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## Simplified synthesis of double-wall carbon nanotubes

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### Abstract

We demonstrate a simplified synthesis technique for double-wall carbon nanotubes that is an adaptation of chemical vapor deposition (CVD) techniques used previously for the production of single-wall nanotubes. Double-wall nanotubes (DWNTs) provide ideal geometries for numerous fundamental structural, electronic, thermal and vibrational studies, as well as providing a unique new platform for practical applications. The diameter distribution of DWNTs is broad, and it is possible that in previous studies using CVD-grown small-diameter nanotubes, presumed to be single-wall, there were significant numbers of DWNTs present.

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The study of carbon nanotubes have, until now, been divided largely into two categories: the study of multi-wall nanotubes (MWNTs) [1,2] and the study of single-wall nanotubes (SWNTs) [3,4]. While some experiments show similarities between the two species, others reveal stark differences. For instance, some transport measurements show that MWNTs are diffusive conductors of electric current while SWNTs are ballistic [5]. In order to examine the differences in detail, it would be ideal to study samples of nanotubes with precisely controlled numbers of walls and study the progression of properties from one to two to many walls. Synthesis of exclusively double-wall nanotubes (DWNTs) is the defining step making this possible.

Arc synthesis methods that produce double-wall boron nitride nanotubes have been known for some time [6–8], and recent studies have also demonstrated that controlled synthesis of double-wall carbon nanotubes is also possible. Temperature or electron-beam induced fusing of  $C_{60}$  encapsulated inside SWNTs has been used to produce double-wall structures, but in this case the inner ‘wall’

formed by the  $C_{60}$  is not continuous for the entire length of the nanotube [9]. More conventional nanotube synthesis methods have had a disappointingly low yield of carbon DWNTs [10–12], and methods that have high yields require specialized apparatus [13], exotic ceramic precursors [10], or sulfur-containing precursors [14–16]. We here describe a simple and reliable method for production of carbon DWNTs that have two walls over their entire length. The method is an adaptation of well-established [11] chemical vapor deposition (CVD) methods of producing SWNTs.

Similar to previous studies [11], we utilized fumed alumina (Degussa Alumina C) as a catalyst support material, and deposited iron salts onto the support from a methanol solution. The alumina particles have a typical size of 13 nm, and thus produce nm-sized particles of iron salts after evaporation of the solvent. The nanotube synthesis is initiated at approximately 900 °C in flowing argon gas. As the alumina/iron salt mixture is heated, the iron salt forms iron oxide, from which the nanotubes grow. To initiate the nanotube growth, the argon is replaced with flowing methane. After 10 min, the gas is switched back to argon and the sample is allowed to cool.

A typical transmission electron microscope (TEM) image of the resulting nanotubes can be seen in Fig. 1. In

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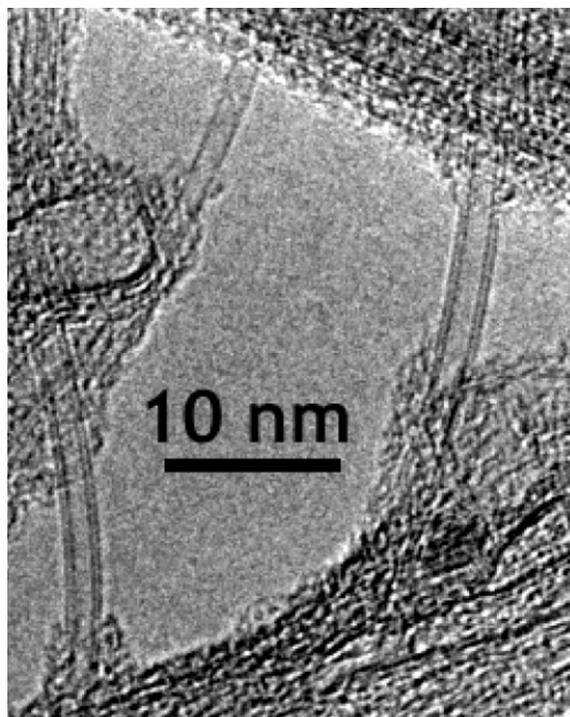


Fig. 1. A typical sample from the CVD synthesis of DWNTs. Clearly visible in the image are two DWNTs and one single-wall nanotube.

this image, two DWNTs can be clearly seen, as well as one SWNT. More extensive TEM imaging shows that the nanotubes throughout the sample have outer diameters ranging from 1 to 4 nm, and that the diameters of the nanotubes are uncorrelated to wall numbering (i.e. whether they have one or two walls). The distribution of wall numbers in a sample from a typical synthesis run is shown in Fig. 2. From the distribution, it can be seen that two-wall nanotubes dominate the synthesis products. The method also produces a limited number of nanotubes with three or more walls, but more than 90% of the nanotubes present have either one or two walls.

Several examples of DWNTs are shown in Fig. 3. As is shown, the diameters of the nanotubes can vary greatly. We have observed DWNT with outer diameters as small as 1.3 nm and as large as 5–6 nm. This demonstrates that by outer diameter alone, it is not possible to conclude that a nanotube grown by similar CVD techniques is a SWNT (unless perhaps the outer diameter is smaller than  $\sim 1$  nm, in which case the inner core nanotube would have to be smaller than the known smallest nanotube diameter of 0.4 nm [17, 18]).

It is not yet known what synthesis parameters cause the preference for DWNTs. Within the precision of our experiment, we have exactly reproduced the conditions that have been previously reported [11] to produce SWNTs, and we have repeated the synthesis several times with

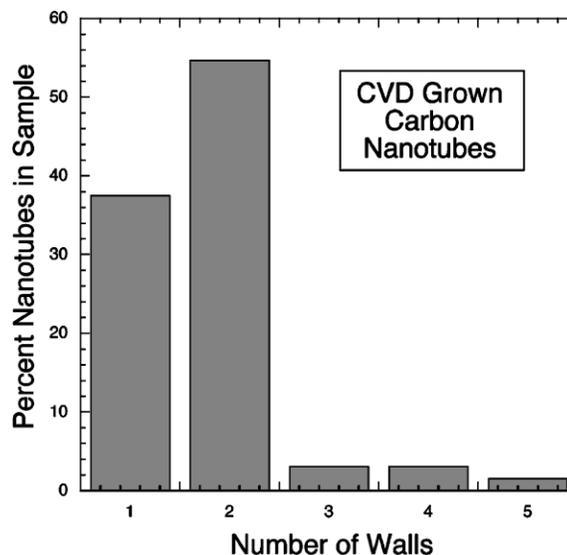


Fig. 2. A histogram from counting nanotubes in TEM images. Note the preference for DWNTs.

identical results. One possibility is that previous experiments did not have the experimental resolution to consistently resolve the difference between SWNTs and DWNTs. As stated previously, the outer diameter of the nanotubes is independent of whether the nanotubes have one or two walls and is in the range of 'typical' SWNTs. Therefore, any characterization technique that only examines the external morphology of the nanotubes, such as

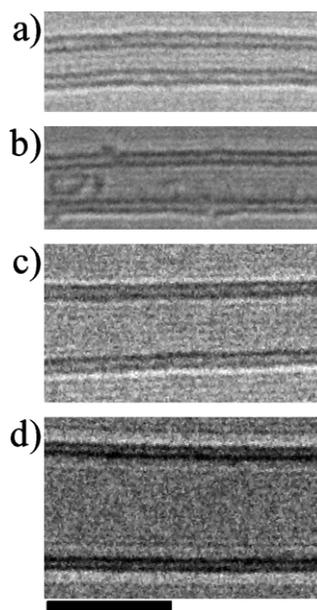


Fig. 3. Four double-wall carbon nanotubes (DWCNT) of different diameters. The respective inner and outer diameters are (a) 1.1 and 1.8 nm; (b) 1.5 and 2.2 nm; (c) 2.4 and 3.2 nm; (d) 4.2 and 4.9 nm. The scale bar is 5 nm.

atomic force microscopy, scanning tunneling microscopy, or scanning electron microscopy (SEM), does not have the capability to distinguish between single-wall and double-wall nanotubes. In fact, we find that in SEM studies of our nanotube products, the morphology of the DWNTs more closely resembles that of SWNTs than traditional MWNTs. Furthermore, the commonly used technique of TEM has the ability to distinguish single-wall structures from double-wall structures only under optimum conditions, as we now demonstrate.

Fig. 4 shows the same DWNT in two separate TEM images. In the top image, both nanotube walls are clearly resolved with inner tube and outer tube diameters of 1.1 and 1.8 nm, respectively. In the bottom image of Fig. 4 the focus of the microscope has been slightly changed, and it is now no longer clear that the nanotube has two walls. In fact, from this bottom image alone one would conclude that it is a SWNT with a diameter of 1.4 nm. Focus conditions are not the only factors that can cause a DWNT to appear like a SWNT in TEM images. Thermal vibration, amorphous material, or other microscope parameters can cause DWNTs to appear single-wall in TEM images. It is possible that in many key previous studies, ostensibly on SWNTs produced by CVD methods [11], DWNTs were present.

In addition to providing a bridge between SWNTs and MWNTs, there are many possibilities for future studies on properties that could be unique to DWNTs. For instance, vibrational coupling between nanotubes has been studied in

the thermal conductivity and heat capacity of SWNTs bundled together [19,20]. DWNTs would be ideal for studying the vibrational coupling between two concentric tubes. Such information could be revealed by heat capacity, thermal conductivity, or low frequency Raman spectrometry. Additionally, if the two walls are indeed decoupled, and can slide easily relative to one another: a DWNT presents the smallest possible geometry for realizing nanoscale bearings [21].

There is also substantial interest in the chiral wrapping angle formed by nanotubes, and whether successive walls of MWNTs have chiral angles that are correlated in any way [22–24]. DWNTs would be ideal for studying these relationships [25]. This type of information could be revealed by either electron diffraction or high-resolution TEM. Specifically, it would be interesting to study whether or not the two walls of a DWNT always form a commensurate structure, or whether incommensurate structures are possible. This would have a significant impact on possible nanobearing applications [26]. The chirality relationships in DWNT's could also have relevance to various growth models that have been proposed for MWNTs.

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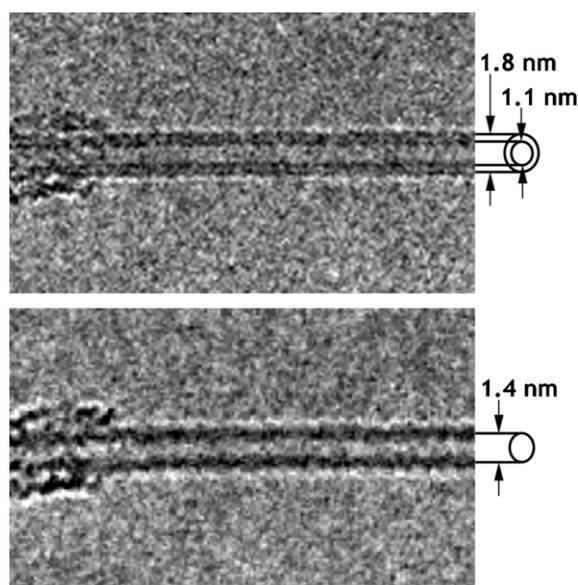


Fig. 4. Two TEM images of the same double-wall nanotube. In the upper image, both walls of the nanotube are resolved. In the lower image, the focus of the microscope has been slightly changed, and it now appears as though the nanotube is a single-wall nanotube. Line drawings have been added to the right of both images as guides to the eye.

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