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Phase transition and restructuring of carbon nanoparticles induced by aerosol laser irradiation

Takafumi Seto [a,*], Ayumi Inoue [a], Hidenori Higashi [a], Yoshio Otani [a], Masamichi Kohno [b], Makoto Hirasawa [c]

[a] Department of Chemical and Material Engineering, Kanazawa University, Kakuma, Kanazawa 920-1192, Japan
[b] Department of Mechanical Engineering, Kyusyu University, Motooka 744, Nishi-ku, Fukuoka 819-0395, Japan
[c] Advanced Manufacturing Research Institute, National Institute of Advanced Industrial Science and Technology, Namiki 1-2-1, Tsukuba 305-8564, Japan

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ABSTRACT

We recently reported that laser irradiation of aerosol amorphous carbon nanoparticles induces formation of onion-like carbon structures. In this study, the further analyses of laser induced phase transitions and restructuring of aerosol carbon nanoparticles were carried out using the combination of off-line and in-flight measurement techniques. Laser-synthesized carbon agglomerates composed of 7-nm amorphous primary nanoparticles were used as starting materials. Irradiation of multiple laser shots to the gas-suspended carbon agglomerates resulted in the formation of variety of unique structures, such as diamond-like, defective graphite, concentric shell structures, and their agglomerates. Evolutions of the carbon nanostructures were found to be responsible for the in-flight mass-to-mobility spectra.

1. Introduction

Nanocarbons are allotropes of carbon that have a characteristic dimension of nanometer range, *e.g.* carbon nanotubes (CNT), fullerenes, carbon nano-onion (CNO). Towards the precise manufacturing of nanocarbon with desirable properties, the control of crystal phase of carbon nanosystem, hereafter called as 'carbon nanophase', is the most important issue. According to the thermodynamic relationship for bulk carbon (Gibbs' phase rule), the phase equilibrium is determined by the pressure and the temperature, *i.e.* the free energy. However, the formation of carbon nanophases may strongly depend on the synthesis routes and kinetics as well as the *size* of the system which limits the amount of reactant. For example, 2-dimensional sp^2 bonding may create one dimensional (CNT) or zero dimensional (fullerene or CNO) nanophases when the amount of carbon is limited. Such transformation process of carbon nanophase has been commonly realized in the vapor phase synthesis processes with the assist of metal catalysts where the *growth sites* are limited in the nanometer scale [1]. In particular, transient metal nanoparticles were widely used as catalysts in the factory-scale production of the CNTs [2].

In contrast to these 'chemical' routes, laser irradiation is an alternative approach to induce phase transition in the carbon nanophase without the use of catalysts. It is well known that the laser irradiation of carbon substances introduces substantial phase transition under non-equilibrium process. Cappelli et al. [3] reported that formation of graphitic structure from amorphous carbon film was observed during the laser annealing. However, synthesis of the carbon nanophase by laser induced phase transformation is still big challenge. The strategies for the laser synthesis of carbon nanophases might be summarized in the following two directions, *i.e.* (1)

* *Corresponding author.*
E-mail address: t.seto@staff.kanazawa-u.ac.jp (T. Seto).
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the use of ultra-short pulsed laser to excite carbon bonding near the top most surface, and (2) the super-focusing of laser beam down to nanometer size. The former could be realized by the non-thermal (non-equilibrium) process using femto- or pico-second laser technologies to generate carbon nanophases, typically graphene [4]. However, the latter is rather difficult because it is hard to focus laser beam much smaller than the wage length of the light.

Laser irradiation of carbon nanoparticles is a possible candidate to overcome these difficulties. In fact, there are several reports to generate the CNOs by the laser irradiation of diamond nanoparticles in liquid [5]. Although the phase transformation from diamond (sp^3) to CNO (sp^2) is energetically favored, building-up processes such as amorphous to graphite, or amorphous/graphite to diamond is of our concern. Hu et al. [6] reported a synthesis of hydrophilic carbon onion with a millisecond-pulsed laser irradiation in carbon black water suspension but the hydrophilicity might result from the surface of generated particles might be contaminated with impurities exist in the liquid solution.

Aerosol laser irradiation is also one of the advantageous methods to cause transition of carbon nanophase in an isolated system. In our previous study [7], we found that the laser irradiation of gas-suspended amorphous carbon nanoparticles generated by laser ablation induced the formation of concentric graphitic shell structure. However detailed analysis of the phase transformation process was not performed. The purpose of this work is to obtain insight into the phase transition and restructuring of carbon nanostructures induced by aerosol laser ablation. Crystal phase transformation associated with the change in the microstructures was evaluated using the combination of off-line analysis (transmission electron microscopy and Raman spectroscopy) as well as in-flight mass (density) measurement of aerosol particles.

2. Experiments

Fig. 1 shows the schematic of experimental system used in this study. The detail procedures of synthesis of onion like carbons (OLCs) have been reported elsewhere (Inoue et al. [7]). Briefly, third harmonic wave of ns-pulsed Nd:YAG laser (λ = 355 nn, 10 Hz, pulsed width about 5 ns) was used as energy source. Carbon target has a cavity drilled at the center of the target rod with the diameter of 2 mm and the depth of 20 mm. The target was rotated to stabilize the particle generation. When the bottom of the cavity in the target was irradiated by the laser beam, carbon agglomerates composed of 7-nm primary nanoparticles were generated. These agglomerates were re-irradiated by periodical laser beam while they traveled to the outlet of cavity. In order to irradiate all of carbon nanoparticles suspended in the cavity, cylindrical laser beam with 2 mm in diameter (equal to the cavity diameter) was formed using a combination of convex and concave lenses. The particle generator was operated at the atmospheric pressure (0.1 MPa) and room temperature (20 °C). During the particle generation, nitrogen (>99.999%) was continuously fed to the generator at the flow rate of 4.0 L/min.

In this study, both off-line and in-flight analyses of phase transition of carbon nanoparticles were conducted. The changes in size, shape and crystal structure of the carbon nanoparticles with/without the aerosol laser irradiation were analyzed using a high resolution transmission electron microscopy (HR-TEM, JEOL JEM-2000EX-II). TEM samples were prepared by directly depositing the generated carbon nanoparticles on a micro-grid using an electrostatic precipitator (Nanometer Aerosol Sampler; model 3089, TSI Inc.) after the electrostatic size classification by a differential mobility analyzer (DMA) (Fig. 1, line (a)). Laser induced structural changes were also analyzed using Raman spectroscopy at room temperature (Xe laser, excitation wavelength: 488 nm). The samples for Raman analysis were prepared on a cupper plate using an inertial impactor without the mobility classification (Fig. 1, line (c)).

Laser-induced morphological change of carbon nanoparticles was also analyzed using in-flight measurement techniques. The mass distribution of mobility-classified particles was measured by an Aerosol Particle Mass Analyzer (APM; model 3061, Kanomax Inc.) as shown in line (b) of Fig. 1. The APM consists of two coaxial cylindrical electrodes (inner and outer radius, r_{in} and r_{out}), which rotate at the same angular velocity (ω). When the electrically q-charged particles (mass of m) are introduced into the annular region of APM, the particles draw the trajectory depending on the balance between centrifugal force ($m\omega^2 r$) and the electrostatic forces (qE; E is the electric field strength). The specific mass of particles penetrating through the APM is determined by the applied voltage (V) and the rotation speed (ω) (Ehara et al. [8]):

$$M\omega^2 r = \frac{qV}{r\ln(r_{in}/r_{out})} \quad (1)$$

The true density of primary carbon particles (ρ) can be calculated from the mass (m), the mobility (Z_p), and the primary particle diameter (d_p) with the fractal dimension (D_f) as:

$$\rho = \frac{m}{(\pi/6)Z_p^{D_f} d_p^{(3/Df)}} \quad (2)$$

The detailed procedures to estimate ρ is shown in the Appendix.

During the multiple laser irradiations of carbon nanoagglomerates, three transitions may take place; (1) phase transition from amorphous to crystal structure, (2) evaporation of carbon atoms and (3) restructuring of agglomerates. The densities of carbon allotropes are $2.30–2.72 \times 10^3$ kg m^{-3} for graphite [9], 3.51×10^3 kg m^{-3} for diamond [9], 1.72×10^3 kg m^{-3} for fullerene (C_{60}) and $2.0–2.7 \times 10^3$ kg m^{-3} for amorphous carbon called diamond-like carbon (DLC) [10]. The comparison of densities obtained from the in-flight density analysis with these referenced values may prove the applicability of in-flight analysis for the study of laser-induced phase transition of nanocarbon materials.

3. Results and discussion

3.1. Phase transition of carbon nanoparticles (off-line analysis)

Fig. 2(a and b) show the typical high resolution TEM images of particles generated by the laser irradiations of carbon target followed by the electrical mobility classification with the DMA at 100 nm. Fig. 2(a) is the TEM image of particles