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Mass production of high-quality single-wall carbon nanotubes by electric-arc technique

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High-crystallinity single-wall carbon nanotubes (SWNTs) with the yield higher than 70 at% have been mass-produced by arc discharge evaporation of carbon electrode containing 1.0 at% Fe catalyst in H_2-Ar, or H_2-N_2 mixed gas. The as-grown SWNTs can be easily purified by a simple purification process (heating in air at 693 K, and then hydrochloric acid treatment). Moreover, Raman scattering studies indicate that the diameter distribution of SWNTs can be controlled by varying the mixing ratio of H_2 and N_2 gas. This new method for producing gram order of quantities of high-quality SWNTs will accelerate the studies of physical properties and practical applications of bulky SWNTs.

Key words: single-wall carbon nanotubes, electric-arc, Raman spectroscopy, HRTEM

1. INTRODUCTION

Single-wall carbon nanotubes (SWNTs) have attracted great attention due to their unique physical properties and potential applications [1,2]. One decade has been left after the discovery of SWNTs [3,4], a challenging problem toward wider applications of SWNTs is to develop a method for mass-production of high-crystallinity SWNTs with controlled diameters at high-yield and low cost. Because metallic catalysts have to be necessarily used for preparing SWNTs, it is also important that the catalyst nanoparticles coexisting with the as-grown SWNTs can be easily removed.

Three methods, laser ablation [5], arc discharge [6,7], and catalytic chemical vapor deposition (CCVD) [8-10] are generally used to synthesize SWNTs. However, high-crystallinity SWNTs can be only prepared by laser ablation or arc discharge method. It has been reported that high-yield SWNTs have been synthesized by laser ablation in argon gas using catalyst of a binary metal mixture [5]. A significant number of metallic catalyst nanoparticles remained in the product even after extensive refluxing in strong nitric acid [11-13], because the metallic nanoparticles are usually embedded in thick amorphous carbon.

Atomic hydrogen can selectively etches the impurities of carbon nanoparticles and amorphous carbon [14-16]. Liu *et al.* [17] and our group [18] have tried to prepare SWNTs by hydrogen arc discharge using a combination of Fe/Co/Ni as a catalyst, with S as a growth promoter. However, the excessive use of multiple metal mixtures as catalyst and the use of a growth promoter of S increased the defects of SWNTs themselves and hampered the purification of SWNTs.

Here, we show that high-yield and high-crystallinity SWNTs can be mass-produced by arc discharge evaporation in H_2-Ar, or H_2-N_2 mixture gas, using only a simple transition metal, iron, as catalyst. Moreover, the as-grown SWNTs can be easily purified to attain those with purity as high as 90 at%.

2. EXPERIMENTAL

SWNTs were prepared using an apparatus of dc arc discharge evaporation, where two electrodes were installed vertically. The lower carbon electrode (anode: 6 mm diameter, 100 mm length, ~ 4 g mass) containing 1.0 at% Fe catalyst was fixed at the center of a vacuum chamber. The upper, pure carbon electrode (cathode: 10 mm diameter, 100 mm length) was automatically fed by computer-controlled step motor so that a constant distance of ~ 2 mm between the two electrodes could be maintained. The vacuum chamber was linked to both H_2 and Ar (or N_2) gas lines through two mass-flow meters as well as a rotary pump to allow continuous flow (2000 sccm) of H_2-Ar (or H_2-N_2) ambient gas with various mixing ratios at 200 Torr. A dc arc discharge was generated by applying a current of 40–60 A, with synthesis time 3–20 min.

To purify as-grown SWNTs, a two-step purification process was used. First, 30 mg of as-grown SWNTs was heated in air at 693 K for 30 min. This resulted in ~ 15% weight loss. The residual material was then soaked in 36% hydrochloric acid (100 ml) for 12 h and centrifuged (11000 rpm, 30 min), leaving a black

sediment and a yellow-green supernatant liquid, which was decanted off. Since the sediment still contained substantially trapped acid, we repeatedly re-suspended the sediment in distilled water (twice) or ethanol (once), followed by centrifuging and decanting of the supernatant liquid. After the ethanol was evaporated using a hot plate at 473 K, the weight of purified SWNTs was measured to determine the mass yield ($m_{purified}/m_{as\text{-}grown}$), which was found to be typically 20–30%. As-grown and purified SWNTs were evaluated mainly by scanning electron microscopy (SEM, Topcon ABT-150F) equipped with an energy-dispersive X-ray analysis system (EDX, Horiba EMAX-5770W). High-resolution transmission electron microscopy (HRTEM, JEOL JEM-2010F) was also used. Raman spectra were recorded using a Raman spectrometer (Jobin Yvon, RAMANOR T64000) with 514.5 nm excitation (Ar^+-laser, ~ 10^6 W/cm^2).

3. RESULTS

3.1 SWNTs prepared by H_2-Ar arc discharge

Figure 1a shows an optical photograph of SWNT web, which was prepared by arc discharge evaporation (dc current, 50 A) of a carbon electrode containing 1 at% Fe in 40%H_2-60% Ar

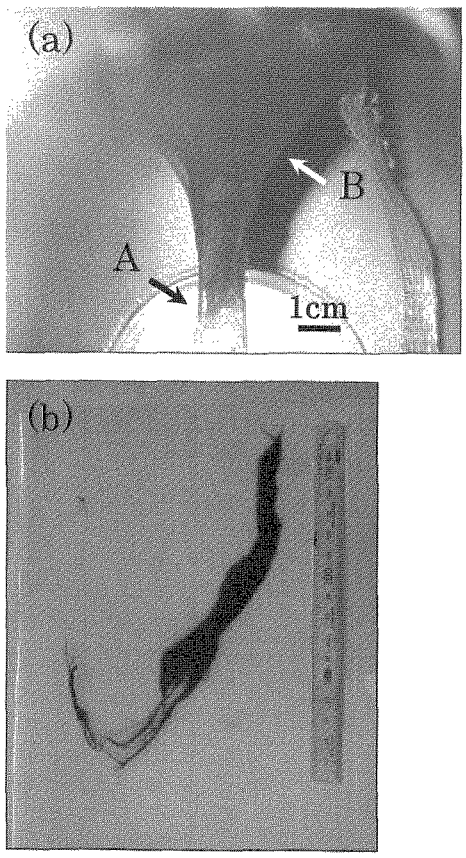

Fig. 1. (a) Optical photograph of SWNT web. Arrows A and B show the starting point and black thick region of SWNT web, respectively. (b) Optical photograph of a macroscopic SWNT belt. mixture gas under pressure of 200 Torr for 3 min. Arrow A shows the starting point of SWNT web, near the bottom end of the cathode, and arrow B indicates the black region of thick web. The web is so long and strong that it can be collected and manipulated easily using tweezers. It is possible to rip the web easily along the A–B direction generating small sound, which perhaps originates from the breaking of individual SWNTs, and even reel a long thread (2–10 cm long, ~ 0.1 mm diameter) of the SWNT web. However, it is difficult to break the web perpendicularly to the A–B direction. SEM observation reveals that the web consists of abundant SWNTs or SWNT bundles, which are roughly aligned along the A–B direction. Obviously, thermal convection of the H_2-Ar mixture gas during the production process plays an important role in the formation of a macroscopic oriented SWNT web. By drawing the SWNT web along the A–B direction, a macroscopic SWNT belt with a length of 150 mm (see Fig. 1b) can be obtained. The production rate of SWNT web can reach 7.7 mg/min [19], which is much higher than that produced by laser ablation [5,11] and CCVD [9].

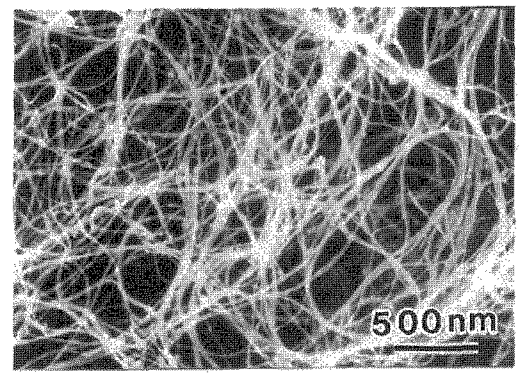

Fig. 2. Typical SEM image of as-grown SWNTs prepared by H_2-Ar arc discharge.

A characteristic SEM image of SWNT web is shown in Fig. 2. Numerous entangled SWNT bundles can be seen, and the SWNT bundles are so long that their end can not be found in the area of this figure. In Fig. 3a, we show a typical low-magnification TEM image of as-grown SWNTs. Long SWNT bundles with various diameters of 10–40 nm can be seen in abundance, and some Fe catalyst nanoparticles attached to the surface of SWNT bundles can be observed as dark dots. HRTEM observations, the inset in Fig. 3a, indicate that as-grown SWNTs possess high crystallinity and clean surfaces, and have a wide diameter distribution, 0.8–2.5 nm, which has been also confirmed by Raman spectroscopic studies [19]. The Fe catalyst nanoparticles are nearly spherical, with diameters of 2–10 nm, and are embedded in a few layers of discontinuous graphene sheets. The arrow in the inset of Fig. 3a shows a 5-nm-diameter Fe particle wrapped by two layers of discontinuous graphene sheets. X-ray diffraction analyses reveal that α(bcc)-Fe is

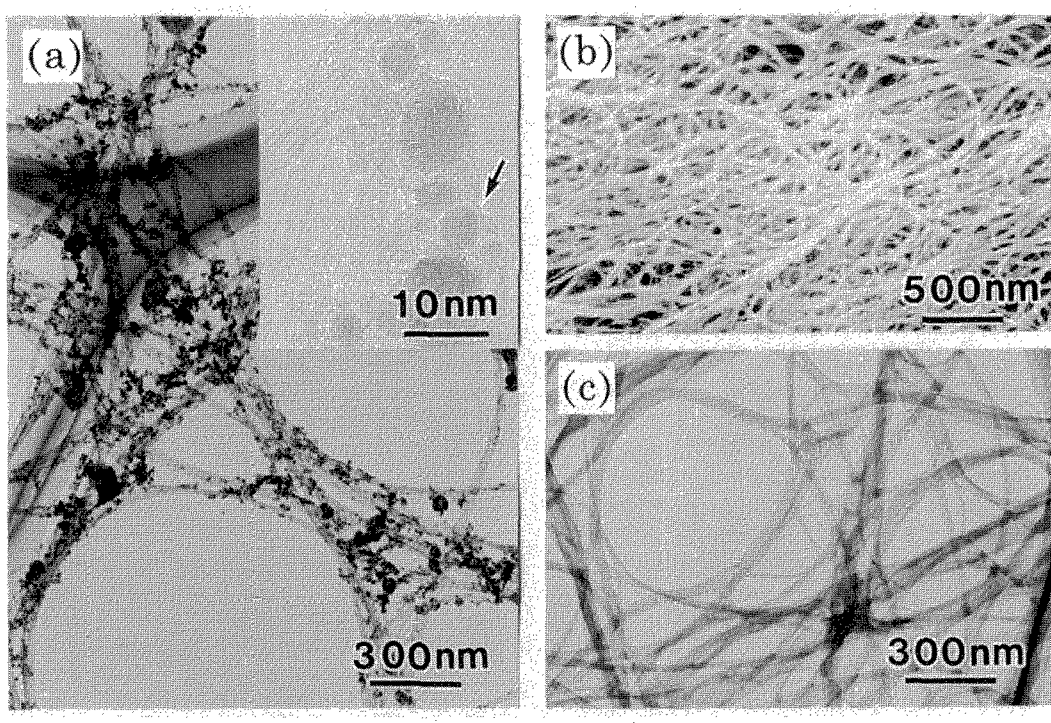

Fig. 3. (a) Low-magnification TEM image of as-grown SWNTs by H_2-Ar arc discharge. The inset in Fig. 3a is a HRTEM image of as-grown SWNTs, and the arrow shows a 5-nm-diameter Fe particle wrapped by only two layers of discontinuous graphene sheets. (b) SEM image of purified SWNTs. (c) Low-magnification TEM image of purified SWNTs.

the major phase in these Fe catalyst nanoparticles, as inferred by the presence of a strong 110 diffraction peak from α-Fe. Although only slight amorphous carbon and no fullerenes exist, a few carbon nanoparticles and pieces of graphitic carbon are also observed as impurities. EDX analyses indicate that the main elements are C (88.62 at%) and Fe (9.43 at%), with a small amount of O (1.60 at%), as shown in Table I. From SEM, TEM observations and EDX analysis, the as-grown SWNT purity is estimated to be higher than 70 at%.

Table I Energy-dispersive X-ray analysis results.

Elements	As-grown (at.%)	Heated (at.%)	Purified (at.%)
C	88.62	78.38	95.58
Fe	9.43	9.79	0.05
O	1.60	11.43	2.55
Cl	-----	-----	1.06

Figure 3b shows a typical SEM image of purified SWNTs, and the morphology of SWNTs is very similar to "buckypaper" [11]. In Fig. 3c, we show a low-magnification TEM image of purified SWNTs. No Fe catalyst nanoparticles can be found in the area of this figure. The HRTEM investigation reveals that the mild treatment with hydrochloric acid does not damage SWNTs, so that the cleanliness of the SWNT surface is maintained. EDX analyses indicate that the percentage of Fe decreases from 9.43 to 0.05 at% by purification, that of C increases from 88.62 to 95.58 at% (see Table I). Remaining impurities are O (2.55 at%), Cl (1.06 at%), and a few other forms of carbon (carbon nanoparticles, pieces of graphitic carbon). The purity of purified SWNTs is estimated to be higher than 90 at%. The high reactivity of Fe catalyst nanoparticles and the presence of very thin layers of discontinuous graphene sheets attached to their surface are crucial in the present purification process. From Table I, it is clear that after heating in air at 693 K for 30 min, the content of C decreases from 88.62 to 78.38 at%, and that of O increases from 1.60 to 11.43 at%. This means that the heat treatment completely removes the discontinuous graphene sheets (perhaps by the catalyzed etching reaction of oxygen by the entrapped α-Fe catalyst nanoparticles). Moreover, the heat treatment transforms α-Fe into iron oxide, which can be easily washed out by mild hydrochloric acid.

It is well known that Fe element is the cheapest one of the transition metals and is an effective catalyst for forming graphite, carbon fiber and SWNTs in CCVD [8,9]. However, the high solubility of Fe in graphite and the high reactivity of Fe with oxygen cause self-deactivation, which hampers the formation of SWNTs. Therefore, a reducing agent, such as H_2 or CO, is essential for mass-production of high-purity SWNTs. In the case mentioned above,

we use H_2 gas as a reducing agent and Ar gas for stabilizing the arc plasma. The atomic hydrogen in reactive H_2-Ar arc discharge plasma can promote the vaporization of carbon anode including Fe catalyst and keep the Fe catalyst active. Moreover, hydrogen also hinders fullerenes from growing and selectively etches the amorphous carbon attached to the surface of Fe catalyst nanoparticles or SWNTs (see Fig. 3a). This serves as an in situ purification process and improves the purity of SWNTs. Because the carbon anode is evaporated in the form of hydrocarbon fragments, radicals and molecules, the H_2-Ar arc discharge process is analogous to that of CCVD [20]. However, the high temperature and steep temperature gradient is different with the case of CCVD. The high temperature applied in the use of a single Fe catalyst favors the growth of high-crystallinity SWNTs. The steep temperature gradient hampers the formation of multiwalled carbon nanotubes (MWNTs) that is usually observed in the SWNT samples obtained by CCVD [8].

3.2 SWNTs prepared by H_2-N_2 arc discharge

H_2-N_2 arc plasma possesses higher enthalpy than that of H_2-Ar arc plasma. As carbon electrode including 1.0 at% Fe catalyst was evaporated by H_2-N_2 arc discharge, much carbon smoke occurs compared with the case of H_2-Ar arc discharge. We have obtained a SWNT web (length, 20 cm; mass, 76 mg) by dc arc discharge evaporation (arc current, 50 A; evaporation time, 6 min) of carbon electrode containing 1.0 at% Fe in 40%H_2-60%N_2 mixture gas under a pressure of 200 Torr. This gives a production rate of ~ 13 mg/min, which value is twice than that by H_2-Ar arc discharge. When a whole C-Fe anode was evaporated for 20 min, a huge SWNT web with the mass of more than 200 mg could be produced. Therefore, it is easy to produce SWNT web in gram quantities in a few hours using the present production apparatus. In Fig. 4, we show an optical photograph of 1 gram SWNT web bottled in 1 liter plastic bin.

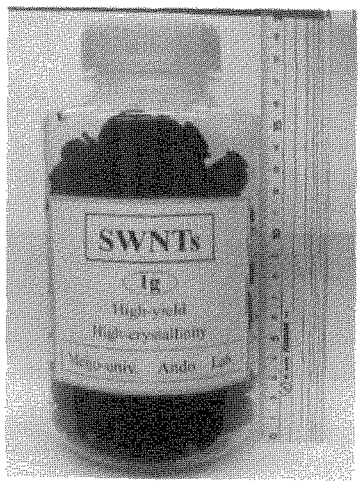

Fig. 4. Optical photograph of 1 gram as-grown SWNT bottled in 1 liter plastic bin.

It should be noted that when atomic hydrogen in H_2-N_2 (or H_2-Ar) arc discharge selectively etch the amorphous carbon attached on the surface of Fe catalyst nanoparticles or SWNTs, gaseous hydrocarbons will be formed. If mass-production of SWNTs was carried out in a sealing chamber filled with these mixture gas, the composition of ambient gas in the chamber would change with the progress of arc discharge evaporation of anode. Therefore, mass-production experiments of SWNTs have been done under H_2-N_2 (or H_2-Ar) mixture gas flow. With the help of the computer-controlled feeder, we can make the as-grown SWNTs to have the same quality.

Figures 5a and 5b illustrate the Raman spectra of SWNT webs prepared by arc discharge in H_2-N_2 mixed gas in total pressure 200 Torr with various mixing ratios, 60%H_2-40%N_2 indicated by A, 50%H_2-50%N_2 by B, 40%H_2-60%N_2 by C, 30%H_2-70%N_2 by D. In Fig. 5b, the multiple splitting of G-band modes (1550–1620 cm^{-1}) can be clearly seen, and a low intensity of the D-band at 1340 cm^{-1} indicates the less amorphous carbon and high-crystallinity of as-grown SWNTs. In low-frequency region, 100–300 cm^{-1}, four peaks of radial breathing modes (RBMs) can be observed at 183, 243, 258 and 265 cm^{-1}, as shown in Fig. 5a. RBM frequencies ω (cm^{-1}) are related with the SWNTs diameter d (nm), and they are affected by van der Waals interaction when SWNTs are in bundles. Using the correlation [21], $d = 224/(\omega\text{-}14)$, the RBM peak at 265 cm^{-1} should originate from the SWNTs with 0.89 nm in diameter, and the RBM peaks at 183, 243 and 258 cm^{-1} can be assigned to the SWNTs with diameters of 1.33, 0.98 and 0.92 nm. Therefore, the as-grown SWNTs have a diameter distribution, 0.89–1.33 nm. This diameter distribution shifts to much thinner region than that of SWNTs prepared by H_2-Ar arc discharge.

It has been shown [22] that as using laser ablation to prepare SWNTs, only the SWNTs grown in N_2 gas have thinner diameter. From Fig. 5a, it can be seen that the peak at 265 cm^{-1} becomes stronger, and the others become weaker when the partial pressure of N_2 is increased. This means that the diameter distribution of SWNTs can be controlled by varying the mixing ratio of H_2 and N_2 gas. When the mixing ratio of H_2 and N_2 gas is 3:7 (see D in Fig.5a), very thin SWNTs with 0.89 nm in diameter can be selectively prepared. This 0.89 nm SWNT may be assigned to metallic SWNT, based on the Kataura plot [23]. The reason why the very thin SWNTs can be grown in high partial pressure of N_2 is probably related to the cooling process of vaporized carbon by collision with each other.

3.3 Tensile strength and *I-V* characteristics of macroscopic SWNT belt

We have measured the tensile strength of a 4-mm-wide belt, and found that this SWNT belt can withstand a pulling force of 1 N. In order to

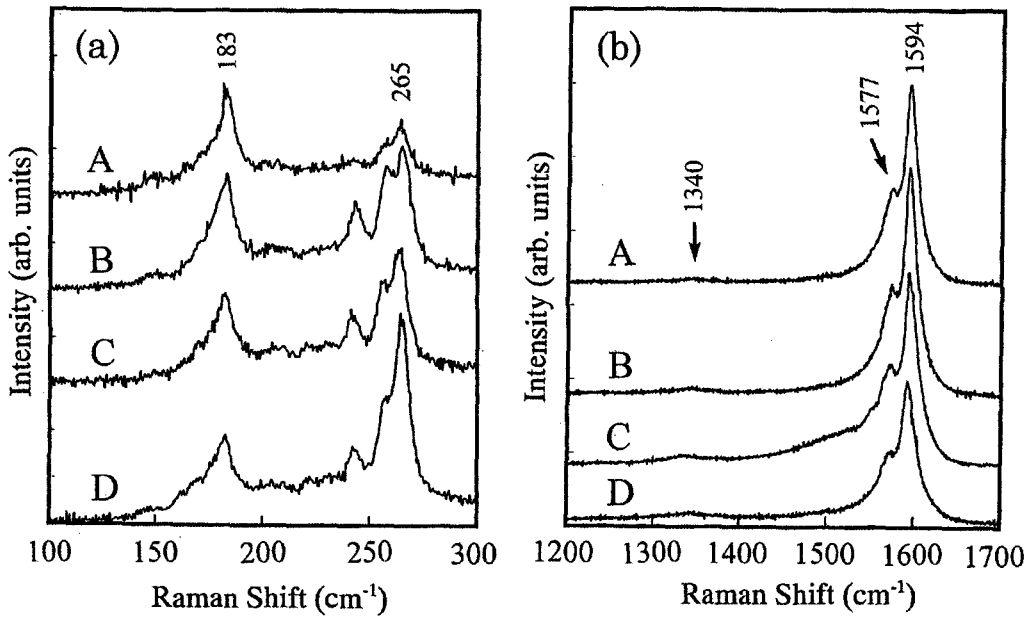

Fig. 5. Raman spectra of SWNT webs prepared by arc discharge in H_2-N_2 ambient gas of various mixing ratios, 60%H_2-40%N_2 indicated by A, 50%H_2-50%N_2 by B, 40%H_2-60%N_2 by C, 30%H_2-70%N_2 by D, at total pressure 200 Torr. (a) Low-frequency region, 100–300 cm^{-1}. (b) High-frequency region, 1200–1700 cm^{-1}.

Measure *I-V* characteristics in vacuum (2×10^{-5} Torr), a SWNT belt (22 mm length, 4 mm width, and 0.02 mm thickness) with a mass of 2.3 mg was used as the sample in the two-probe method. When a dc voltage of 40 V was applied, a strong current of 1.5 A was observed, and the SWNT belt emitted strong incandescent light. Under the assumption that the SWNT belt has an identical cross section area of 8×10^{-4} cm^2, the current density and electric resistivity are calculated to be 2×10^3 A/ cm^2 and 1×10^{-2} Ωcm, respectively.

4. DISCUSSIONS

It has been reported [24] that aligned super bundles (> 20 cm length) of SWNTs can be grown on top of a bowl-shaped cathode surface by helium arc discharge, and high-purity SWNTs can also be prepared as a "collar" around the cathode deposit [6]. However, except for the SWNTs collected from these restricted positions, the rubbery soot condensed on the chamber walls usually contains a large quantity of impurities, such as amorphous carbon, metallic catalyst nanoparticles, and fullerene. In the present experiments, the atomic hydrogen in arc discharge plasma selectively etches the amorphous carbon attached to the surface of Fe catalyst nanoparticles or SWNTs. This serves as an in situ purification process and dramatically improves the purity of SWNTs grown in the vacuum chamber. However, the yield of production, i.e. the ratios of the obtained SWNT mass to the evaporated anode mass, is only ~ 10%. Most of the evaporated carbon from anode seems to become gaseous hydrocarbons and cathode deposit. It has been found that more than half part of evaporated carbon from anode becomes the cathode deposit, which does not contain SWNTs. For eliminating the cathode deposit, application of ac arc discharge may be a better choice. It has been shown that no carbonaceous deposit is formed on either of the two electrodes [25]. Although some of the evaporated carbon will still form gaseous hydrocarbons due to etching effect of H_2, it can be expected that the use of ac arc discharge will significantly increase the yield of production.

From our earlier experience in the preparation of high-quality MWNTs by hydrogen arc discharge [14,15], we note that atomic hydrogen selectively etches the impurities of carbon nanoparticles and amorphous carbon. Moreover, atomic hydrogen terminates the dangling carbon bonds at the growing edge of MWNTs, keeping them open [16]. Since some carbon species are trapped inside SWNTs, we believe that hydrogen can also terminate dangling carbon bonds at the growing edge of SWNTs, thereby preventing the end from closing. We think that our results should be explained using "scooter" mechanism [5], where Ni or Co atom is replaced by Fe atom, because the Fe catalyst nanoparticles are always attached on the surface of SWNTs.

It was experimentally confirmed that other simple transition metals, Co or Ni, and their mixtures (Fe/Co, Fe/Ni, Co/Ni, Fe/Co/Ni) were not effective catalysts for preparing SWNTs by the present arc discharge method in H_2-Ar (or H_2-N_2) mixture gas. Although addition of a growth promoter, sulfur, can activate these metal catalysts [18], this will result in an increase in the diameter

and amount of defects of SWNTs. On the other hand, the instability of arc discharge plasma in pure H_2 gas is disadvantageous for the mass-production with high purity of SWNTs. Addition of He gas into H_2 gas may be effective for stabilizing an arc discharge plasma. However, no SWNTs have been produced in the soot obtained by H_2-He arc discharge. From these results, it may be understood that arc plasma with too high temperature is not proper to produce SWNTs.

5. CONCLUSIONS

The present study provides a new method for producing gram quantities of high-quality SWNTs by H_2-Ar or H_2-N_2 arc discharge evaporation of carbon electrode containing only Fe catalyst. The diameter distribution of SWNTs can be controlled by varying the mixing ratio between H_2 and N_2 gas. By exploiting the etching effects of hydrogen and the high reactivity of Fe, we are able to remove coexisting Fe catalyst nanoparticles and obtain SWNTs with purity greater than 90 at%. The use of electric-arc technique for commercial-scale synthesis of high-quality SWNTs is foreseen. In addition, studies of the physical properties and practical applications of bulky SWNTs will be accelerated.

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