High-Quality Double-Walled Carbon Nanotube Super Bundles Grown in a Hydrogen-Free Atmosphere

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High-quality double-walled carbon nanotube (DWNT) super bundles were selectively grown above a bowl-like cathode by arc discharge in a hydrogen-free atmosphere. These DWNTs can resist high-temperature (up to 720 °C) oxidation in air without additional annealing even after acid treatment, which is due to an in-situ defect-healing effect of the bowl-like cathode and the absence of reactive gases during arc discharge. Selective formation of DWNTs is ascribed to the increased presence of carbon clusters in the enlarged hot plasma region inside the cathode and optimized composition of the catalysts.

Introduction

Double-walled carbon nanotubes (DWNTs) have recently attracted much attention because of their unique structure and physical properties that are not found in other types of carbon nanotubes.[1−3] For an application to field emission, for example, DWNTs possess the advantages of both single-walled carbon nanotubes (SWNTs) and multiwalled carbon nanotubes (MWNTs), i.e., their threshold voltage for electron emission is as low as that of SWNTs and their durability is as good as that of MWNTs.[4] The advantages of DWNTs for applications such as field emission or composite material, however, can only be fully realized when they are essentially defect free, because the defects in nanotubes are closely related to their electrical and mechanical failure.[5,6]

Compared to SWNTs, DWNTs remain largely unexplored due to the difficulties involved in producing them with both high quality and sufficient quantity. DWNTs were first found in arc-discharge cathode deposits.[7,8] A small amount of DWNTs can now be produced using such techniques as high-temperature treatment of C_{60}@SWNT peapods,[9,10] catalytic chemical-vapor deposition (CVD),[11,12] and arc discharge in hydrogen.[13,14] Economical up-scalable production using the first procedure was yet to be achieved, while for the latter two techniques, further research is needed to improve structural integrity of the DWNTs because of the presence of reactive gases, in particular hydrogen during synthesis, and to produce purer DWNTs. In addition, very long DWNTs have yet to be reported.

In our recent report on the generation of SWNT super bundles,[15] we noted that DWNTs are frequently found in the product. In this work, we focus on the production of DWNTs. Under certain conditions, DWNTs are the major product. The high quality of DWNTs is reflected not only in their large quantity relative to other carbon structures, but also in their structural perfection, which is evidenced in their very high oxidation resistance, even in the presence of metal catalysts and after acid treatment. A growth model of the DWNTs is also proposed.

Experimental Section

DWNTs in super bundles were grown on the surface of a bowl-like cathode in an arc-discharge chamber. The anode was a square (15 × 15 mm, 250 mm long) graphite rod doped evenly with Ni, Co, and FeS (12:3:5, 4.5 wt % in total). The cathode was a much larger graphite bowl shown in the inset of Figure 1. Additional catalysts containing NiS, CoS, and FeS in the ratio 1:1:1, together with a small amount of Sn (1wt %), were mixed with crushed cathodic deposit (obtained from previous arc discharges using the same anode), and filled in the holes and bottom of the cathode. A metal mesh plate was positioned about 30 cm away from the cathode to collect the carbon threadlike material. The buffer gas was helium (>99.9999% in purity). The pressure was kept at 8×10^4 Pa during the reaction. The arc current was maintained at 180 A.

The collected carbon threadlike material was then subjected to purification. The material was stirred in 3 N nitric acid at room temperature for 24 h, followed by repeated centrifuging and ultrasonic dispersing to remove residual acid and water-soluble impurities. The acid-treated soot was then dried at 60 °C for over 20 h.

For TEM (HRTEM, HF2000, Hitachi) observation, the carbon threadlike material was dispersed in acetone via ultrasonication, and then deposited on a TEM copper grid by simply dipping and lifting. Thermal gravimetric analysis (TGA, Perkin-Elmer, Pylis 1 TGA) was performed in air with a temperature ramping rate of 5 °C/min.

Results and Discussion

Figure 1 shows a photo of the carbon threadlike material grown on the surface of the bowl-like cathode. The image was taken through an observation window about 10 min after the beginning of arc discharge. The carbon threadlike material seems to be white, which may be due to the thermal effect and/or strong UV irradiation of arc plasma. At the beginning of arc discharge, groups of carbon threads several centimeters long were rooted to catalytic particles that may have been dispersed from the arc plasma region. Many thus rooted carbon threads quickly grew to as long as 30 cm and filled the space between the cathode and the web collector above. A 300−500 mg quantity of these carbon threads can be collected in a 20 min operation under optimized conditions, which is much faster than the time required by the experimental catalytic CVD method used for DWNT production.[11,12]

Figure 2 shows SEM images of the carbon threadlike material. The diameter of these threads is in the range of 1−100 μm.

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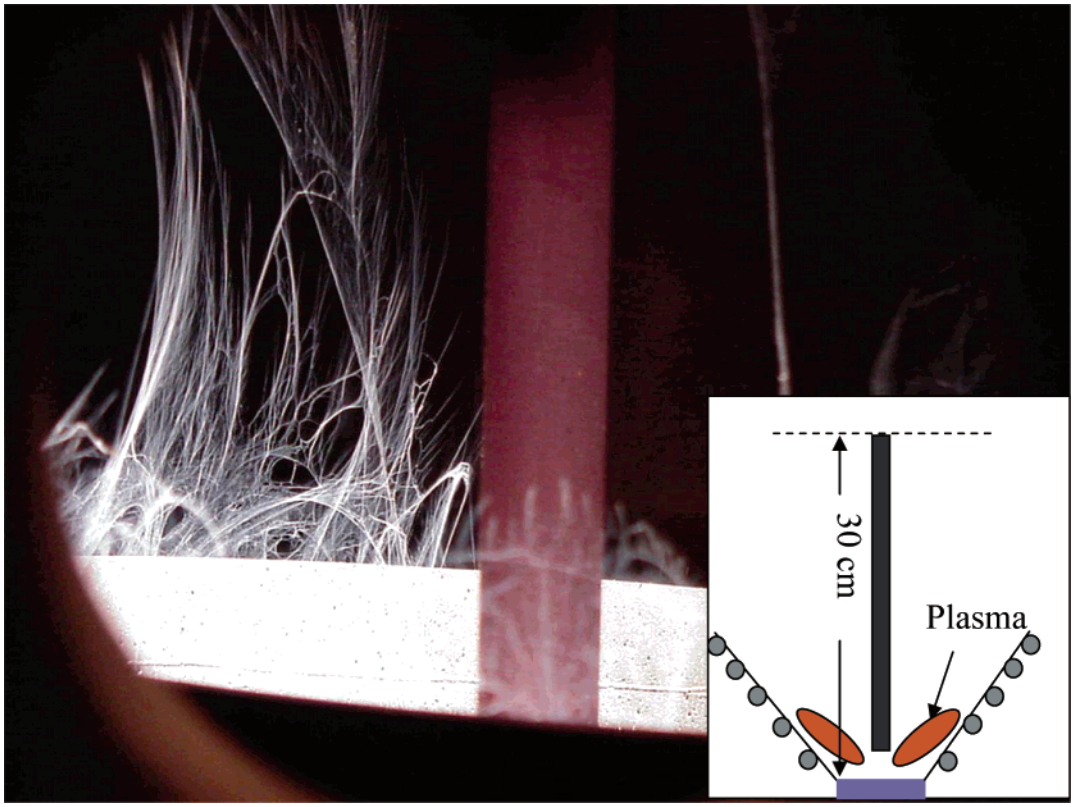

Figure 1. Photograph taken through the observation window (ϕ8 cm) of the arc-discharge chamber, showing the abundant DWNT super bundles over the cathode surface. The inset is a schematic of the setup. Note that the length of the super bundles reaches 30 cm.

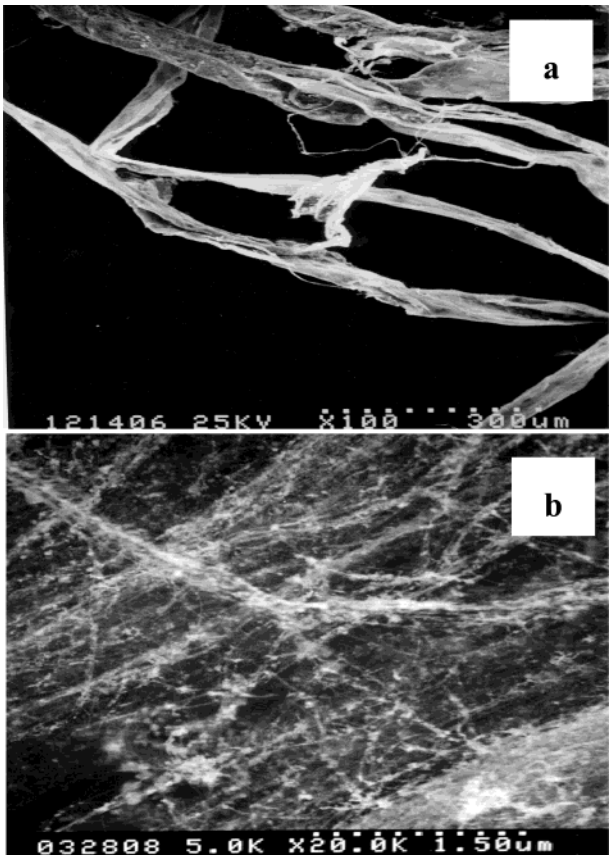

Figure 2. SEM images of DWNT super bundles: (a) low magnification; (b) high magnification.

The apparent difference between this material and soot produced by conventional arc discharge is its mechanical toughness. It is difficult to break these threads manually by trying to pull them apart. Because the carbon threads are very long, they have to be cut or twisted in order to be able to mount them on the SEM stand. At the high magnification shown in Figure 2b, we can see that numerous carbon nanotubes and bundles with diameters of a few to tens of nanometers are roughly aligned.

Figure 3a is a typical TEM image of the carbon threadlike material after being dispersed in acetone. Though the metal content is high in this specimen, the content of amorphous carbon is very low even after vigorous ultrasonication. This is in contrast to soot prepared using the conventional arc-discharge method. The double-wall nature of the carbon nanotubes is clearly seen in Figure 3b, and is confirmed by cross sections of the bundles, as shown in the inset of Figure 3b. The outer diameter of the DWNTs ranges from 2 to 7 nm, similar to that of DWNTs prepared using the arc discharge in hydrogen and catalytic CVD methods. The interlayer spacing falls in the range of 0.36 to 0.42 nm, slightly larger than that of graphitic carbon and MWNTs (typically 0.34 nm in interlayer spacing). The portion of DWNTs generated compared to that of all carbon nanotubes (SWNTs and MWNTs) is about 80%.

Figure 4 shows the results of a thermogravimetric analysis (TGA) of the threadlike material before and after purification. Though the raw material contains metal catalysts up to 60 wt %, the burning starting point appears at around 600 °C, which is much higher than that of raw soot prepared from the same anode by conventional arc discharge (~300 °C).[16] Obviously, in our material the metals are not catalysts for lowering the burning temperature of the carbon nanotubes. After simple acid treatment at room temperature, the metal content is reduced to 6.8 wt %, suggesting that most of the metals are not well sealed with carbon. The oxidation resistance of the DWNTs is not much changed after acid treatment, as suggested by the nearly overlap of the TG derivative peaks (~720 °C).

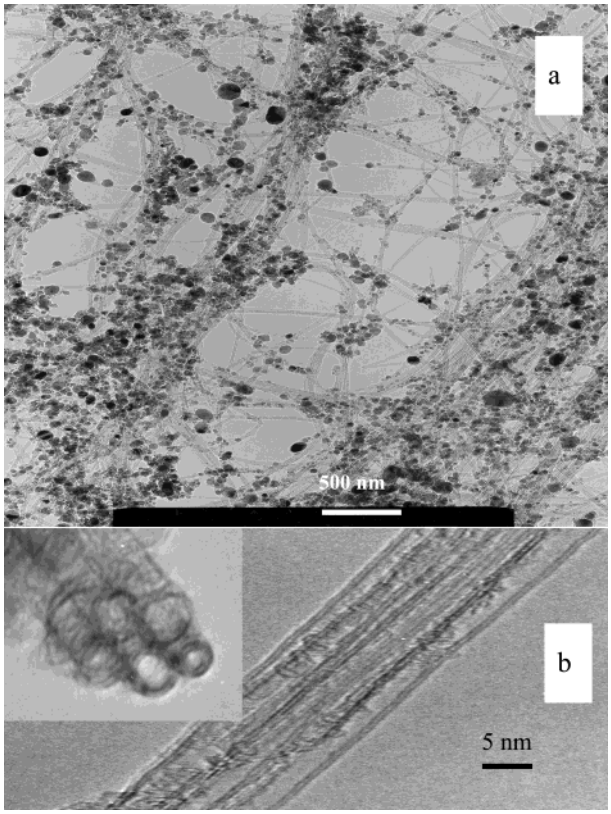

Figure 3. TEM images of DWNTs released from their super bundles via ultrasonication. (a) General view; (b) selected area showing the double-layer nature of the carbon nanotubes. The inset shows the cross section of a small bundle.

In our recent report on the production of SWNTs with improved oxidation resistance, we suggest that the bowl-like cathode possesses a defect-healing effect which can be induced by in-situ annealing.[17] The very high oxidation resistance of DWNTs in this work may be partially due to the same factors.

It is also important to note here that no reactive elements such as hydrogen or oxygen were added to the reaction system. It has been reported that CNTs grown by arc discharge in hydrogen atmosphere have many defects.[18] We have also noted that, when catalysts for CNT growth are added in oxides, it is difficult to anneal all carbon soot components so they become highly oxidation resistive (>600 °C), even after heat treatment at 1600 °C for several hours. We believe that the DWNTs with very high oxidation resistance produced in this work benefit from two things: the absence of reactive elements for minimizing defects and use of the bowl-like cathode for healing defects.

The high production selectivity of DWNTs over other carbon nanotubes produced in pure He is another striking feature of this work. Hutchison et al. found hydrogen to be indispensable for the selective formation of DWNTs.[13] Saito et al. also noted that no DWNTs were observed when pure He was used. The percentage of DWNTs became much less when He was added into H_2 atmosphere.[14] Saito et al. then argued that the balance between the processes of hydrogen etching and sulfur promoting of carbon layer formation in CNTs therefore accounts for the selective growth of DWNTs. These results suggest that a high percentage of DWNTs cannot be produced without hydrogen, which our results do not support.

Hutchison et al. have noted that, when H_2 was added to Ar atmosphere in arc discharge, the anode evaporation became much faster than that in H_2-free atmosphere.[13] The arc-discharge process is then transferred into a gas-phase analogue of a catalytic pyrolysis process.[13] Indeed, in hydrogen arc discharge, we have recently found a high-purity fibrous carbon deposit on the anode surface. The fibrous carbon deposit consists of bamboo-shaped and amorphous carbon fibers, which were formed by thermal deposition of hydrocarbon clusters (C_nH_m) generated during hydrogen arc discharge.[19] In Hutchison's experiment, DWNTs were mainly collected from the electrodes but not from the cooled chamber walls. It is thus believed that some carbon in DWNTs may come from the gas-phase hydrocarbon clusters. Hydrogen appears to be an important

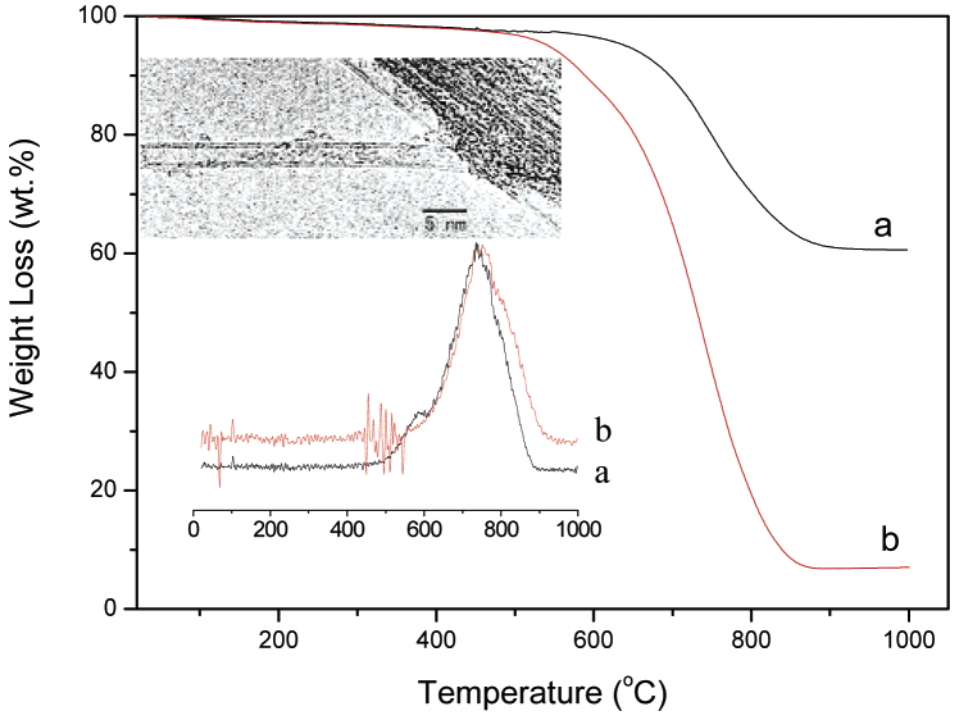

Figure 4. Thermogravimetric analyses (TGA) of DWNT super bundles (a) before acid treatment, and (b) after acid treatment. Their TGA derivative curves are shown in the inset. A high-resolution TEM image of an acid-treated sample is also shown in the inset.

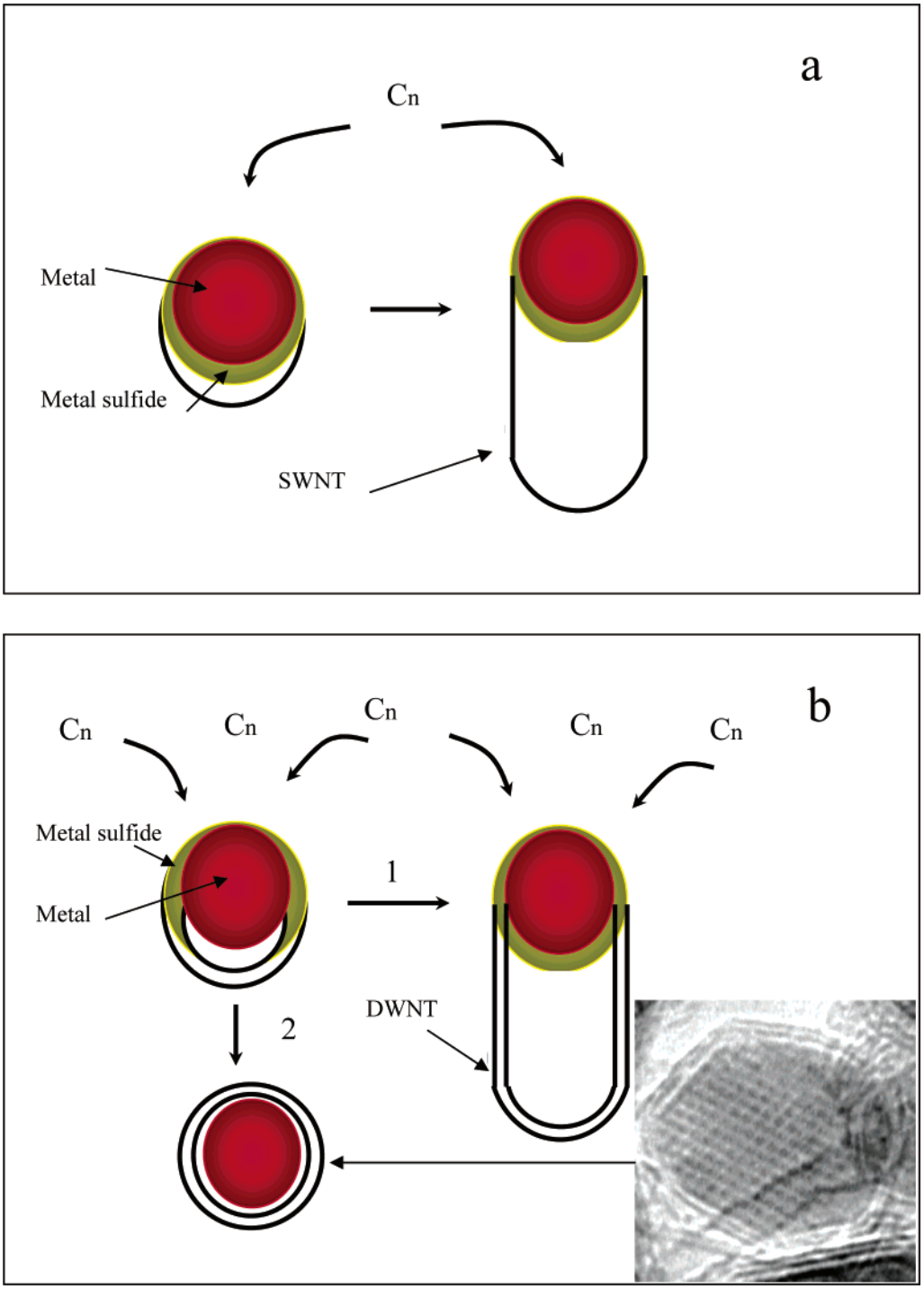

Figure 5. Schematic growth mechanisms for CNTs using the same metal−metal sulfide catalysts. (a) SWNTs formed in conventional arc discharge, and (b) DWNTs formed in our modified arc discharge.

carrier gas of carbon for the formation of DWNTs in conventional arc discharge.

The bowl-like cathode plays a crucial role in the formation of DWNTs in our H_2-free process. In fact, without using the bowl-like cathode, DWNTs could hardly be observed in the soot collected from both the chamber wall and electrode deposit, even using the same anode and discharge conditions.[16] Compared to the conventional arc discharge, the bowl-like cathode is able to enlarge the reaction zone and confine carbon clusters (C_n) in the reaction zone. The enlarged hot reaction zone may provide these carbon clusters more opportunities to form CNTs, while the enhanced concentration of carbon clusters increases the supply of nanotube precursors, which is an analogue of the addition of hydrogen for DWNTs, though the composition of the precursors is different.

The catalyst is another important issue for efficient transformation of carbon clusters into DWNTs. We noted that SWNTs, while not DWNTs, were the major product when metals only instead of metal sulfides were doped in the anode.[15] Metal sulfides are believed to be promoting elements for the formation of DWNTs in our modified arc-discharge method, while it has been shown that addition of sulfur to the catalyst Co could significantly increase the yield of SWNTs in the conventional arc discharge.[20] It was suggested that sulfur might affect the kinetics by removing terminating species from the growing ends of the tubes. Considering the stronger bonding strength of C−S

(714.1 kJ/mol) compared to that of C═C (614 kJ/mol), as well as the low melting point of metal sulfides (for example, NiS, mp 797 °C), we prefer to ascribe the yield enhancement and widening of tube diameters to the easier availability of active catalyst particles upon addition of sulfides. In fact, we have already confirmed the possibility of metal sulfide-catalyzed growth of CNTs.[21]

The growth models of SWNTs and DWNTs in the conventional and our modified arc discharge, using the same catalyst system, i.e., a mixture of metals and metal sulfides, are sketched in Figure 5a and 5b, respectively. In arc plasmas, both metals and metal sulfides are liquefied, and tend to form core/shell particles during their solidification process due to their different melting points. CNTs may be formed as tails of the nonequilibrium catalytic particles, while carbon clusters enter through the uncoated particle heads. In conventional arc-discharge, carbon clusters and catalysts are quickly dispersed out of the plasma region and quenched, and do not have enough time to reach the catalyst core portion. These carbon clusters are then rearranged and extruded only along the shell layer surface to form SWNTs, as shown in Figure 5a.

While in our modified arc discharge, with the presence of a higher concentration of carbon clusters, as well as an elongated reaction time due to the enlarged reaction zone, carbon clusters may dissolve in both core and shell portions of the catalyst particles. Carbon nanotube layers may precipitate out from both surfaces of core and shell portions, leading to the formation of DWNTs, as shown in Figure 5b. Double-layer carbon-coated particles, which are the major form of non-DWNT species in the modified arc-discharge soot, as shown in the inset of Figure 5b, are speculated to have the same origin as DWNTs.

In summary, high-quality DWNT super bundles have been abundantly synthesized by arc discharge in a bowl-like cathode without the addition of hydrogen. The cathode geometry and catalysts are found to be crucial factors for the formation of DWNTs. These high-quality DWNTs are highly resistive to oxidation and acid treatment, which is attributed to their being largely free of defects. These DWNTs may find applications in which highly ordered tube walls are critical, such as field emission with a long-term stability.

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