Appl. Phys. A 76, 285–286 (2003)
DOI: 10.1007/s00339-002-1718-8

Applied Physics A
Materials Science & Processing

S.-H. JUNG[1]
M.-R. KIM[1]
S.-H. JEONG[1]
S.-U. KIM[1]
O.-J. LEE[1]
K.-H. LEE[1,✉]
J.-H. SUH[2]
C.-K. PARK[2]

High-yield synthesis of multi-walled carbon nanotubes by arc discharge in liquid nitrogen

[1] Department of Chemical Engineering, Computer & Electrical Engineering Division, Pohang University of Science and Technology (POSTECH), Pohang 790-784, Korea
[2] Department of Materials Science and Engineering, Pohang University of Science and Technology (POSTECH), Pohang 790-784, Korea

Received: 5 July 2002/Accepted: 8 July 2002
Published online: 10 September 2002 •

ABSTRACT Synthesis of multi-walled carbon nanotubes (MWNTs) by arc discharge in liquid nitrogen is reported. As liquid nitrogen substituted both vacuum and cooling systems, high-quality MWNTs were produced at a low cost. The content of the MWNTs can be as high as 70% of the reaction product. Auger-spectroscopy analysis revealed that no nitrogen is incorporated in the MWNTs. This method can be an economical route for the mass production of highly crystalline MWNTs.

PACS 81.01.O; 82.80.P; 82.80.G

Carbon nanotubes (CNTs) are thin and hollow cylinders composed of carbon atoms. Because CNTs can realize new material properties required in nanotechnology, the importance of basic research has been highlighted [1, 2]. The availability of CNTs in mass quantity, however, is equally important for more conventional applications such as carbon electrodes of batteries and of fuel cells or super-strong composites. There are various synthesis methods for the production of CNTs, including electric arc discharge, laser ablation, chemical vapor deposition, catalytic decomposition of hydrocarbons, solar energy, and electrolysis [3]. While various methods can produce CNTs of different qualities, electric arc discharge is advantageous for obtaining highly crystalline CNTs. The conventional arc discharge method, however, requires a complicated vacuum apparatus with an efficient cooling system. Olk [4] and Ishigami et al. [5] proposed a modified method for the synthesis of CNTs, in which liquid nitrogen was filled in the arc discharge chamber. Liquid nitrogen prevents the electrodes from contamination with unwanted gases and effectively lowers the temperature of the electrodes. Moreover, CNTs do not stick to the wall of the chamber, so that a clean sample of CNTs can be obtained. In this letter, we report that the content of the CNTs in the reaction products can be as high as 70% with an arc discharge in liquid nitrogen, so that this method can be an economical route for the mass production of highly crystalline CNTs.

Multi-walled carbon nanotubes (MWNTs) were produced using the arc discharge technique, in which a vacuum is replaced with liquid nitrogen. Figure 1a shows a schematic drawing of the arc discharge apparatus used in our experiments. Direct current was supplied to the apparatus using a power supply. The anode is a pure carbon rod of 8-mm diameter and the cathode is a pure carbon rod of 10-mm diameter. The Dewar flask was filled with liquid nitrogen and the electrode assembly was immersed in nitrogen. The voltage was set between 20 V and 27.5 V, and then the distance between the two electrodes was adjusted until arc discharge occurred between the anode and the cathode. Arc discharge occurred as the distance between the electrodes became less than 1 mm, and a current of up to 80 A flowed between the electrodes. Carbon was evaporated from the anode and was deposited to the cathode. When the arc discharge was over, carbon materials deposited on the cathode were recovered for further analysis after removing liquid nitrogen. Figure 1b shows the carbon deposit on the cathode.

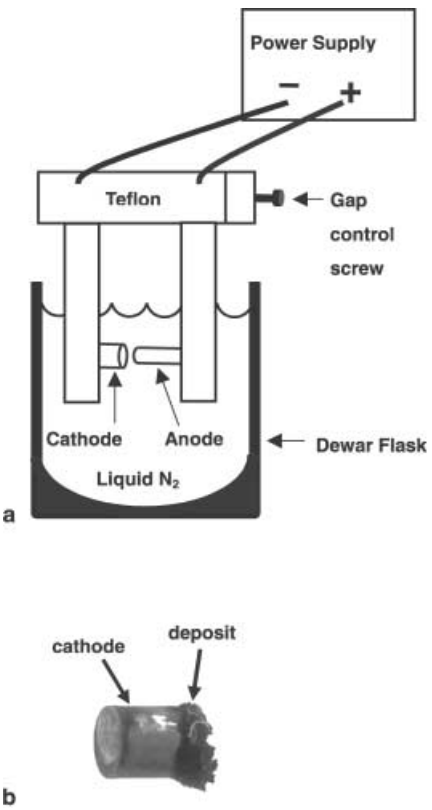

FIGURE 1 **a** Schematic drawing of the arc discharge apparatus. **b** Side image of the MWNTs-rich material deposited on the cathode

A field emission scanning electron microscope (FE-SEM, Hitachi S-4200) was used to observe the morphology of the carbon deposit. The specimens were dried in a desiccator for at least an hour and then coated with Pt prior to FE-SEM observation. The acceleration

✉ Fax: +82-54/279-8298, E-mail: ce20047@postech.ac.kr

voltage was 8 kV. The wall structure of a MWNT was examined by a transmission electron microscope (TEM, Philips CM 20). As-synthesized carbon deposit was ground using a mortar, dispersed in ethanol, and then transferred onto a TEM grid. TEM observation was performed at 200 keV. The surface morphology and the wall structure of the carbon deposit are shown in Fig. 2.

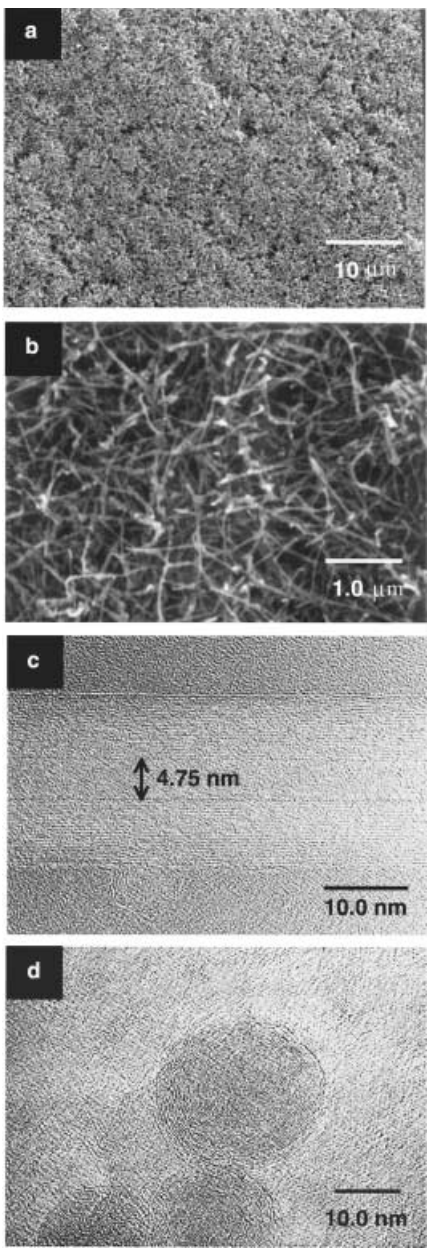

FIGURE 2 MWNTs synthesized at 27.5 V by arc discharge in liquid nitrogen. **a** Low magnification SEM image. **b** High magnification SEM image. **c** TEM image of a MWNT. **d** TEM image of a carbon onion particle

Fibrous structures as well as round particles are observed in the SEM image as shown in Fig. 2a and b. A TEM investigation of Fig. 2c and d reveals that they are MWNTs and carbon onions [6]. Amorphous carbon particles are also present. The particular sample shown in Fig. 2 was synthesized at 27.5 V DC. It is obvious that the amount of MWNTs is much larger than that of carbon particles. The diameter of the MWNTs is in the range of 20–50 nm and the length of the MWNTs is up to a few μm.

Crystallinity of the carbon deposit was examined by a Raman spectroscope (Renishaw Raman System 3000). Figure 3 shows the first-order and the second-order peaks of the Raman spectra of the carbon deposit. The first-order peak (1575.2 cm^{-1}, G-band) represents a graphite-sheet structure and the disorder-induced peak (1331.6 cm^{-1}, D-band) represents a defect structure. The integrated intensity ratio calculated from the areas of the peaks, $I_{1331.6\ cm^{-1}}/I_{1575.2\ cm^{-1}}$, is 0.4204. The area of a peak was calculated from the product of the peak height and the half-peak width. This value is roughly equivalent to the amount of the MWNTs of 70% of the sample, provided that the G-band mainly comes from MWNTs. This estimation can be supported by the SEM observation.

We have analyzed the atomic composition of the surface and the inner part of the carbon deposit using Auger electron spectroscopy (Perkin-Elmer PHI 600 scanning Auger multiprobe). As shown in Fig. 4a, only one sharp peak exists at 270 eV, which is due to the pure carbon element [7]. Figure 4b confirmed

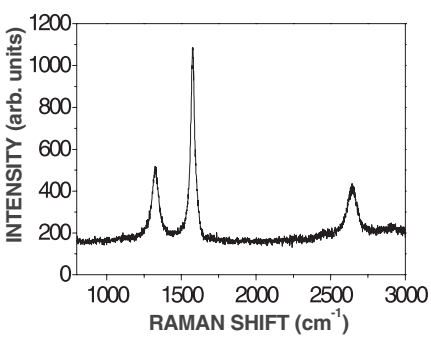

FIGURE 3 Raman spectrum of the carbon deposit synthesized at 27.5 V by arc discharge in liquid nitrogen

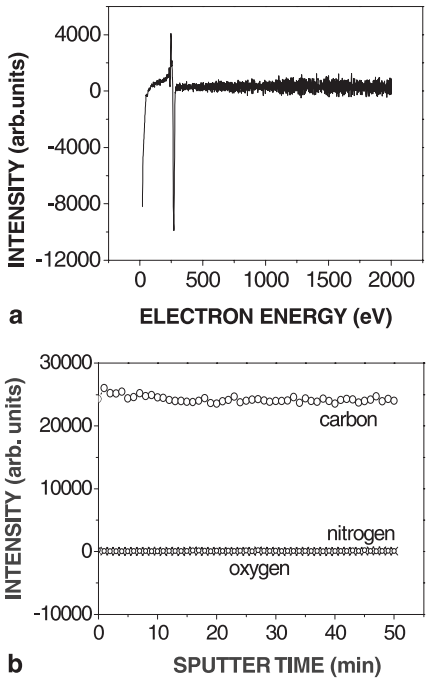

FIGURE 4 Auger electron spectroscopy of the carbon deposit synthesized at 27.5 V by arc discharge in liquid nitrogen. **a** The first derivative of the Raman spectrum. **b** Depth profile of elements of the carbon deposit (excavation rate : 24 Å/min)

that there is no composition change with the depth of the carbon deposit and the inner part of the deposit is composed of pure carbon. One should note that MWNTs synthesized by arc discharge in liquid nitrogen do not contain any nitrogen.

In conclusion, MWNTs can be synthesized at high purity by arc discharge in liquid nitrogen. Since the apparatus and its operation are simple, and the scale-up is straightforward, this technique can be a practical option for the large-scale synthesis of MWNTs with high purity. There is a strong possibility to synthesize SWNTs with the identical apparatus with catalyst-containing graphite rods.

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