# LARGE-SCALE PRODUCTION OF HIGH-YIELD SINGLE-WALL CARBON NANOTUBES BY $H_2$-$N_2$ ARC DISCHARGE

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## Introduction

One decade has been left after the discovery of single-wall carbon nanotubes (SWNTs). A challenging problem toward wider applications of SWNTs is to develop a method for mass-production of high crystallinity SWNTs at high-yield and low cost. Moreover, it is also important that the produced SWNTs can be easily purified. Laser ablation [1], arc discharge [2], and catalytic chemical vapor deposition [3] are generally used to prepare SWNTs. However, SWNTs with high crystallinity can be prepared only by laser ablation or arc discharge. Using a single metal catalyst of Fe, a macroscopic oriented web of SWNTs has been prepared by $H_2$-Ar arc discharge [4]. Here, we report the large-scale production of high-quality SWNTs by $H_2$-$N_2$ arc discharge. We also show that as-grown SWNTs can be easily purified to attain those with purity as high as > 90 at.%.

## Experimental

High-yield 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 long, ~ 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 long) was adjustable to maintain a constant distance of ~ 2 mm between the two electrodes. A dc arc discharge was generated by applying 40~70 A in $H_2$-$N_2$ atmosphere of various mixing ratios at 100~500 Torr. Typical synthesis times were ~ 15 min.

A two-step purification process was used to purify as-grown SWNTs. First, 30 mg of as-grown SWNTs was heated in air at 693 K for 30 min. The residual material was then soaked in 36% hydrochloric acid (100 ml) for 12 h and centrifuged, leaving black sediment and yellow-green supernatant liquid, which was decanted off. We repeatedly re-suspended the sediment in distilled water (twice) or ethanol (once), followed by centrifuging and decanting of the supernatant liquid. 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), and by high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2010F). Raman spectra were recorded using a Raman spectrometer (Jobin Yvon, RAMANOR T64000) with 514.5 nm excitation.

## Results and Discussion

Figure 1 shows an optical photograph of SWNT web, which was produced 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 SWNT web has a length of 20 cm and a mass of 76 mg, giving high production rate of ~ 13 mg/min. 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 obtained. $H_2$-$N_2$ arc plasma possesses higher enthalpy than that of $H_2$-Ar arc plasma [4]. This promotes the evaporation of C-Fe electrode, and increases the production rate of SWNTs. SEM observation shows that the web consists of abundant SWNTs or SWNT bundles, as shown in Fig. 2. The SWNT purity is estimated by SEM and EDX to be higher than 70 at.%.

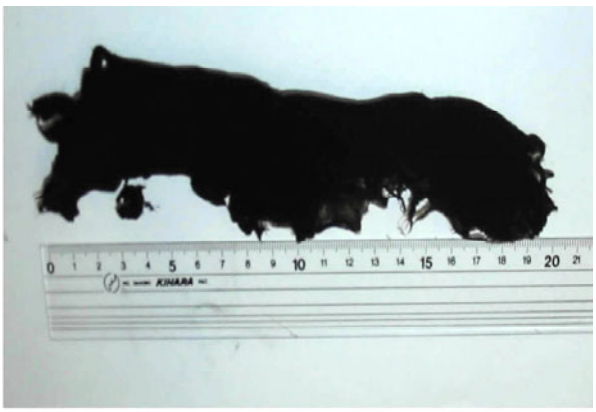


Figure 1. Optical photograph of SWNT web

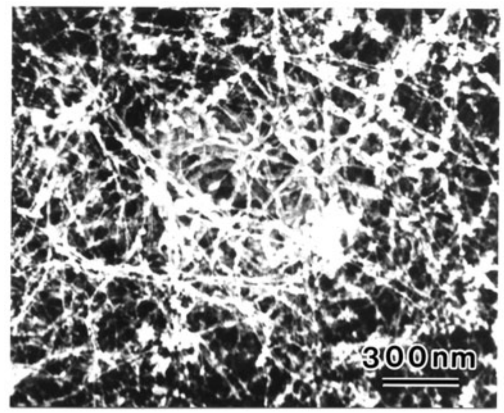


Figure 2. SEM image of SWNTs

The investigations of HRTEM indicate that SWNTs possess high crystallinity and "clean" surface. Some Fe catalyst nanoparticles attach to the surface of SWNT bundles, and they are embedded in very thin amorphous carbon. The amount of Fe element is ~ 10 at.% by EDX analyses. Obviously, the high temperature of arc discharge favors the growth of high crystallinity SWNTs, and hydrogen atoms etch amorphous carbon during the formation of SWNTs.

Raman scattering technique can be also used to characterize the crystallinity and to determine the diameter of SWNTs. Figure 3 shows a Raman spectrum of SWNT web in high-frequency region, 1200–1700 $cm^{-1}$, and the inset shows the

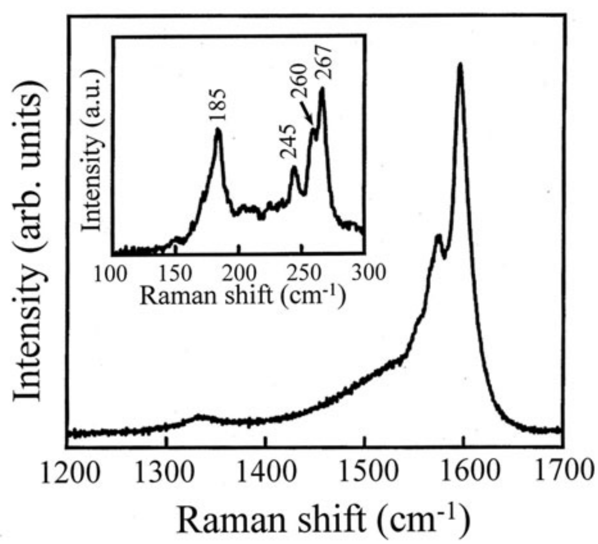


Figure 3. Raman spectrum of SWNTs

Raman spectrum in low-frequency region, 100–300 $cm^{-1}$. The multiple splitting of *G*-band modes (1500–1700 $cm^{-1}$) can be clearly seen, and a low intensity of the *D*-band at 1340 $cm^{-1}$ indicates the high purity and high crystallinity of as-grown SWNTs. In low-frequency region, strong peaks of radial breathing modes (RBMs) can be observed. Using the correlation between SWNT diameter *d* (nm) and RBM frequency ω($cm^{-1}$): $d = 224/(\omega-14)$, the strong RBM peak at 267 $cm^{-1}$, which can be assigned to metallic SWNTs, should originate from the SWNTs with 0.8 nm in diameter. The as-grown SWNTs have a distribution with a wider diameter, 0.8–2.0 nm.

Figure 4 shows a low-magnification TEM image of purified SWNTs, and few Fe catalyst nanoparticle can be found. EDX analyses indicate that the percentage of Fe decreases to < 0.5 at.%. The high reactivity of Fe catalyst nanoparticles and the presence of very thin amorphous carbon attached to their surface are crucial in the present purification process. Heating in air removes the amorphous carbon and also changes Fe into iron oxide, which can be easily washed out by mild hydrochloric acid. The purified SWNTs have purity higher than 90 at.%.

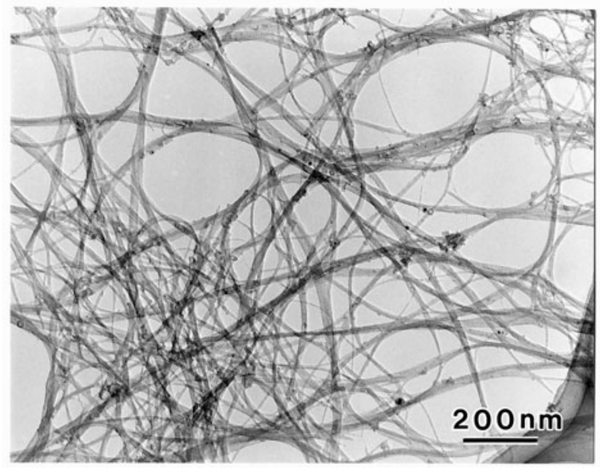

Figure 4. TEM image of purified SWNTs

**Conclusions**

The present study provides a new method for producing gram quantities of high quality SWNTs by $H_2$-$N_2$ arc discharge evaporation of carbon electrode containing only Fe catalyst. Mass-production of high crystallinity SWNTs will accelerate the studies of physical properties of bulky SWNTs, and their practical applications for field emission, electronics, compound materials etc.

**References**

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