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Time evolution of emission by carbon nanoparticles generated with a laser furnace technique

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Abstract. Time evolution of emission by carbon nanoparticles generated with a laser furnace technique was investigated with a high-speed video camera. Assuming blackbody radiation formula for small spherical particle, the internal temperature of these carbon nanoparticles was determined as a function of time delay (Δt) after laser vaporization. It was found that the internal temperature of them drastically decreased at $\Delta t < 400$ μs through collision with the surrounding rare gas inside the furnace. On the other hand, in particular laser vaporization condition where yields of C_{60} and other higher fullerenes in the soot were found to be high, an increase in the blackbody emission intensity could be recognized for longer wavelength ($660 < \lambda < 830$ nm) at $\Delta t > 400$ μs. This finding suggests that a certain exothermic process related to the formation of C_{60} and other higher fullerenes should occur at $\Delta t > 400$ μs inside the furnace.

PACS. 36.40.-c Atomic and molecular clusters

1 Introduction

After the discovery to produce C_{60} and other fullerenes in preparative amounts [1], the formation mechanism of them has been extensively discussed. However, up to now no clear image has emerged. To attack this problem experimentally, we applied the laser furnace technique, which was first introduced by Smalley and others for the production of endohedral fullerenes and single wall carbon nanotubes [2]. Compared to the arc technique, the laser furnace method allows better control of the key parameters such as ambient temperature of the furnace, laser fluence, buffer gas pressure etc. By the laser furnace technique, one can find that the yield of C_{60} and other large fullerenes increases if the temperature of the furnace, *i.e.* the buffer gas temperature is increased. In particular, Wakabayashi *et al.* reported that the furnace temperature does not only determine the yield of C_{60} and larger fullerenes but also strongly influences the relative yields of different conformational isomers of larger fullerenes [3].

It is well known that carbon nanoparticles generated by laser vaporization of a graphite rod are initially rather hot. The particle emission spectra can be interpreted as black-body emissions [4–10]. In this paper we study the time evolution of the emission spectra under several different source conditions in order to obtain information on the internal temperature of the carbon nanoparticles and to gain insight into the conditions under which fullerene formation takes place.

2 Experimental

We measured the emission from the plume of carbon fine particles from the surface of a graphite rod (6 mm in diameter) as a function of the delay after the vaporization laser was fired. We used the 2nd harmonic of a Nd:YAG laser (600 mJ/cm^2, 10 Hz) and recorded the emission continuously using a high-speed video camera (KODAK EKTAPRO H4540) with 25 μs time window. Throughout the experiment argon buffer gas (200 torr) did flow very slowly (*ca.* 10 ml/min) through the quartz tube surrounded by an electric furnace. The emission images were recorded using several band pass filters ($\Delta\lambda = 10$ nm) at 435.8, 488.0, 514.5, 546.8, 632.8, 660.0, 694.3, 720.0, 760.0, and 830.0 nm, respectively. The emission intensity of the entire cloud of carbon nanoparticles at each wavelength and time delay was investigated and the emission spectrum as a function of delay time was obtained.

Since the continuous emission can be described by the black-body radiation of small (radius $\ll$ wavelength) spherical particles exhibiting a $1/\lambda$ emissivity and disregarding the contribution of C_2 line-emission (Swan band), an effective internal temperature of the carbon nanoparticles could be derived [4,6]. Only data for $\Delta t \geq 200$ μs were used for further analysis, because fitting could be

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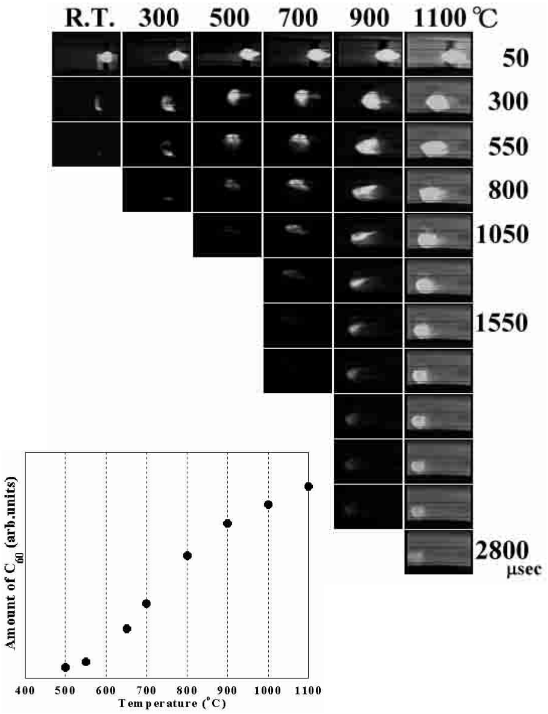

Fig. 1. Time and spatial evolution of emission by the plume of carbon nanoparticles immediately after laser irradiation of a graphite rod (each image covers an area of 28 mm × 16 mm).

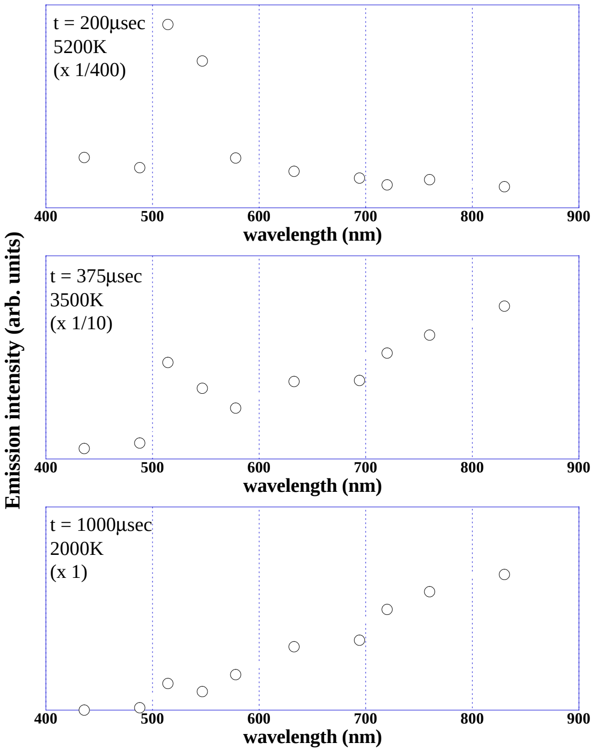

Fig. 2. Typical emission profiles of carbon nanoparticles ejected from the surface of graphite rod at $\Delta t = 200$ μs, 375 μs, and 1 ms, respectively. The ambient gas temperature is kept at 1150 °C.

achieved only for $\Delta t \geq 200$ μs. By this procedure we obtained the internal temperature of particles as a function of the delay time after laser vaporization, Measurements at different ambient temperature of the furnace (550 °C, 700 °C, 1000 °C, and 1150 °C) were carried out because it is well known that the yield of C_{60} and other higher fullerenes is drastically increasing with the temperature of the buffer gas.

3 Results and discussion

Figure 1 shows high-speed video camera images of the time and spatial evolution of the carbon nanoparticle emission after laser evaporation, obtained at several different ambient temperatures [8]. Please notice that the intensity of emitting particles is very sensitive to the ambient temperature inside the furnace. The insert in Fig. 1 shows the result of a separate measurement, namely the yield of in the recovered soot *vs.* ambient buffer gas temperature. As can be recognized, the C_{60} yield increases as the ambient temperature increases up to 1100 °C with a threshold at around 500 °C. Remarkably, the observed emission decays with a clearly longer lifetime under the same conditions under which C_{60} is produced in high yields [8].

Figure 2 shows typical emission spectra of carbon nano-particles ejected from the surface of a graphite rod at the time delay (Δt) of 200 μs, 375 μs, and 1000 μs after laser vaporization, respectively. The recording of the emission of these carbon nanoparticles was carried out at 1150 °C furnace temperature, and at a laser fluence of 600 mJ/cm^2, where the yield of C_{60} was found to be high [9]. As outlined in the previous section, the emission intensity at each wavelength was obtained by accumulating the emission of the carbon nanoparticle cloud as a whole. Curves shown in Fig. 2 display the best fits for the wavelength distribution assuming blackbody radiation formula modified for the emissivity of small spherical particles [6]. Data obtained for 514.5 nm and 546.8 nm at 100 μs and 375 μs delay were omitted in the fitting, because the emission by C_2 Swan band ($d{:}^3\Pi_g \rightarrow a{:}^3\Pi_u$) overlaps heavily with the blackbody emission of carbon nanoparticles. Actually no C_2 emission was observed after $\Delta t > 500$ μs. Fig. 1 clearly demonstrates that the fit well reproduces the obtained emission profile, supporting that this blackbody emission comes from carbon nanoparticles ejected from the surface of the graphite rod immediately after laser vaporization. This figure also shows that the internal temperature of carbon fine particles becomes highest (5200 K) in the early stage ($\Delta t = 200$ μs), then decreases to the about 3500 K at $\Delta t = 375$ μs, and finally decreases down to 2000 K at $\Delta t = 1000$ μs.

Figure 3 shows a summary of the change of the derived internal temperature of carbon nanoparticles as a function of time delay after laser vaporization. In this figure, results obtained at different ambient temperatures of the furnace (1150 °C, 1000 °C, 700 °C and 550 °C, respectively) are also included. Other physical parameters were kept constant throughout the experiment. It can be seen that the internal temperature of the carbon nanoparticles

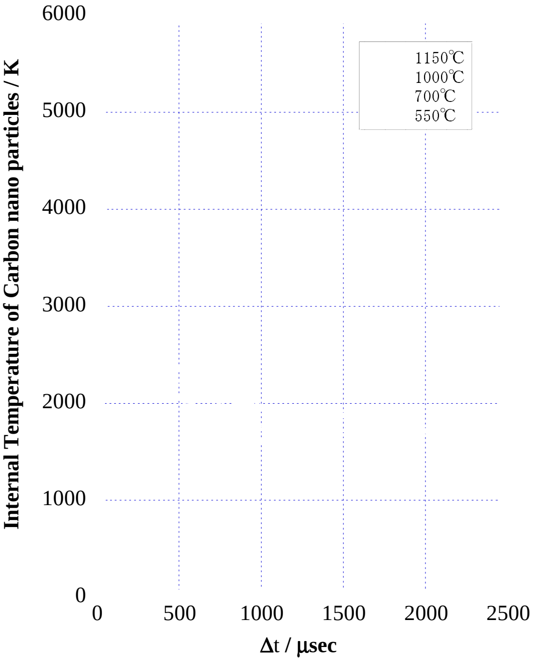

Fig. 3. Summary of the change of the internal temperature of carbon nanoparticles with delay after laser vaporization. each data was obtained at the indicated furnace temperature (1150 °C, 1000 °C, 700 °C, and 550 °C, respectively).

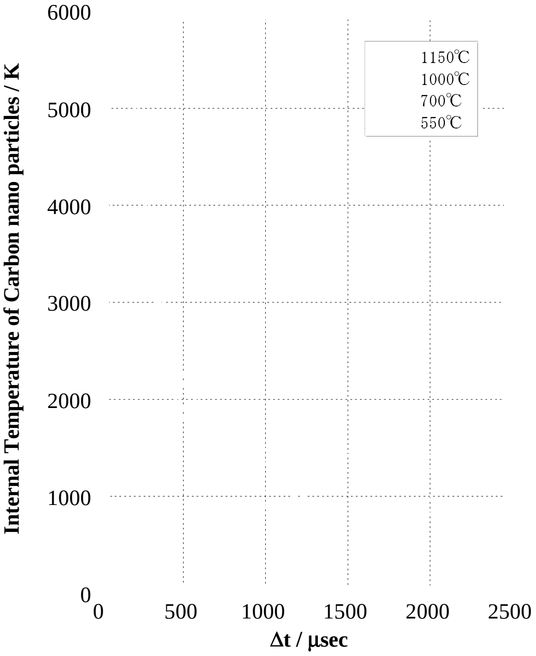

Fig. 4. Temperature-time ($T - \Delta t$) curves based on the formula $dT/dt = -C(T - T_e)$ obtained with different ambient temperature T_e.

rapidly decreases at $\Delta t < 400$ μs, where the decay of the internal temperature does not seem to be so sensitive to the ambient furnace, *i.e.* buffer gas temperature. However, after $\Delta t > 400$ μs, the decreasing tendency of the internal temperature is influenced by the buffer gas temperature. Particularly, when the furnace is set 1150 °C, where the yield of C_{60} was found to reach a maximum, the internal temperature decreases most slowly, and the total emission intensity itself is found to last rather long, *i.e.* for more than a few milliseconds (see Fig. 1).

To gain insight into the cooling of carbon nanoparticles, we refer to the work of Mitzner *et al.* [5], who considered several different kinds of cooling mechanisms for laser desorbed C_{60} in vacuum. According to the discussion of these authors, C_2-losses or other fragmentation processes are the main cooling mechanism for C_{60} at $T \geq 2400$ K in vacuum. However, the cooling rate (dT/dt) by this processes strongly depends on the absolute value of the temperature T through the term $\exp(-E_0/k_BT)$, where E_0 denotes the apparent excitation energy for dissociation. By using such an expression, we could not reasonably fit our $T - \Delta t$ cooling curves shown in Fig. 3. Radiative cooling mechanism, for which the cooling rate (dT/dt) is proportional to T^4, was also considered, but it could not reproduce our obtained $T - \Delta t$ curves either. In the present investigation, also the heat transfer from carbon fine particles to the ambient argon gas has to be considered. For this process, the cooling rate (dT/dt), it can be expressed by the following equation,

$$dT/dt = -C(T - T_e)$$

where T_e denotes the ambient buffer gas temperature given by the electric furnace, and C represents a constant which depends on the thermal diffusion between gas and particle, and also on the heat capacity and size of the carbon fine particles [11]. Fig. 4 shows the $T - \Delta t$ curves obtained by this equation setting $C \approx 5000(\mathrm{s}^{-1})$. At $\Delta t < 400$ μs, the cooling rate does not depend very much on the ambient temperature of the furnace. This behavior well corresponds to $T - \Delta t$ curves shown in Fig. 3. However, Fig. 4 also indicates that at $\Delta t > 400$ μs the temperature should drop faster as compared to the cooling curve shown in Fig. 3. The internal temperatures of carbon nanoparticles do not seem to converge sufficiently fast to the values of the ambient temperature. This suggests that an additional process sets in at $\Delta t > 400$ μs which delays the cooling of carbon nanoparticles.

The anomalies in the cooling of the nanoparticles can also be derived from our raw emission data. Fig. 5 shows the change in the emission intensity of carbon nanoparticles obtained using a band pass filter of 694.3 nm as a function of delay time. When the furnace temperature is set 1150 °C, it can be clearly seen that the emission intensity at this wavelength increases during 400 μs $< \Delta t <$ 800 μs, then gradually decreases thereafter. Similar increasing tendency was recognized for longer wavelength (632.8, 660.0, 720.0, 760.0, and 830.0 nm). However, when the ambient temperature of the furnace is set to 1000 °C or below, this increasing tendency becomes weak, and at 550 °C or below there is almost no indication of such an increasing tendency.

It is important to note that this increasing tendency in the emission of carbon nanoparticles at longer wavelength can only be recognized when the furnace temperature is

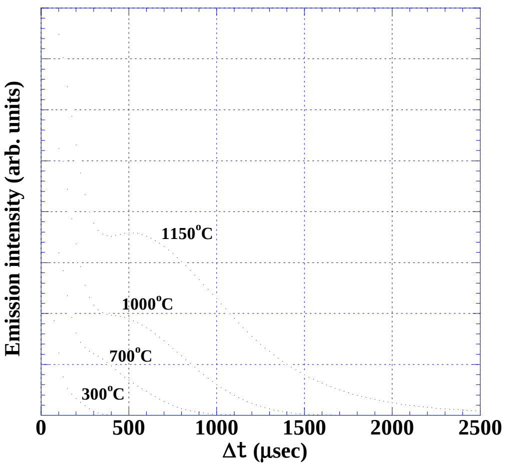

Fig. 5. Change in the emission intensity of carbon nanoparticles obtained with a bandpass filter at 694.3 nm. Each set of data was obtained at different ambient temperature (1150 °C, 1000 °C, 700 °C, and 300 °C, respectively).

kept high where also the yield of C_{60} or larger fullerenes is known to become high [9]. Since the blackbody radiation formula itself assures that the emission intensity at a certain wavelength monotonously increases with the temperature of the emitter (provided the total volume of all emitting particles remains the same), it is natural to think that a certain new source of blackbody radiation emerges at $\Delta t > 400\ \mu$s.

As a most probable candidate, this new source of blackbody radiation comes from the newly formed carbon clusters at $\Delta t > 400\ \mu$s by association of small carbon species, those of which can not give blackbody radiation by themselves. During the course of formation of these new clusters, exothermic processes would occur *e.g.* by the formation of C-C bonds. These processes are considered to be the heat source of blackbody radiation observed at $400\ \mu\text{s} < \Delta t < 1000\ \mu$s. It is interesting to point out that this exothermic process seems to be strongly correlated with the formation of C_{60} and other higher fullerenes, since only under the condition where C_{60} yields are high, this particular radiation appears and lasts as long as $\Delta t > 400\ \mu$s. As an alternative explanation, the emitting nanoparticles may possess internal energy, which is released as an additional blackbody emission and delays the cooling. However, in this case, it is highly likely that the internal temperature of carbon nanoparticles will increase at $\Delta t > 400\ \mu$s in order to give more blackbody emission intensity without changing the number of emitting particles. Fig. 3 shows that the internal temperature does not increase at $\Delta t > 400\ \mu$s. This picture is also consistent with a recent study by Kasuya *et al.* [9] suggesting that the key reaction for fullerene formation takes place in the reaction zone which lies about 20 mm far from the surface of the target rod. The position of this reaction zone is about the same location where in the present investigation the thermal emission of the nanoparticles lasts rather long, in the range of $400\ \mu\text{s} < \Delta t < 800\ \mu$s.

In summary, at $200\ \mu\text{s} < \Delta t < 400\ \mu$s, all of the observed blackbody radiation comes from carbon nanoparticles generated by laser vaporization of graphite rod. It is also considered that there exist small carbon clusters, which can not give blackbody emission by themselves. After $\Delta t > 400\ \mu$s, these small carbon clusters are used for the formation of C_{60} and other higher fullerene species under appropriate experimental condition. In this case new blackbody emission appears as an result of exothermic process required for fullerene formation, at the location about 20 mm far from the target within that time scale. Such an exothermic process diminishes after $\Delta t > 1000\ \mu$s, and thereafter only aggregation of carbon nanoparticles is possible, which does not include an exothermic process.

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