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# Multiwalled Carbon Nanotubes Produced by Direct-Current Arc Discharge in Foam

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The arc discharge method was the first method developed for producing multiwalled carbon nanotubes (MWNTs). Generally, this method is carried out in low-pressure He gas or other neutral atmospheres, which requires the use of sealed reaction chambers and vacuum equipment. At high temperatures, the method produces well-graphitized MWNTs. Here, we report the first successful trial of the facile synthesis of high-quality MWNTs in a high yield using the arc discharge method in foam. [DOI: 10.1380/ejssnt.2008.167]

Keywords: Multiwalled carbon nanotube; DC arc discharge; Foam

## I. INTRODUCTION

High-quality crystalline multiwalled carbon nanotubes (MWNTs) have been generated by the arc discharge method in gas phase; they were first prepared by Ebbesen and Ajayan in helium gas phase [1]. Generally, the arc discharge method is carried out in low-pressure He gas or other neutral atmospheres, which requires the use of sealed reaction chambers and vacuum equipment. To eliminate this requirement, arc discharge in liquid phase has been investigated by some groups as an effective method of CNT formation [2–5]. For example, Sano *et al.* have described the formation of carbon nano-onions using DC arc discharge in water [6, 7]. Moreover, Lange *et al.* have generated CNTs by arc discharge in water between pure graphite electrodes [8]. It is interesting to study the arc discharge process in liquid phase. Such a method has the advantages of not requiring a vacuum system because it is not carried out in gas phase, and of using simple cost-effective approaches to CNT formation. These advantages will not only promote fundamental research but will also foster industrial applications of CNTs.

In this study, we examine the arc discharge method in the gas and liquid phases to determine the more cost-effective means of achieving a high yield of highly crystalline CNTs. We used the foam phase for arc discharge, which is the critical phase between gas and liquid. We used a non-vacuum system, thereby eliminating almost all the complex and expensive machinery usually required in the arc discharge method. The technique used in this study facilitated the collection of fine particles including CNT clusters with a high yield of MWNTs from the foam surface.

## II. EXPERIMENTS

A schematic of the apparatus for arc discharge in foam is shown in Fig. 1. The equipment is composed of a chamber, graphite electrodes as the cathode and anode, and a DC power supply (Kenwood: PD36-20A). We used beer foam, which is a multiphase flow of liquid and gas, as the environment for the gas discharge.

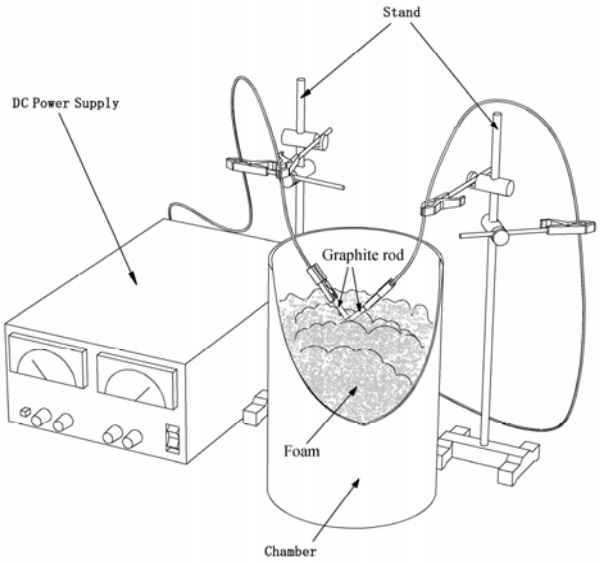


FIG. 1: Schematic of the experimental setup for MWNT preparation by the DC arc discharge method in foam.

It is known that foam generally has the ability to attract substances floating inside liquids. More specifically, hydrophobic substances, such as solid particles, are attracted to foam, whereas hydrophilic substances are not. There are selective separation methods based on floatation which utilize this difference in the attractability to foam, for example, the separation of target minerals from unnecessary ones. Furthermore, in everyday life, the principle according to which dirt particles are attracted to foam when doing laundry, as well as the principle where the impurities released while boiling certain foods float and become attached, are all related to the property of foam to "attract solid particles floating inside liquids".

Similarly, beer froth comprises liquid membranes that include proteins, and the structure allows liquid to be captured between the surfaces of two membranes made of proteins. Therefore, beer froth has the effect of attracting and agglomerating astringent impurity compounds, and this can be felt as astringent taste. Consequently, by utilizing the agglomerating effect of beer froth as well as the property of nanotubes, which are hydrophobic in nature, to generate attraction to the film of beer froth due to the Coulomb interaction, we were able to investigate both the coupling and the decoupling of nanotubes at the

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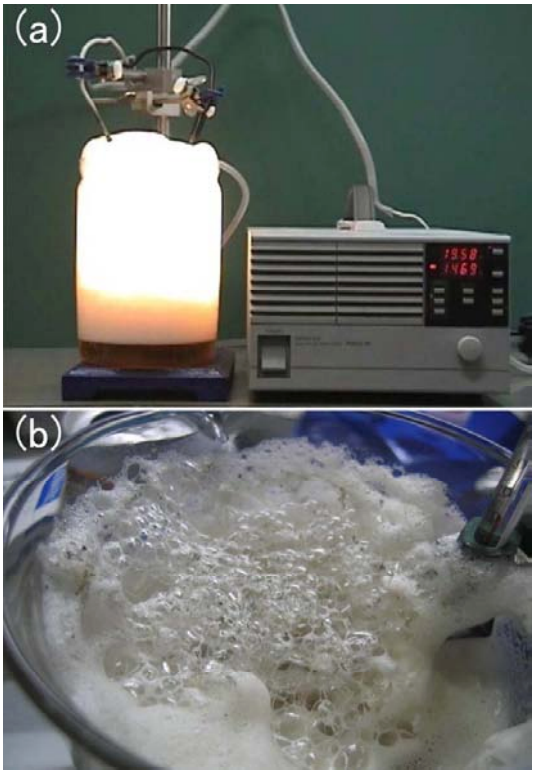


FIG. 2: DC arc discharge in foam: (a) Arc discharge in foam; (b) Surface of the foam after DC arc discharge.

same time.

We used a beer dispenser (Fukushima Industries Corporation: FTN-38S1) as the beer foam supply, and the pressure of the carbon dioxide gas in the dispenser was set to 2.4 kg/cm$^2$. Generally, foam can be prepared by using surfactants, which are primarily proteins in the case of beer. Moreover, because the foaming ingredients create viscous membranes, it is possible to obtain a highly dense foam phase that entraps the carbon dioxide gas from the beer. In addition, there is not enough surface tension in the foam to break the membranes, so direct current arc plasma inside the foam can be entrapped for comparatively long periods of time. The average free path of an arc discharge in foam is longer in comparison with that in water, and it is possible to achieve good arc discharge, as in gas phase.

Arc discharge was conducted as follows. Both graphite electrodes were dipped in an open container filled with high-density foam from a beer dispenser. They were momentarily brought into contact, and arc discharge was initiated as shown in Fig. 2(a). Discharge voltage and current were optimized and maintained at 20 V and 10 A, respectively. The synthesis time was 2 min. Note that during continuous operation large quantities of fine particles adhered onto the surface of the foam.

Figure 2(b) shows the foam surface after the arc discharge. The products of the arc discharge in the foam were separated into fine particles trapped on the foam surface and fine particles at the bottom of the beaker. We placed some of the fine particles on a microscope specimen grid and examined them under a high-resolution transmission electron microscopy (HR-TEM) system operating at

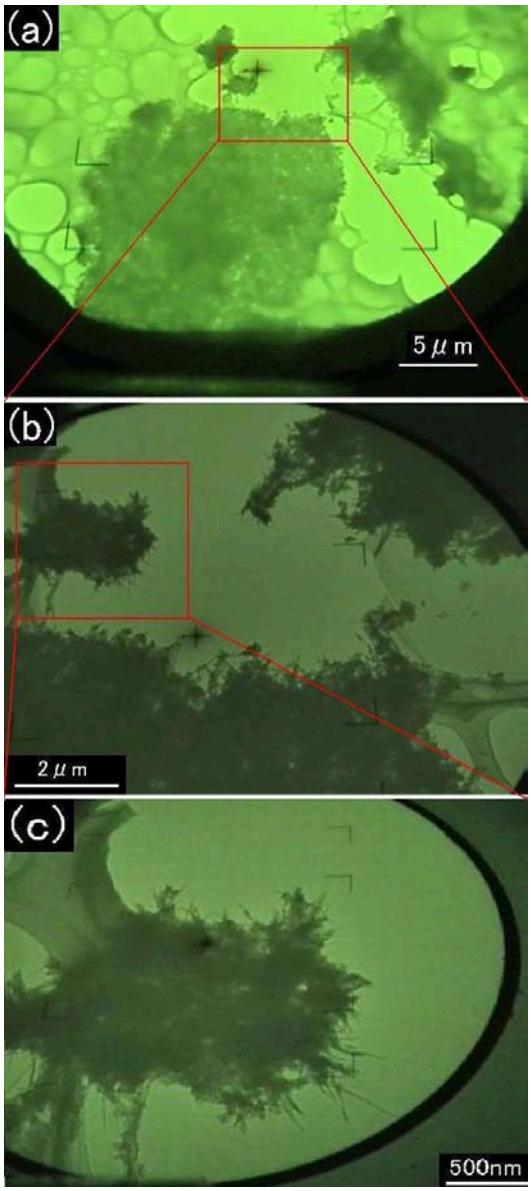


FIG. 3: (a)-(c) TEM images of fine particles at the bottom of the beaker. (b) and (c) are high-magnification views of (a).

200 kV (HR-TEM model H9000; Hitachi Co., Ltd.).

## III. RESULTS AND DISCUSSION

Figures 3(a)-(c) show HRTEM images of the fine particles at the bottom of the beaker. Figures 3(b) and 3(c) are enlarged views of Fig. 3(a). These micrographs show a large cluster of 2 $\mu$m diameter and consisting of numerous MWNTs, as shown in Fig. 3(c). From the fine particles at the bottom of the beaker, clusters of approximately 1-10 $\mu$m diameter and a small cluster of 1 $\mu$m diameter were observed.

Figures 4(a)-(c) show the fine particles on the foam surface. Figures 4(b) and 4(c) are enlarged views of Fig. 4(a). The cluster from the foam surface was different from the cluster at the bottom of the beaker. Many small clusters were observed from the sample of the foam surface.

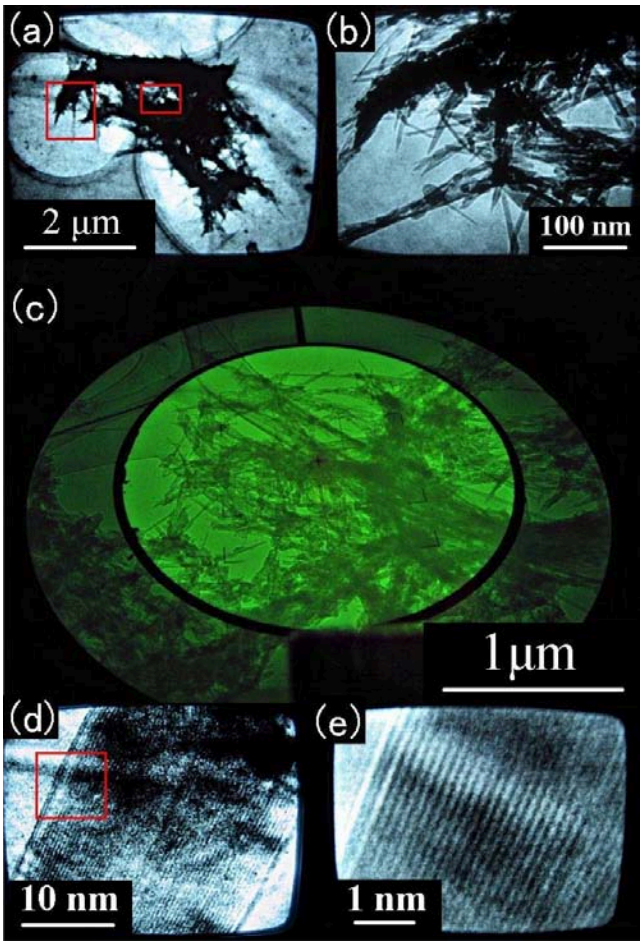


FIG. 4: TEM images of fine particles on the foam surface: (a)-(c) low-magnification views; (e) high-magnification view of (d).

These small clusters were typically 500-1000 nm in diameter. Compared with that at the bottom of the beaker, the cluster on the foam surface showed high-purity MWNTs with a small percentage of amorphous carbon or onions, as shown in Figs. 4(b) and 4(c).

The TEM images provided valuable information on the quality of the nanotubes produced. On the other hand, the HR-TEM images revealed that such nanotubes were MWNTs of 25 nm diameter and tended to be very straight and clean, as shown in Figs. 4(d) and 4(e).

Table I shows the percentages of fine particles in the clusters collected at the bottom of the beaker and the surface of the foam. We took 10 samples each from the bottom of the beaker and on the foam surface, and divided them into MWNTs, onions and amorphous carbon by TEM observation. In particular, we have defined clusters with an MWNT ratio of 50 % or more as CNT clusters, and the first column of Table I provides the CNT cluster ratio at the two sampling sites. In the second column of Table I, we have defined spherical graphite as "Onion" and shapeless amorphous carbon as "Amorphous", where both are non-CNT materials, and have presented the component ratios of the materials included in the CNT clusters.

As seen from the table, most of the CNT clusters were included in the foam. We observed more than 60 % CNT clusters from the foam, and less than 20 % CNT clusters at the bottom of the beaker. In addition, CNT clusters of small diameter ($< 1$ $\mu$m) were often found on the foam surface, whereas CNT clusters of large diameter ($> 1$ $\mu$m) were found at the bottom of the beaker with small CNT clusters of more than 1 $\mu$m diameter.

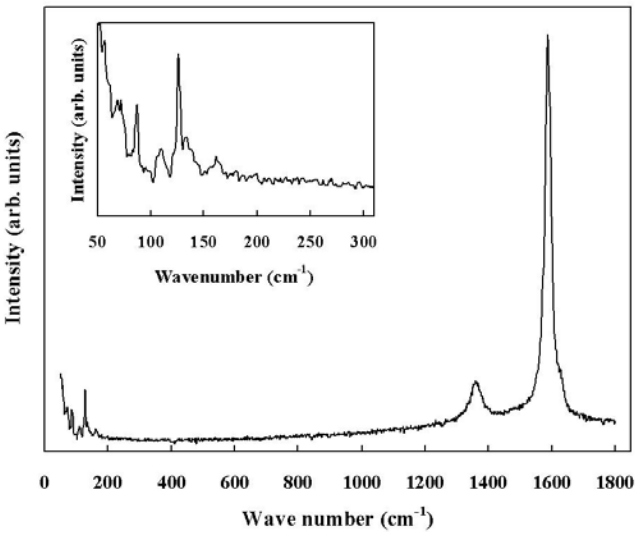


FIG. 5: Raman spectra of CNT cluster produced by arc discharge in foam.

In addition, Table I shows the material ratio of the CNT clusters. CNT clusters containing high-purity MWNTs were those containing MWNTs at greater than 60 %; however, these CNT clusters contained onions and amorphous carbon from 5 % to 40 %. In particular, CNT clusters with many MWNTs but with few of onions or amorphous carbon, and CNT clusters with a purity of MWNT exceeding 90 % were often found.

From the TEM observation, CNT clusters of small diameter were often found on the foam surface, whereas CNT clusters of large diameter were found at the bottom of the beaker. Therefore, it is considered that CNT clusters separated by size or mass into the foam surface and the bottom of the beaker.

Figure 5 shows the Raman scattering spectra of the CNT cluster in the regions of 50-1800 cm$^{-1}$. The excitation wavelength of the Raman spectrum device (JASCO Corporation: NRS-3000) used green laser of 532.03 nm.

A strong peak at 1587 cm$^{-1}$ and a weak peak at 1367 cm$^{-1}$ can be observed, which were assigned to the D-band and G-band signals, respectively. The signal intensity ratio of the G-band to the D-band (G/D) is high, indicating that high-quality MWNTs contain few impurities. Low-frequency peaks (at -220 cm$^{-1}$) can also be

TABLE I: Percentages of production collected from the foam.

| CNT clusters | | Material ratio of CNT clusters |
|---|---|---|
| Form surface | 20-40 % | MWNT 60-95 %; Others |
| Bottom of beaker | 5-20 % | (onion, amorphous) 5-40 % |

observed, which are assigned to RBM vibrations. The tube diameter d (in nm) can be estimated using the relation d=223.75/w [9], where w (in $cm^{-1}$) denotes the RBM vibrational wave number observed. The RBM peaks at 72, 86, 107 and 126 $cm^{-1}$ correspond to MWNTs with diameters of 3.1, 2.6, 2.1 and 1.7 nm, respectively.

## IV. CONCLUSION

We reported the characteristics of MWNTs produced by arc discharge in foam as determined from the TEM images and Raman spectra of the nanotubes. From the TEM observation, CNT clusters containing high-purity MWNTs were often found. These clusters also contained small percentages of onions and amorphous carbon, but a large percentage MWNTs at more than 90 %. CNT clusters with a large percentage of high-quality MWNTs were easily collected on the foam surface. We observed more than 40 % CNT clusters on the foam surface and less than 20 % CNT clusters at the bottom of the beaker. From these results, it is considered that CNT clusters separate by size or mass into the foam surface and the bottom of the beaker. The yield of MWNTs by the arc synthesis method is highest in foam, and might be increased with further research.

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