Fabrication of Carbon Nanostructures by Pulsed Electric Discharge between Metal Electrodes Using Fluorine-containing Organic Liquid

Katsuhiko Hosoi, Shin-ichi Kuroda,* and Hitoshi Kubota
Department of Chemistry, Faculty of Engineering, Gunma University, 1-5-1 Ten'jin-cho, Kiryu 376-8515

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The carbon nanotube and carbon nanoparticle that contain fluorine on the surface were prepared by the pulsed electric discharge in fluorine-containing organic liquid. The production rate of carbon nanostructures by this method was found to be about 50 times faster than that by the "arc in liquid" method previously reported.

Since the discoveries of fullerene[1] and carbon nanotubes (CNTs),[2] several kinds of carbon nanostructures have attracted increasing attention.[3–6] Among others, CNTs are expected to be applicable in varieties of area from electronics to energy, and their mass-production methods have been extensively investigated. There are already many methods for the production of CNTs, e.g., vacuum arc discharge[7,8] and chemical vapor deposition.[9,10] We have also developed a method based on the polymer blend technique.[11–13]

On the other hand, Ishigami et al. used the arc discharge between graphite electrodes in liquid nitrogen for the fabrication of multiwalled carbon nanotubes (MWCNTs).[14] After this paper, several reports have been appeared on the fabrication of various carbon nanostructures by arc discharge in liquid nitrogen and deionized water.[15,16] These methods do not require any vacuum system nor large-scale equipment which is necessary for the traditional arc discharging method. Recently, some "arc in liquid" methods in organic liquids were reported.[17,18] This "arc in liquid" method in organic liquid is expected to increase the variation of resulted carbon nanostructures as the organic liquid becomes the source of carbon. Some aromatic hydrocarbons, such as benzene and toluene, have been used as the organic liquid in "arc in liquid" methods.

In this paper, we report the novel procedure as electric discharge in a fluorine-containing organic liquid with applying pulsed voltage between metal electrodes. This is to realize more efficient fabrication of carbon nanostructures and fluorine-containing surface which improves solubility of the products.[19]

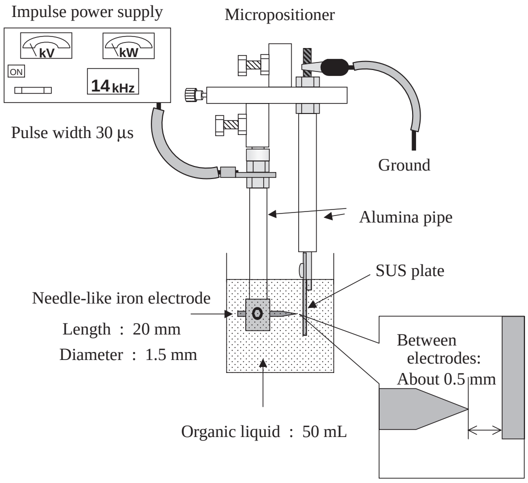

Figure 1. Apparatus for "arc in liquid" with pulse-modulated applied voltage.

Ethyl nonafluoroisobutyl ether ($C_4F_9OC_2H_5$ (HFE-7200): 3M Co.) was used as the organic liquid in "arc in liquid" method. Apparatus used is shown in Figure 1. The length and diameter of iron needle-like electrode are approximately 20 and 1.5 mm, respectively. It is attached to the holder made of brass, and the high-voltage power supply is connected. An insulated micropositioner is attached at the upper end. A SUS plate ($15 \times 84 \times 3\,mm^3$) is connected to the ground. The high-voltage power supply is PHF-2K (Heiden Institute) that generates pulse-modulated sinusoidal potential with pulse width of 30 µs. The gap between the needle-like electrode and SUS plate was adjusted to 0.5 mm using a micropositioner. Arc discharge was generated between iron electrodes submerged in HFE-7200 (50 mL) in a beaker. As the applied voltage rose, the electric current observed increased gradually, and when the former reached the dielectric break down voltage the arc discharge began and the voltage fell down. The applied voltage and power between electrodes were monitored during discharge. Experiments were carried out by changing the pulse frequency (5–60 kHz) and discharge period (5–30 s).

The obtained carbon material was analyzed by transmittance electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). Little discharged solution was dropped on a micro grid and dried before the observation using TEM (JEOL JEM-1200EXII, acceleration voltage of 80 kV). XPS (Perkin-Elmer ESCA-5600, X-ray source of Mg Kα 15 kV, 400 W) measurement was carried out for the surface composition analysis after washing the products with 50 mL of acetone three times. Raman spectra were collected for evaluation of the crystallinity of products (JASCO NRS-1000, $\lambda = 532\,nm$). The formation rate of carbon product was calculated using the total discharge current and dry weight of carbon product.

The colorless transparent solution generated soot-like product by electric discharge and became muddy black. The electric voltage and power during discharge were 3.5–5.5 kV and 0.35–0.45 kW, respectively. The product formation rate was 20.5 mg/A·s, which is about 50 times faster than that previously reported for another "arc in liquid" method.[17] When the pulse frequency of applied voltage was 5 kHz, discharge hardly occurred, and high voltage was required. However, the surface composition of product did not change for different pulse frequency. Typical TEM micrographs of obtained product are shown in Figure 2. The dominant product was nanoparticles. The diameter of carbon nanoparticles was approximately 5–100 nm in all experiments (Figure 2a). Some nanotubes were also observed except for the discharge with pulse frequency of 5 kHz or electric

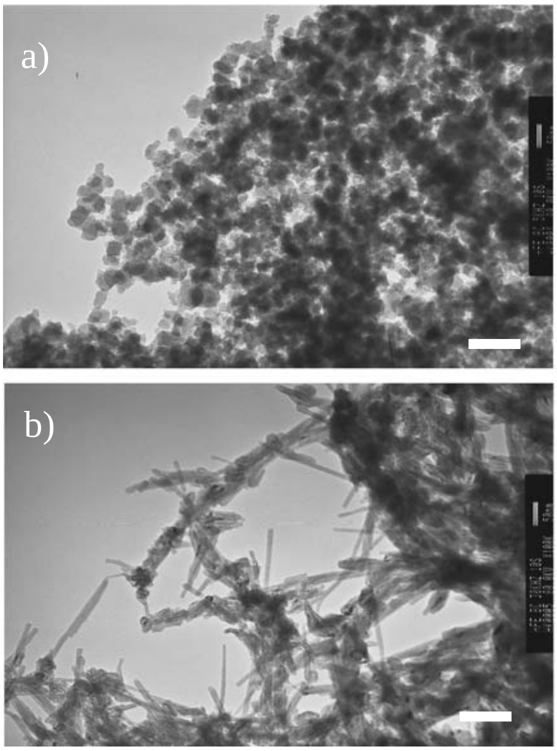

Figure 2. Typical TEM micrograph of carbon products, a) carbon nanoparticles, b) carbon nanotubes. Scale Bar: 100 nm. Surface composition of the product was estimated as C, 81.07; O, 4.40; F, 14.53% by XPS.

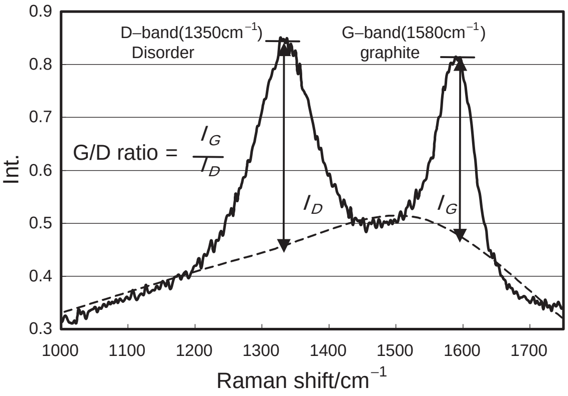

Figure 3. A typical Raman spectrum of carbon product.

discharge period of 5 s. The nanotubes were MWCNTs and their diameter was approximately 10 nm. Aggregation of CNTs was observed when the pulse frequency was 30 kHz and discharge period was 10 s (Figure 2b). A typical Raman spectrum observed is shown in Figure 3. The intensity ratio (G/D ratio) of G-band (1580 cm^{-1}) and D-band (1350 cm^{-1}) of the Raman spectrum was estimated as shown in Figure 3. G/D ratio increased with the increase of discharge frequency, and it increased with prolong discharge time (Figure 4).

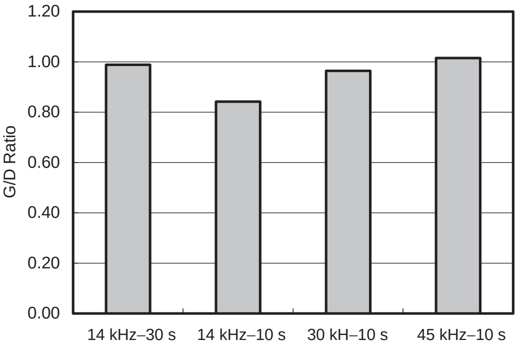

Figure 4. Dependence of G/D ratio on the discharge frequency and period.

Carbon nanostructures were prepared by pulse-modulated discharge in fluorine-containing organic liquid without using graphite electrodes. The formation rate of product was found to be about 50 times faster than that by the "arc in liquid" method previously reported. The product consisted of nanoparticles and MWCNTs with fluorine covalently bonded on their surface. The crystallinity of products depended on discharge frequency.

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