Discharge characteristics in liquid helium preparatory to fabrication of carbon nanomaterials

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Arc discharge in liquid helium is a promising method for fabricating high-quality carbon nanomaterials. Measurements of the discharge characteristics of the resulting plasma and observation of the associated optical emission spectra show that the behaviour of discharge current over time and the associated spectra depend strongly on discharge voltage and both may be related to the temperature of the carbon target.

Key words: Carbon nanotube, arc discharge, superfluidity liquid helium

1. INTRODUCTION
Nanosize materials have become important in industrial production and applications in the past several years. Carbon nanomaterials—including fullerene molecules, carbon nanotubes (CNTs), nanohorns and nano-onions—are particularly promising for a variety of applications [1–5]. Among effective methods for synthesizing CNTs are the contact arc method, laser ablation method and chemical vapour deposition method. However, the reactions and mechanisms of CNT fabrication are not yet well understood because production speeds are too high to measure.

Carbon nanomaterials have been synthesized by arc discharge generated in liquid water [6–11]. For example, Sano et al. prepared single-walled nanohorns by arc discharge in liquid nitrogen [7]. These results suggest that two fabrication parameters, reaction-field temperature and the energies of the carbon atoms and molecules may be particularly important.

Our group has reported that, at low temperature, liquid carbon atoms emitted by discharge cool quickly and start to combine with some amount of energy, enabling creation of carbon nanomaterials with basic structures [12–14]. Our subsequent work has focused on CNT fabrication in liquid helium, with the goals of achieving both high reproducibility and a better understanding of the details of fabrication that will enable us eventually to fabricate nanomaterials with new characteristics. Herein, we investigate the conditions for fabrication of carbon nanomaterials by arc discharge in low-temperature liquid such as liquid helium by studying the discharge characteristics in liquid helium and the obtained emission spectra of the discharges.

2. EXPERIMENTAL
Schematics of our pulsed arc-discharge setup are shown in our previous papers [12–14]. Two high-purity carbon rod electrodes (Nilaco Corp., Japan; 99.99% purity) were set in either pure water, liquid nitrogen or liquid helium in a glass chamber. The chamber was surrounded by a vacuum jacket and a top plate was secured by a quick coupling method. Direct current (DC) from a DC power supply (Kikusui PWR1600L) was applied to the electrodes. Because most of the arc energy is absorbed by the liquid, inducing significant evaporation, the chamber was equipped with an evaporation cryostat of liquid nitrogen and liquid helium dewars as well as with a leak valve (10 L/s) to prevent evaporation. The electrode gap was set initially to 3 mm, but changed over time by arc-induced erosion. Arc discharge was generated between the electrodes by opening and closing. Short sparking times are important for the production of carbon materials; our discharge times were 100–400 ms.

The maximum discharge current and discharge voltage were set by the power supply. The following three conditions were set: (1) 10 V, 80 A; (2) 40 V, 40 A; and (3) 80 V, 10 A. Opening and closing discharge voltages and currents were measured by oscilloscope (Iwatsu DS-5324). Optical emission spectra in the arc plasma were observed by a USB-interface multichannel spectrometer (Soma Optics S2431). The wavelength range for simultaneous measurement was 300–800 nm. The effective light-receiving area of the optical fibre was 1 mm². Wavelength integrated light emission from the intermittent arc discharge during the discharge on time was measured with a pin-photodiode (Ophir, FPS-1).
3. RESULTS AND DISCUSSION

3.1 Discharge voltage and current

Figure 1 shows plots of opening and closing discharge current and voltage in liquid helium as a function of time. At all three maximum discharge voltages (10, 40 and 80 V), the mean discharge currents are very small, about 0.5–2 A. Thus, discharge current can be determined by the impedance of the electric circuit. Vibration in the figures may be caused by bubbles generated between the electrodes.

Figure 2 shows plots of discharge current and voltage at the very early stage of the discharge in liquid helium as a function of time. At all three maximum discharge voltages, discharge current is very high during the very early stages of discharge. At 10 V, discharge current increases slightly, saturates at 1.4 A, and remains almost constant until the electrode closes as shown in Fig. 1(a). At 40 V, it increases to 7 A and then decreases slightly to < 6 A. At 80 V, it increases to 16 A and then decreases to < 5 A. These results suggest that peak discharge current increases with increasing setup voltage of the source. Plots of opening and closing discharge current and voltage in liquid nitrogen and pure water were also measured as a function of time, not shown here. At all three maximum discharge voltages, the mean current is almost the same, 1–2 A, similar to the results in liquid helium.
3.2 Emission spectra of the discharge plasma

Figure 3 shows emission spectra of the discharge plasma in liquid helium. Spectra were made integration during the measurement time. HeI (388.9 and 587.5 nm), C⁺ (426.7, 657.8 and 723.6 nm) and C₂ swan band emissions are evident with a kind of black-body radiation. At 10 V (the lowest maximum discharge voltage), black-body radiation is strong and emission from the C₂ swan band is weak. At 40 V, both black-body radiation and emission from the He atoms, carbon ions and C₂ swan band are clearly evident. At 80 V (the highest maximum discharge voltage), black-body radiation is weak and emission from the He atoms, carbon ions and C₂ swan band are strong. Black-body radiation is thought to be related to the temperature of the carbon target. Thus, these results suggest that electric power heats the electrode at a low-discharge voltage condition. In the low discharge voltage, emission intensity was very weak. On the other hand, emission intensity was very strong and small bubbles were generated between electrodes in the high voltage discharge.

We reported previously that, at low maximum discharge voltages (< 10 V), CNTs cannot be prepared. However, at a high voltage (80 V), we were able to prepare needle-shaped carbon nanoclusters in liquid helium, as confirmed by scanning electron microscopy [14]. The cluster diameters are 10–30 nm, and some of the lengths are > 1 μm. Transmission electron microscopy images show that the clusters are multi-wall tubes.

3.3 Voltage and current waveforms of the intermittent arc discharge

Figure 4 shows typical waveforms of voltage, current and light emission for intermittent arc discharge in liquid helium. In the initial portion of the waveforms, the cathode is detached from the anode, voltage remains at 30 V and no arc discharge is generated. During phase I of the waveforms, the cathode is moved into contact with the anode, voltage drops, transient current is evident, but light emission is not yet detected, indicating that the measured current is not due to arc discharge but rather to the short circuit between the electrodes. The fluctuation of discharge voltage and current is considered for generating of bubbles. During phase II of the waveforms, the cathode is detached from the anode, voltage is 10 ~ 20 V, current remains constant at 1 ~ 2 A. In this phase, light emission is detected and it increased

Fig. 3 Emission spectra of the discharge in liquid helium.
with the time at 380 ~ 420 ms. This result indicating that the measured current is due to arc discharge between electrode. The intermittent arc discharge is in the form of a DC-chopped pulse. At the conclusion of the experiment, arc discharge is disrupted by further separation of the cathode from the anode.

4. CONCLUSION

The discharge characteristics and optical emission of plasma discharge in low-temperature liquid were measured with the ultimate goal of preparing high-quality carbon nanotubes. Changes in discharge voltage and current with time are almost the same regardless of whether the liquid is pure water, liquid nitrogen or liquid helium. Emission spectra from the discharge show a strong dependence on discharge voltage.

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6. REFERENCES