Water-assisted fabrication of aligned microsized carbon tubes made of self-assembled multi-wall carbon nanotubes

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Aligned micro-sized carbon tubes have been successfully synthesized on silicon substrate by pyrolysis of cyclohexane/ferrocene in the presence of water, a spectacular feature of which is that the multi-wall carbon nanotubes formed *in situ* act as the basic building blocks for the construction of micro-tubes *via* a "multi-scale" self-assembly process.

Fabrication of carbon nanotubes (CNTs) with well-defined arrangements and configurations has attracted much attention in the past decade because of their paramount importance for making CNT-based devices with exceptional properties such as field emitters, sensors and nanoelectronics.[1] The intensive research has led to controlled synthesis of various CNT architectures by adopting the strategies of pre-designed catalyst patterns or substrate patterns, which were constructed by a variety of techniques such as offset printing,[2] standard lithography, and soft lithography.[3,4] Using Fe/Si substrates, Fan *et al.* successfully prepared regular arrays of oriented CNTs with a high uniformity.[5] Wei *et al.* reported a site selective growth of multi-direction aligned CNTs by pyrolysis of xylene/ferrocene on a patterned SiO_2/Si substrate.[6] Very recently, Iijima and his colleagues demonstrated the efficient synthesis of highly organized intrinsic single-wall carbon nanotube (SWNT) structures with the assistance of water.[7] In addition to the patterned CNTs at micrometer level, fabricating CNTs with well-arranged forms in macro-scale is also being actively investigated with the aim of making materials from CNTs for practical uses. In this area, Ajayan and his colleagues pioneered the fabrication of a macro-sized hollow CNT cylinder with diameter and length up to several centimeters;[8] this was made on a well-defined cylindrically curved surface (a removable silica tube) and were found to be of potential as filters for separation purposes. However, the utilization of self-assembly to assemble architectures composed of CNTs has seldom been addressed.[9] Here we describe a simple method for simultaneous growth and construction of aligned micron-sized CNT cylinders on silicon substrate *via* self-assembly of *in-situ* formed multi-wall CNTs, which is achieved by pyrolysis of cyclohexane and ferrocene mixtures in the presence of water. During the whole process, no pre- or post-synthesis manipulations are required.

The fabrication experiments were conducted in a horizontal quartz tube reactor (i.d. 21 mm) which was heated in a two-stage furnace system.[10] Ferrocene was put inside a quartz boat which was placed in the middle of the first-stage furnace, while a Si (100) substrate (5 mm × 7 mm) was put in the middle of the second-stage furnace. To avoid undesired vaporization of ferrocene during the ramping step, the quartz tube was pulled out a little to keep ferrocene just out of the first furnace before the two furnaces were heated. After both furnaces reached the preset temperatures, the tube reactor was pushed back to keep ferrocene and Si substrate at the centers of the first furnace and the second furnace, respectively, then cyclohexane was carried into the reactor by a gas mixture of N_2 (140 sccm) and H_2 (60 sccm) through a bubbler. In addition, water vapor was carried into the reactor with flowing N_2 (50 sccm) through another bubbler to assist the growth of CNT cylinders. The optimal results were obtained by controlling the temperatures of water and cyclohexane at 0 °C and 45 °C, respectively. For typical runs, the first-stage furnace (for vaporization) was set at 150 °C while the second-stage furnace for growth of CNTs was set at 850–900 °C. Each run normally lasted for 15–20 min. The as-obtained products were examined using scanning electron microscopy (SEM, JSM-5600LV), transmission electron microscopy (TEM, Philips Tecnai G^2 20) and Raman spectroscopy (JY LabRam HR800).

The SEM study reveals that some aligned cylinders or microtubes are formed on the Si substrate surface, as shown in Fig. 1a. Further SEM examination under high magnification shows that the walls of the cylinders are tightly packed by fiber-like materials with only a few individual fibers protruding out of the walls randomly, as can be seen in the inset of Fig. 1a and in Fig. 1b. The diameters of the microtubes or cylinders vary in a wide range, from several microns to more than seventy microns. It is noteworthy that cylinders with a big diameter are straight and rigid, while cylinders with smaller diameters are flexible and tilted. On average, the height and wall thickness of the microtubes vary from *ca.* 120 μm to 190 μm and 3 μm to 7 μm, respectively. The inset in Fig. 1a shows a typical well-formed cylinder with sharp edges, uniform wall thickness, and smooth surfaces. It should be further noted that in addition to microtubes or cylinders with perfect morphology, there also exist a number of imperfect microtubes, curly sheets, and semi-tubes. Whatever the morphologies of the products are, the fiber-like materials in the walls are approximately parallel to the axis of the cylinders or semi-microtubes (Fig. 2a,b). This is strikingly different from Ajayan's macro-tubes,[8] in their case the CNTs consisting of the tube wall are perpendicular to the axis of the cylinder. The fundamental reason for the different orientation of nanotubes in the macro- or micro-tubes is that Ajayan's macro-tube was made with a well-defined cylindrically curved surface as a template through the well-established pyrolysis method, while in our case the micro-tubes were formed by the nature of self-organization. Fig. 2b shows two

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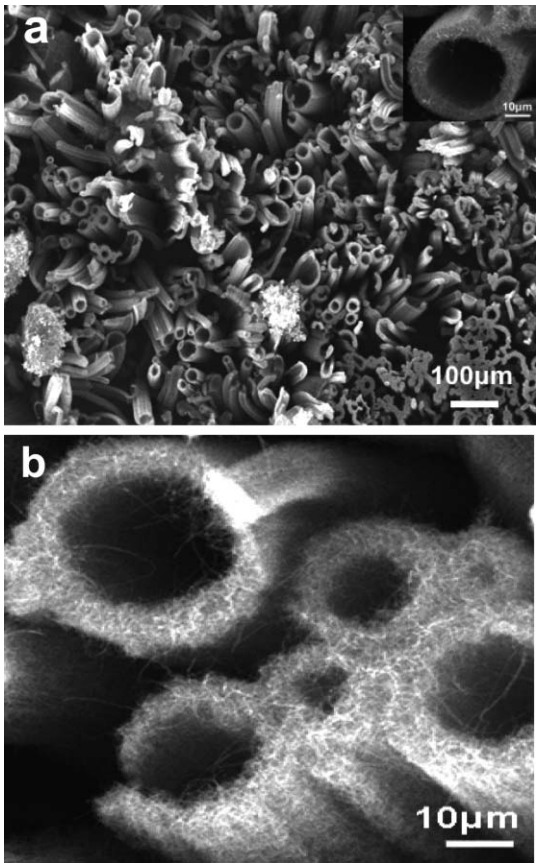

Fig. 1 (a) SEM image of microtubes or CNT cylinders on silicon substrate (inset; a typical CNT cylinder with perfect morphology), (b) high magnification SEM image of several CNT cylinders.

microtubes with similar diameter and wall thickness, of which one common feature is that there exists a fissure in their walls (as pointed to by the white arrows). The information available now leads one to believe that cylinders with their walls made of self-assembled fibers are composed of a single curly sheet. Occasionally, a cylinder with its wall made of sandwich-like double-sheets can also be seen (as shown in Fig. 2c), of which the outer diameter is *ca.* 20 μm, and the thickness of one single sheet in the sandwich-like wall is *ca.* 2 μm. It seems there exists a gap between these two sheets in the sandwich-like cylinder wall that consists of thread-like fibers.

The thread-like fibers that form the cylinder walls were examined by TEM, revealing that these fiber-like materials are actually multi-wall CNTs (MWCNTs) with a thick wall and thin central cavity, as shown in Fig. 3. The inner and outer diameters of these MWCNTs vary in the ranges 10–15 nm and 60–70 nm, respectively.

To further examine the quality and crystallinity of the carbon tubes, Raman spectroscopy was used to study the basic structure of the CNTs and to work out the intensity ratio of the D and G bands (I_D/I_G) that is often regarded as indicative of disorders in CNTs.[11] Fig. 4 is the Raman spectra of the carbon nanotubes obtained with and without water in the reaction system, showing clearly that the crystallinity of the CNTs obtained in the presence of water was not inversely affected by water. The I_D/I_G ratio for the CNTs prepared with and without water is 0.75 and 0.98,

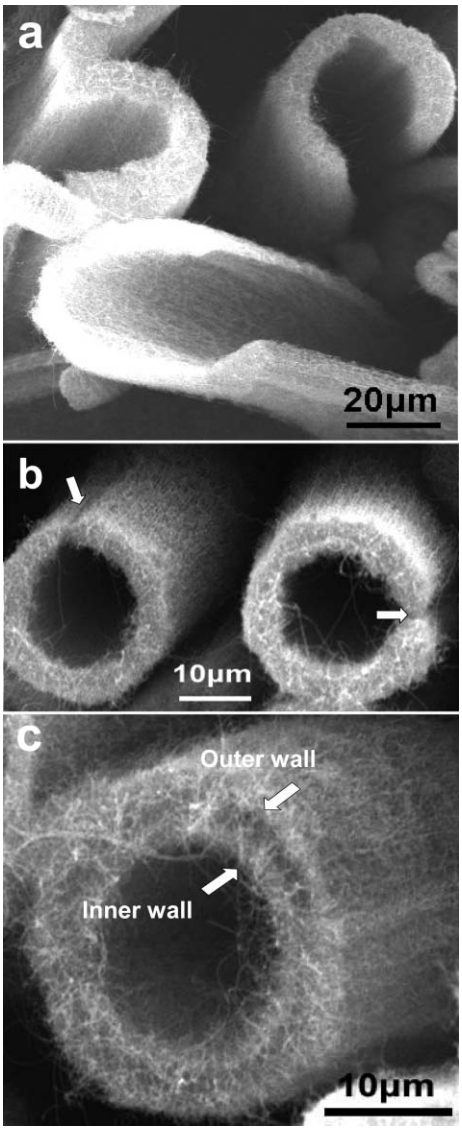

Fig. 2 (a) SEM image of semi-cylinder; (b) SEM image of two cylinders with a fissure on the wall; (c) a perfect cylinder with its wall made of a sandwich-like double-sheet.

respectively, indicating that CNTs obtained in the presence of water have fewer disorders. One possible reason for this is that water helps to remove amorphous carbons formed *in situ*, which naturally results in cleaner CNTs.

The self-assembly mechanism of CNTs for forming cylinders reported here is not clear right now because the available information is still very limited. Nevertheless, water present in the reaction system is believed to be one of the key factors which must become involved in the growth process of the carbon cylinders in some way. We also found that the balancing level of carbon source, floating catalyst and water is crucial for the growth of CNT cylinders. It should be noted that our results are remarkably different from the CNT growth reported by Ajayan's group.[6] They demonstrated the substrate-selective growth of CNTs on SiO_2 not on Si during the chemical vapor deposition of ferrocene and xylene mixtures, however, our CNT cylinders grow on Si substrate without any pretreatment. In our case the

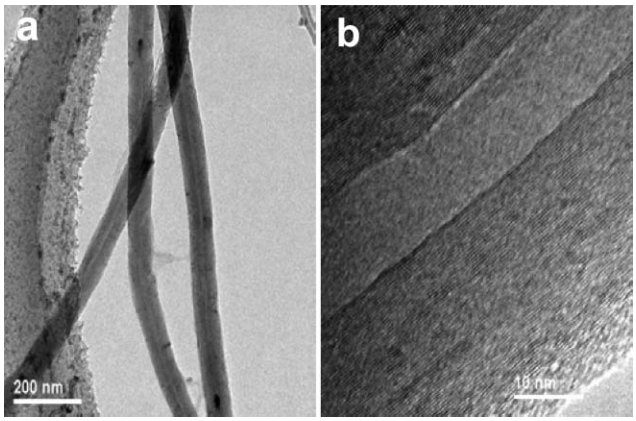

Fig. 3 (a) Low-magnification TEM image of the thread-like fibers consisting of the cylinder walls, of which a typical HRTEM image is shown in Fig. 3(b), showing that the fibers are actually multi-wall CNTs with well-developed graphitic structure.

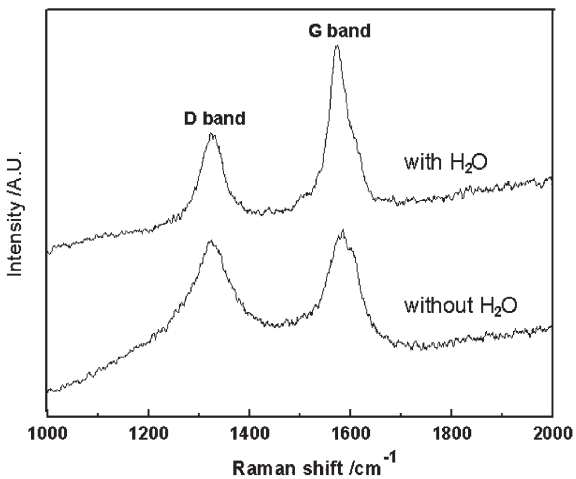

Fig. 4 Raman spectra of CNTs that were obtained with and without H_2O in the reaction system.

growth of CNTs on Si substrate might be due to the higher catalyst concentration ($\sim$ 0.05 g/ml) used in the reaction than that used in Ajayan's group ($\sim$ 0.01 g/ml). In addition, the formation of the SiOx on Si substrate by the *in situ* oxidation in the presence of water should also be taken into account. It is believed that the interaction between the substrate and the catalyst/carbon flux under this condition must play a critical role in the initial stage of reaction, which may create circular patterns that favor the nucleation of catalyst. Consequently, the deposited catalyst functions to initiate and catalyze the growth of aligned CNTs on the circular patterns that form microtubes or cylinders. Undoubtedly, the growth of the microtubes is a complex multi-component reaction process. More detailed work is needed to clarify the formation mechanism of these carbon cylinders. The successful synthesis of CNT cylinders in the presence of water leads us to believe that the growth of CNT cylinders might be also possible with the assistance of other weak oxidants such as CO_2. The effects of the process parameters and types of oxidants are currently under investigation with the aim of elucidating the growth mechanism of CNT-made cylinders, which will pave the way to tuning the diameter and wall thickness of the microtubes and creating uniform arrays and highly oriented carbon cylinders.

In summary, we have demonstrated for the first time that carbon cylinders consisting of multi-wall CNTs *via* a multi-scale self-assembly scheme can be obtained in a one step process. This method has potential for making hollow carbon cylinders that would find uses in the field of separation and catalysis. It is believed that the synthesis of those carbon cylinders may open up new possibilities for making use of CNTs to fabricate functional carbons with unique geometry and specific properties in a controllable way, which may also shed some light on further understanding, both experimentally and theoretically, of the self-assembly of CNTs.

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