAHs such as alkyl- and alkylphenyl-substituted hexa-*peri*-hexabenzocoronenes (HBC) show exceptional mesomorphic properties and form highly ordered columnar architectures in the liquid-crystalline phase owing to the strong π–π interactions between the HBC discs. These discotic liquid crystals usually display an edge-on orientation in thin films on different substrates such as glass, PTFE and highly oriented pyrolyzed graphite (HOPG).[9] Our recent studies showed that in the absence of a catalyst, pyrolysis of this kind of disclike graphite-structured molecules in the bulk state resulted in different types of carbon nano- and microobjects with graphitic structures.[10] Herein, we report a novel synthetic approach to fabricate graphite-structured carbon nanotubes by carbonization of the preorganized disclike molecules in porous alumina membranes (Scheme 1). The molecules were preorganized by π–π stacking into highly ordered columnar architectures that were maintained to form ordered graphene sheets after carbonization at high temperatures. By removal of the template, carbon nanotubes with ordered graphene layers that lie perpendicular to the tube axis were obtained.



Scheme 1. The formation of carbon nanotubes with controlled orientation of graphene layers.

Commercially available anodic alumina membranes were chosen as a template because of their relatively narrow pore size distribution and as they comprise mostly open and separated straight channels. Hexa(4-dodecylphenyl)-*peri*-hexabenzocoronene (HBC-PhC$_{12}$, **1**; Scheme 2) was chosen as a carbon precursor in this work because of its good solubility and as it forms stable columnar liquid-crystalline phases.[11] A solution of **1** in dichloromethane was added dropwise onto the surface of the alumina template. The

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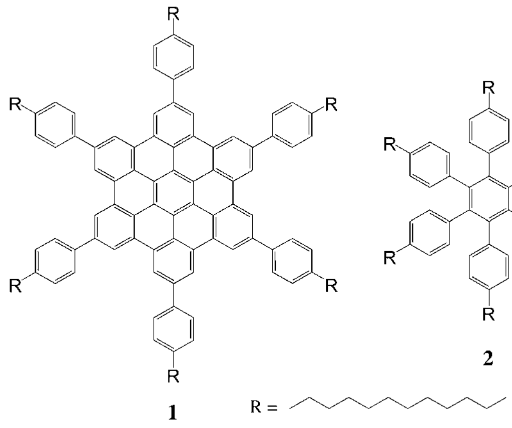

Scheme 2. The discotic molecules used in the carbonization process. R is a C_{12} alkyl chain.

solution spread along the inner surfaces of the nanoscale channels of the template and completely filled the pore. As a result, the alumina film became transparent. When the solvent was evaporated, the film became opaque again which indicated that HBC-PhC_{12} (**1**) had coated the surface of the channel to form a tube instead of a fiber. Tubes are formed because the cohesive driving forces for complete filling are much weaker than the adhesive forces, as explained by Steinhart et al.[12] After heating the HBC-PhC_{12}-loaded template at 400 °C for 5 h, then at 600 °C for 5 h, and finally at 900 °C for 5 h, with a rate of increase in temperature of 2 °C min^{-1}, completely carbonized and uniformly sized carbon nanotubes formed in the channels of the alumina membrane.

Figure 1 shows an image obtained by scanning electronic microscopy (SEM) of the aligned carbon nanotubes that formed in the channels of the template, which was partially etched with an aqueous solution of sodium hydroxide. The shape and size of the tubes are in agreement with the dimensions of the template channels. Most of the tubes are cylindrically shaped with open ends. Tubes with a closed end were occasionally observed, as shown in Figure 1 b, and were produced in a channel with one closed end. After complete removal of the template, single carbon nanotubes with lengths of several to tens of micrometers were obtained. The average outer diameter is about 100 nm and the wall thickness is around 20 nm. High resolution transmission electronic microscopy (HR-TEM) measurements showed that graphitic structured walls were formed and highly ordered graphene layers with a layer-to-layer distance of about 0.34 nm were aligned, as expected, perpendicular to the tube axis (Figure 2). The same architecture was found at every tube and at every position studied by HR-TEM. Raman spectra of the nanotubes also confirmed the graphitic structure of the tube walls (see Supporting Information). Because of the special graphene sheet orientation, we predict that this kind of carbon nanotube will display quite different properties relative to catalytically prepared carbon nanotubes. For example, the tubes here should have a relatively higher density of active sites on the surface,[8b] and the tube walls will be more reactive toward functionalization by chemical or physical methods. Electron transport along the tube wall should also be quite different from that of normal carbon tubes, and this difference will be interesting from the standpoint of microelectronic devices.

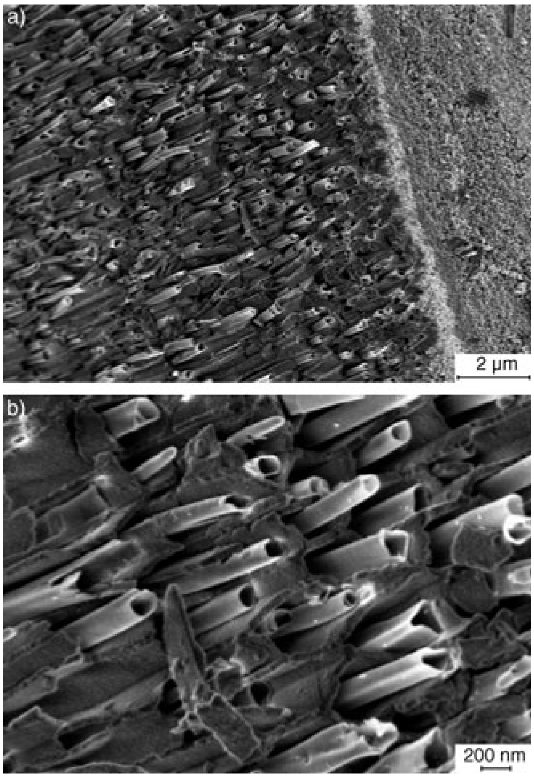

Figure 1. Aligned carbon nanotubes formed in the template channels. Most of the tubes are cylindrically shaped with open ends. Tubes with a closed end or special shapes can be seen occasionally.

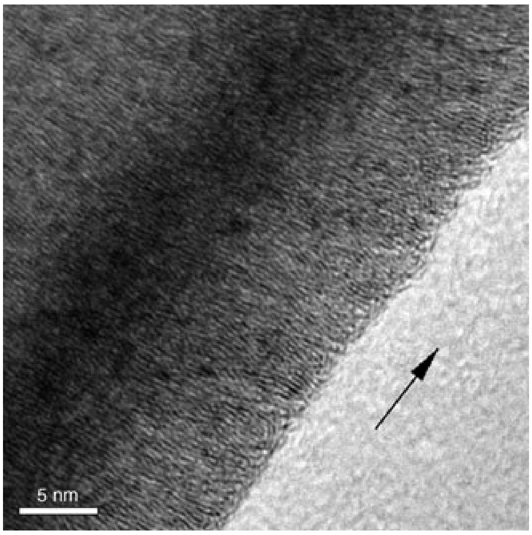

Figure 2. HR-TEM image of as-prepared carbon nanotubes with highly ordered graphene layers oriented perpendicularly to the tube axis. The arrow indicates the tube axis.

The ordered preorganization of the HBC molecules at the inner surface is thought to play an important role in the final unique graphene wall structures. Previously, we reported that

HBC molecules substituted with alkyl chains formed uniaxially oriented columnar architectures on a glass surface by a "zone-casting" technique.[9a] Given the similar hydrophilic properties of alumina and the glass surface, the HBC molecules in the alumina pores could also adopt an edge-on stacking and orient along the channel during the diffusion and evaporation processes of the solution. This prediction is supported by the TEM measurements of the samples after heat treatment at the relatively "low" temperature of 400 °C for 5 h. After removal of the template, formation of carbon-like nanotubes was observed, and the HR-TEM measurement of the tubes revealed that the ordered columnar superstructures with the graphene layer aligned perpendicular to the tube axis had been formed at this stage, although the alignment was not perfect (see Supporting Information). According to thermogravimetric analysis (TGA), HBC-PhC$_{12}$ (**1**) loses its alkyl chains at 400 °C and cross-linking reactions take place at this stage. This process was confirmed to be effective for cross-linking the graphitic disc units together and preserving the discotic mesophase.[10] After this stage, a stabilized ordered supercolumnar architecture formed which could be preserved at higher carbonization temperatures. Instead of using the three-step heat treatment, we also performed the carbonization by heating the HBC-PhC$_{12}$-loaded template from 25 °C to 900 °C with a heating rate of 10 °C min^{-1} and holding the temperature at 900 °C for 5 h. Graphitic carbon nanotubes were also formed, however, the graphene layers of thus-formed carbon tubes were not as highly ordered as those of carbon tubes prepared by the stepwise carbonization, although most of the graphene layers were still oriented perpendicular to the tube axis (Figure 3). This experiment further reinforced the importance of the stepwise heat treatment of the HBC discs in the mesophase.

Similar carbon nanotubes were also formed by this method from another discotic molecule, hexa(4-dodecylphenyl)benzene (HPB-C$_{12}$, **2**; Scheme 2), by the same procedure as used for HBC-PhC$_{12}$ (**1**). However, the carbon nanotubes that formed did not have an ordered graphitic architecture and the graphene layers did not orient fully perpendicularly to the tube axis, as shown in Figure 4. In this case, we did not observe the ordered columnar structures after treatment at 400 °C because this temperature is much higher than the melting point of HPB-C$_{12}$; that is, the order is disrupted before the intermolecular cross-linking reactions take place. Other disclike molecules such as HBCs substituted with oxygen-containing alkyl chains, and the alkylated larger graphite disc C96-C$_{12}$,[13] which has a core of 96 carbon atoms, were also chosen as carbon precursors in our work and detailed investigations are ongoing. It is clear that the stabilized preorganization of the discs is essential for effective control of the orientation of the graphene layers in carbon nanotubes.

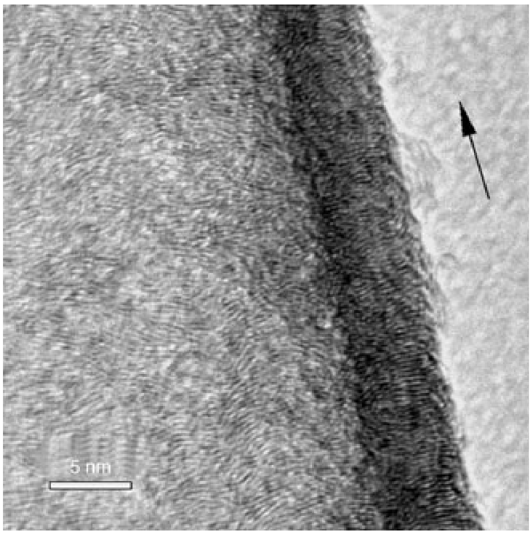

Figure 3. HR-TEM image of carbon nanotubes prepared from HBC-PhC$_{12}$ (**1**) by rapid heating to 900 °C with a heating rate of 10 °C min^{-1}. The arrow indicates the tube axis. The graphene layers are not as highly ordered as those shown in Figure 2.

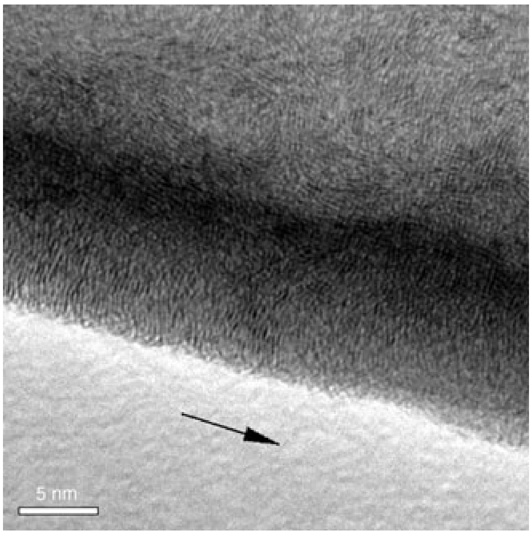

Figure 4. HR-TEM image of carbon nanotube prepared from HPB-C$_{12}$ (**2**). The graphene layers do not orient fully perpendicular to the tube axis. The arrow indicates the tube axis.

Different types of carbon nanotubes were observed in our products, for example, the tubes with triangular and quadrate shapes as shown in Figure 1 b. Some Y-shaped tubes were also observed after complete removal of the template. These special types of carbon nanotubes were formed following the types of channels within the template. In fact, different shapes of carbon tubes have been prepared from different types of template by chemical vapor deposition (CVD) methods.[14] Thus, by using differently shaped template channels,[14,15] different types of carbon nanotubes with controlled orientation of graphene sheets can be synthesized following our method.

In conclusion, a novel molecular engineering approach has been developed to prepare carbon nanotubes with controlled orientation of graphene layers from graphitic molecules preorganized in a porous template. Graphitic carbon nanotubes were synthesized successfully in the absence of metal catalysts, and the graphene layers of the as-formed carbon nanotubes were orderly stacked and oriented perpendicular to the tube axis. The orthogonally oriented carbon nanotubes are of interest for use as chemical or biological sensors, absorbants, catalyst supports, nanoreactors, battery electrodes, and many other microscale investigations. Because of the controllable orientation of graphene layers and alignment, shape, and size of the tubes, our process should also allow fabrication of special carbon materials for microelectronic devices.

Experimental Section

Anodic alumina membranes were purchased from Whatman International Ltd. The average pore size of the membrane was around 100 nm (evaluated by SEM) and the thickness was 60 μm. The membranes were washed in ethanol with sonication for 10 min and then dried under vacuum. Compounds **1** and **2** were synthesized according to procedures described elsewhere[16] and then dissolved separately in dichloromethane (10–30 mg mL^{-1}). The solution of **1** or **2** was then added dropwise onto the membrane surface. The amount of substance loaded in the membrane can be controlled by the concentration of the solution and by the volume of solution applied to the membrane. All heat treatments of the samples were carried out in quartz ampoules sealed under high vacuum in an electric furnace. Alumina templates were removed by dissolving the templates in a solution of NaOH (3 M). The template-free samples were washed with water and ethanol, dried under vacuum, and submitted for SEM and TEM measurements. SEM measurements were performed on a LEO 1530 field emission scanning electron microscope. High resolution TEM studies were conducted on an EM420 electron microscope at an operating voltage of 120 kV. The sample was dispersed in ethanol under ultrasonication, and the suspension was dropped onto a copper grid. TGA measurements were performed on a Mettler TG50 thermobalance. Raman spectra were recorded with a Bruker RFS100/S spectrometer.

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