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Growth Processes of Nanomaterials using Plasma Process in Liquid

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Carbon nanomaterials have been prepared using pulsed laser ablation method in liquid. Field emission scanning electron microscopic observation revealed that most of nanomaterials produced in a deionized water were sphere shape nanoparticles, and small amount of products like nanofiber can be observed in the same sample. The ratio of the products in the ethanol is high compared with those in the deionized water. The particles produced in the super-low temperature, superfluid helium liquid, shows ring shape nanofibers. Several kind of liquid type nanomaterials were observed in that particles.

Key words: plasma, nano-materials, superfluidity, helium, liquid

1. INTRODUCTION

Interest in nanomaterials has been rapidly growing for the past several years. In particular, carbon nanomaterials including fullerene molecules, carbon nanotubes, nanohorns and nanoonions are promising new materials for a variety of potential applications. These carbon nanomaterials have been produced by various methods such as arc discharge in a buffer gas, laser ablation, chemical vapor deposition (CVD) and annealing of nanodiamonds. Among them, the arc discharge method is the most common and is widely used by many researchers and manufacturers. Recently, several kinds of arc-discharge and pulsed laser ablation in liquid method have been developed as a cost-effective technique to fabricate various kinds of nanomaterials [1–6]. These methods have some advantages in the mass production of carbon nanomaterials compared with any other well-known conventional methods as mentioned above. In the past few years, single-wall carbon nanotubes (SWNTs), single-wall carbon nanohorns (SWNHs), and their metal included forms, have been successfully synthesized by the arc in liquid method using water and liquid nitrogen to host arc discharge. However, the high-quality single-walled structures such as SWNTs and SWNHs have been produced only when liquid nitrogen was used in the simple arc in liquid method, and the value of those nano materials was small. On the other hand, pulsed laser ablation in liquid method has been also developed for fabricating high quality nano materials [6-8]. Sugiyama et. al. prepared oxo(phtalocyaninato)vanadium(IV) (VOP) nanoparticles dispersed in water by using femtosecond laser ablation of its bulk crystals. They found that the mean size of the VOP nanoparticles was 17 nm, estimated by a scanning electron microscope (SEM) analysis. Furthermore, they suggest that cooling process of the carbon atoms and molecules in the liquid affect the produced carbon nanomaterials. Therefore, nanoparticle formation process can be controlled precisely by temperature in the liquid using this laser ablation method.

In this paper, carbon nanomaterials have been prepared using pulsed laser ablation methods in the deionized water and low temperature superfluid helium liquid. Morphology, size and density of the particles are observed by field emission scanning electron microscopy (FESEM), and analyzed using computer software. Measurements of optical emission spectra were performed to estimate the processing plasma state in liquid using high speed photonic multichannel spectral analyzer.

2. EXPERIMENTAL

A schematic of the pulsed laser ablation system is shown in Fig. 1. High purity carbon target (purchased from Nilaco Corp., Japan; 99.99% purity, 30mmϕ × 5mm) are suspended in 30 ml of a deionized water (0.2 mS/m conductivity) or ethanol in a Pyrex beaker. In the present work, we demonstrate the formation of carbon nanoparticles by using a pulsed Nd:YAG laser (Continuum SureliteIII; wavelength of 532 nm, pulse duration of 3.5 ns, maximum output energy of 340 mJ). The laser beam was focused on the center of the target with a lens, and the spot size was about 3 mm^2. Repetition rate of the pulsed laser was 10 Hz, and nanomaterials were produced at 6000 shots. Nanomaterials formed in the liquid are collected on the water surface and in the water bottom.

Morphology, size and density of those nanomaterials were observed by FESEM (Joel JSM-6800, 3kV, 8μA). Optical emission spectra in the arc plasma were observed by high speed photonic multichannel spectral analyzer (PMA-11: Hamamatsu Photonics) with ICCD detector (C8808-01: Hamamatsu Photonics). Simultaneous measurement wavelength range of this system was from 200nm to 860nm. Effective light-receiving area of optical fiber was 1mmϕ and A/D resolution was 16bits.

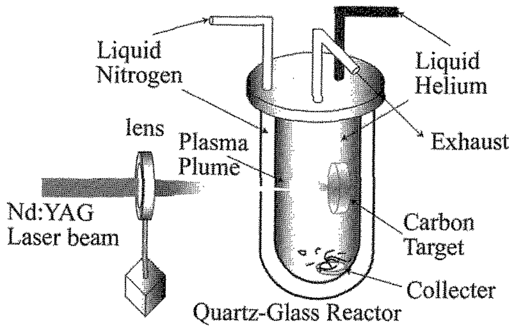

Fig. 1 A schematic of the pulsed laser ablation system.

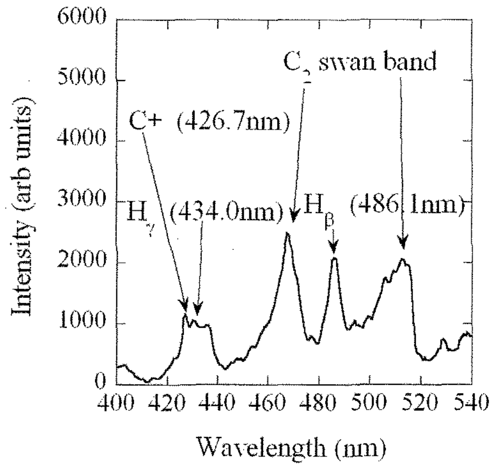

Fig. 3 Emission spectroscopy of the discharge plasma in the deionized water.

3. RESULTS AND DISCUSSION

3.1 Pulsed laser ablation in deionized water

Figure 2 shows the FESEM image of the nanomaterial products using pulsed laser ablation in pure deionized water. After the pulsed laser ablations, there are two kinds of nano products can be obtained. One of them is powdery products floating on the water surface, and another one is bulky deposits sank down in the water bottom. This result is agree with our previous experiment measured by high resolution transmission electron microscopy (HRTEM; Hitachi H-9000 operated at 300 kV) [9]. In this obserbation, most of the products are the sphere shape particles and some of them are coagurated each other. The FESEM images were further analyzed using computer software (Mitani Syoji ; Winroof) to obtain the diameter distribution of individual nanofibers. The diameter of the particles was distributed from 10 nm to 200 nm. Mean diameter of the particles was approximately 70 nm. In addition, very small amount of nanofibers are observed. Size of the nanofibers is 10~100 nm in diameter and several 100 nm in length.

Figure 3 shows the emission spectroscopy of the arc discharge plasma in the deionized water. As the results, C^+(426.7nm), H_β(486.1nm), H_γ(434.0nm) and C_2 swan bands can be observed. Strong peak of H_α(656.3nm) can be also observed, not shown here. Emission spectroscopy from the arc plasma is almost same compared with that in the deionized water described elsewhere [10].

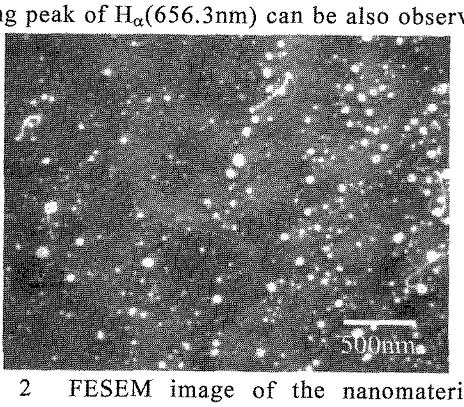

Fig. 2 FESEM image of the nanomaterial products using pulsed laser ablation in pure deionized water.

3.2 Pulsed laser ablation in ethanol

Figure 4 shows the FESEM image of the nanomaterial products using pulsed laser ablation in ethanol. After the pulsed laser ablations, there are two kinds of nanoproducts can be obtained. One of them is powdery products floating on the water surface, and another one is bulky deposits sank down in the water bottom. This result agrees with our previous experiment measured by HRTEM [9]. In this observation, most of the products are the sphere shape particles and some of them are coagurated each other. The FESEM images were further analyzed using computer to obtain the diameter distribution of individual nanofibers. The diameter of the particles was distributed from 20 nm to 300 nm. Mean diameter of the particles was approximately 80 nm. In addition, very small amount of nanofibers are observed. Size of the nanofibers is 10~100 nm in diameter and several 100 nm in length.

The ratio of the products like nanofiber

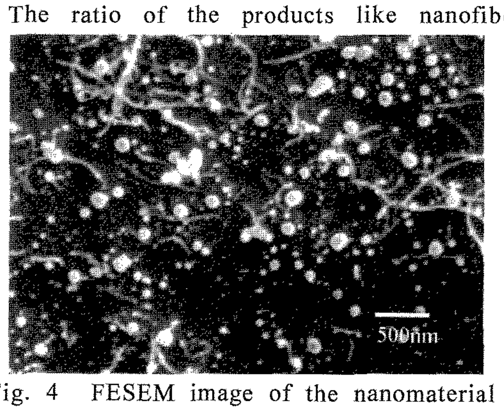

Fig. 4 FESEM image of the nanomaterial products using pulsed laser ablation in ethanol.

produced in the ethanol water with sodium dodecylsulfate (SDS) is high compared with those produced in the deionized water, not shown here.

Figure 5 shows the emission spectroscopy of the arc discharge plasma in the ethanol. As the results, C^+(426.7nm), H_β(486.1nm), H_γ(434.0nm) and C_2 swan bands can be observed. Emission spectroscopy in ethanol is almost same compared with that in the deionized water. However, the emission intensity of the C^+(426.7nm) and C_2 swan bands are stronger than those in deionized water.

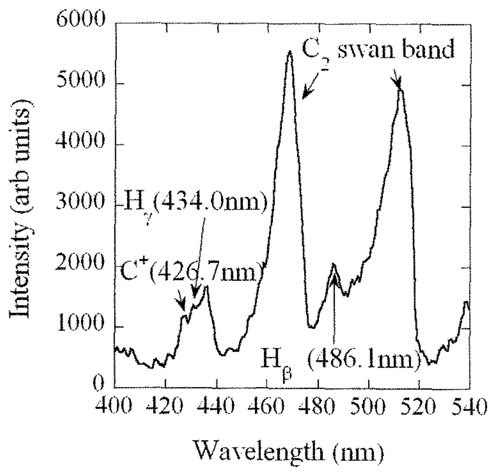

Fig. 5 Emission spectroscopy of the discharge plasma in the ethanol.

3.3 Pulsed laser ablation in superfluid helium liquid

Figure 6 shows the FESEM images of the nanomaterial products using pulsed laser ablation in superfluid helium liquid (4K). In this experiment, most of the helium gas are evaporated, therefore the experiment are performed in the pressure of the atmosphere and liquid. As shown in Fig. 6, there are a lot of ring shaped nanotubes (nano-ring) on the substrate. Figure 7 shows the detail image of the nano-ring. The diameter of the ring is about 10~20nm. In addition, some strange-shaped materials can be observed in the same figure. Those materials are columnar shape and the diameter is about 300~500nm, and the surface looks like very smooth like glass.

In general, quality of nanomaterial is influenced by the atmospheric gas temperature and gas flow rate. Therefore, it is considered that cooling process is important for the nanomaterial growth processes. On the other hand, cooling effect of the superfluid helium liquid is much higher than the nitrogen liquid, because the viscosity disappears in the superfluid liquid. In addition, several kinds of new type nanomaterials, such as glass-coated liquid-carbon, have been prepared in pure helium gas. Walt A. de Heer et al. suggest that glass-coated liquid-carbon is formed in pure helium gas using pure carbon arc discharge [11]. They suggest that liquid-carbon drops are formed at the anode, which acquire a carbon-glass surface due to rapid evaporative

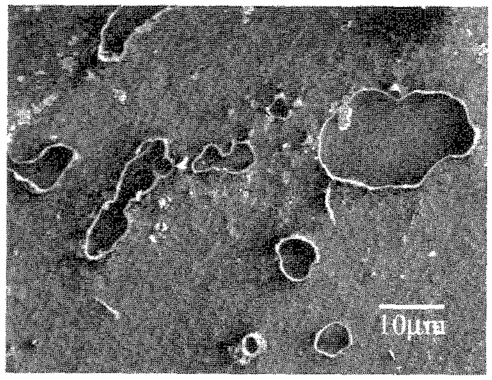

Fig. 6 FESEM images of the nanomaterial products using pulsed laser ablation in superfluid helium liquid (4K).

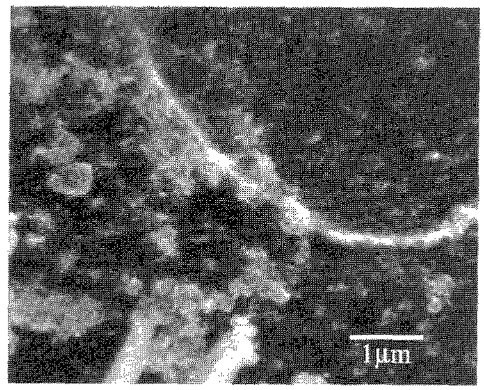

Fig. 7 Detail image of the nano-ring as shown in Fig. 6

cooling. Apparently, the strange-shaped material prepared in our experiment, looks like coagulated glass-coated liquid-carbon. As we don't have enough experimental data to analyze about that, the formation mechanism of the carbon nano-ring and strange-shaped material is not clear yet. However, they may be formed due to rapid cooling by the liquid-helium.

4. CONCLUSION

Carbon nanomaterials have been prepared using pulsed laser ablation method in liquid. Field emission scanning electron microscopic observation revealed that most of nanomaterials produced in a deionized water were sphere shape nanoparticles, and small amount of products like nanofiber can be observed in the same sumple. The ratio of the products in the ethanol is high compared with those in the deionized water. Ring shaped nanotubes and strange–shaped nanomaterials, looks like glass-coated liquid-carbon, were produced in the superfluid helium liquid, which may be due to maybe formed due to rapid cooling by the liquid-helium.

5. References

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