Influence of Pulse Frequency on Synthesis of Nano and Submicrometer Spherical Particles by Pulsed Laser Melting in Liquid

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Abstract

Submicrometer spherical particles (SMSPs) are reported to be fabricated by pulsed laser irradiation with a frequency of 10 or 30 Hz onto raw nanoparticles dispersed in liquid. Here, the effect of the pulse frequency on particles obtained by laser irradiation onto the suspension in a vessel, especially at higher pulse frequencies up to 800 Hz, is investigated. At 200 Hz or lower, SMSPs of similar size can be fabricated, as at 10 or 30 Hz, by the same number of pulses. This indicates that the time required for particle fabrication can be greatly reduced and production efficiency can be improved using a high-frequency laser. In contrast, at 400 Hz or above, nanospherical particles (NSPs) are formed in addition to SMSPs, and the mass fraction of SMSPs is drastically decreased. This result suggests that consecutive laser pulse irradiation induces heat accumulation in particles and suspensions, resulting in a temperature increase and partial evaporation of the particles at 400 Hz or above. From the temperature increase of the suspension, the local temperature of the liquid surrounding the particles is believed to be increased by heat dissipation from the heated particles. Calculations suggest that an increase in the local liquid temperature would cause further heating of the particles.

Keywords
Zinc oxide; Pulsed laser melting; Colloids; Nanoparticles; Submicrometer particles

1. Introduction

In recent years, much attention has been focused on nanoparticle fabrication by pulsed laser ablation in liquid (PLAL) [1–6]. In PLAL, a bulk target immersed in liquid is irradiated with a high power pulsed laser, and nanoparticles are formed through explosive interaction between the bulk target and the laser pulses [5]. Size reduction of nanoparticles caused by pulsed laser fragmentation in liquid (PLFL) has also been investigated [6–12]. In PLFL, dispersed particles interact explosively with a high power pulsed laser, and nanoparticles are formed [12]. These techniques require fewer chemical reagents and no vacuum equipment.

SMSPs of various materials are fabricated by pulsed laser irradiation with relatively low laser fluence onto colloidal nanoparticles dispersed in liquid [6, 13–20]. In this method, a suspension in a glass vessel is generally irradiated for an appropriate time with magnetic stirring. Parts of the raw nanoparticles dispersed in the suspension are irradiated and absorb laser energy; SMSPs are then formed by particle melting, fusing, and quenching [20]. By repeating this process, almost all the agglomerates consisting of raw nanoparticles in the suspension are modified to form SMSPs. NSPs are also fabricated by this method at higher laser fluence than that used to form submicrometer particles [21]. Raw particles that absorb the laser energy are heated above the boiling point of the material and evaporated, resulting in NSP formation at relatively high laser fluence.

In this method, an Nd:YAG laser with a pulse frequency of several tens of hertz is usually used [15]. Therefore, laser irradiation at higher pulse frequencies is probably effective in reducing the total irradiation time required to treat almost all the raw particles in the vessel. In PLAL, ablated mass linearly increases with

pulse frequency in the kHz and MHz regime until the temporal bubble-shielding effect arises [22, 23]. In PLML, kHz laser is also used to fabricate SMSPs [24]. However, the pulse frequency might affect particle cooling, because the interval between two consecutive laser pulses, that is, the maximum available time to cool particles heated over the melting point, would be comparable to the cooling time reported as 10^{-4} to 10^{-3} s when a high-frequency pulsed laser is used [25]. If the pulse interval is shorter than the cooling time, heat energy acquired from a single laser pulse cannot be completely dissipated within the pulse interval and will persist until a subsequent pulse arrives, resulting in a gradual temperature increase by heat accumulation in a particle even during the pulse interval. In this study, SMSPs are fabricated by KrF excimer laser irradiation at higher pulse frequencies than before to study the pulse frequency effect on the obtained particles.

2. Experimental section

Commercial ZnO particles (Sigma-Aldrich Co., LLC, < 100 nm) were dispersed in deionized water at a concentration of 200 ppm. Then, 6 ml of the suspension in a glass vessel was irradiated with a KrF excimer laser (Gigaphoton Inc., wavelength 248 nm, pulse width 50 ns) at various pulse frequencies (25–800 Hz). The beam size was 0.13 cm^2 (1.5 mm × 8.7 mm rectangle). The total number of pulses was fixed at 48,000 irrespective of the pulse frequency. Therefore, laser irradiation with a higher pulse frequency requires a shorter time to produce 48,000 pulses. The suspension temperature was measured with a thermocouple immersed in the liquid. After laser irradiation, the suspension was dropped onto a Si substrate to observe the particle morphology using a field-emission scanning electron microscope (FE-SEM, JSM-7001FA, JEOL Ltd.). To measure the size of the obtained SMSPs, the suspension was settled for a day to separate the NSPs from the produced SMSPs. A precipitate of the suspension was also dropped onto a Si substrate for FE-SEM observation.

3. Results and discussion

3.1. Particle morphology

SEM images of raw ZnO particles and particles obtained by KrF excimer laser irradiation at 100 Hz are presented in Fig. 1. Raw particles have angular morphology, and the average diameter of the raw particles is about 60 nm (Figure 1a). At a laser fluence of 182 mJ $pulse^{-1}$ cm^{-2}, agglomerates of raw particles melted, and SMSPs with an average diameter of 324 nm were formed (Fig. 1(b)). In contrast, at a laser fluence of 203 mJ $pulse^{-1}$ cm^{-2}, NSPs with an average diameter of 44 nm were formed in addition to SMSPs with an average diameter of 327 nm (Fig. 1(c)). In this case, agglomerates of raw ZnO particles would be vaporized by high-fluence laser irradiation. The vapor condenses and then solidifies to form spherical nanoparticles.

Fig. 2 shows SEM images of particles obtained after KrF excimer laser irradiation (182 mJ $pulse^{-1}$ cm^{-2}) at various pulse frequencies. The time taken to produce 48,000 pulses is 1,920 seconds at 25 Hz, 240 seconds at 200 Hz, 120 seconds at 400 Hz, and 60 seconds at 800 Hz. At pulse frequencies of 25 Hz to 200 Hz, almost all the obtained particles were SMSPs (Figs. 2(a) and 2(b)). In contrast, at a pulse frequency of 400 Hz and above (Figs. 2(c) and 2(d)), NSPs were formed in addition to SMSPs, although a laser fluence of 182 mJ $pulse^{-1}$ cm^{-2} was insufficient to obtain NSPs by vaporization at a pulse frequency of 100 Hz, as indicated in Fig. 1. This result suggests that heat energy absorbed by a particle is not completely dissipated during the pulse interval and subsequently accumulates with consecutive laser pulses. Figs. 3(a-d) shows SEM images of ZnO particle precipitates by natural sedimentation of the suspension irradiated with a KrF excimer laser at various pulse frequencies as depicted in Fig. 2. NSPs were easily separated from the suspension by natural sedimentation over one day. By counting the SMSPs in the SEM images of Figs. 3(a-d), histograms of particle diameter distribution are graphed, respectively (Figs. 3(e-f)).

Fig. 4(a) shows the pulse frequency dependence of the mass fraction of SMSPs in the products estimated from SEM images shown in Fig. 2. The mass fraction of the SMSPs to the all particles (SMSPs and NSPs) in the products was estimated by converting the size distribution data of all the SMSPs and NSPs in the SEM images into

mass ratio of SMSPs to NSPs assuming that all particles are spherical and no compositional change from ZnO. Since the particle mass is proportional to the cube of the particle diameter, SMSPs are much heavier than NSPs. Before natural sedimentation, most particles obtained were SMSPs at a pulse frequency of 25 to 200 Hz. In contrast, at 400 Hz or higher, the mass fraction of SMSPs was drastically decreased through vaporization. Therefore, laser irradiation at a pulse frequency of 200 Hz and below is appropriate for effectively obtaining SMSPs. By natural sedimentation over one day, we could remove NSPs from the suspension and prepare an SMSP suspension with a mass fraction of over 90%.

The pulse frequency dependence on the average diameter of SMSPs measured from the histograms of particle diameter distribution (Figs. 3(e-h)) at a laser fluence of 182 mJ pulse^{-1} cm^{-2} is depicted in Fig. 4(b). For a pulse frequency range where mainly SMSPs are obtained, as shown in Fig. 2 ($\leq$ 200 Hz), obtained particles have similar sizes of about 300 nm. Thus, a larger pulse frequency up to 200 Hz is effective in reducing the irradiation time for SMSP synthesis. Above the threshold for NSP formation in Fig. 2 ($\geq$400 Hz), however, the obtained large particles have a submicrometer size of about 240 nm, which is smaller than those obtained at a lower pulse frequency ($\leq$ 200 Hz). This result suggests that particles irradiated with a pulsed laser at high frequency might be heated, resulting in size reduction of the SMSPs due to partial evaporation.

Fig. 4(b) also shows the pulse frequency dependence on the average diameter of NSPs measured from SEM images in Fig. 2. The average particle diameter decreases with the pulse frequency above the threshold for NSP formation determined from Fig. 2 ($\geq$400 Hz). The average diameter of nanoparticles obtained by pulsed laser irradiation is reported to gradually decrease as the laser fluence increases [9, 10]. Therefore, above the threshold for NSP formation, the effect of the pulse frequency on the change in nanoparticle size would correspond to the effect of laser fluence reported earlier. Heat accumulation resulting from consecutive high-frequency laser pulses would cause further heating of the particles.

3.2. Liquid temperature

The average suspension temperature during laser irradiation is gradually elevated by heat dissipation from the particles that absorb laser energy to the surrounding liquid. Fig. 5 shows the suspension temperature increase in a glass vessel during laser irradiation at various pulse frequencies. The highest attained suspension temperature increases with pulse frequency because the input energy per unit time increases in proportion to the pulse frequency. However, the temperature of the liquid adjacent to the particles in the laser-irradiated region is higher than that of the laser-irradiated region remote from the particles, because the particles irradiated with laser pulses are the heat source for the suspension. Therefore, the temperature of the liquid adjacent to the particles is much higher than the average suspension temperature, and adjacent liquid would probably evaporate depending on the laser irradiation conditions, especially at the high input energy per unit time accompanying a high pulse frequency. Such a high liquid temperature would induce vaporization of the liquid at the interface and affect the highest attained temperature discussed in the following section.

3.3. Calculation of particle temperature

These experimental results suggest that the heat energy absorbed from a single laser pulse is not completely dissipated before the arrival of the subsequent laser pulse, and it accumulates in a particle as a result of consecutive laser pulses at high frequencies. Thus, the time required to completely dissipate the energy supplied by a laser pulse is estimated to be longer than 2.5 ms, which is the corresponding laser pulse interval for a pulse frequency of 400 Hz. However, this cooling time is much longer than the value estimated by conductive heat transfer calculation using the particle heating-cooling model [26]. The heat energy dissipated from the particles q_p is described by the following equation:

$$\frac{dq_p}{dt} = h \cdot \pi d^2 \cdot \{T_p - T_0\} \quad (1)$$

where

$$h = \frac{Nu_d \cdot k}{d} \quad (2)$$

Here, h is the heat transfer coefficient, d is the particle diameter, T_p is the particle temperature, T_0 is the

temperature of the surrounding liquid, Nu_d is the Nusselt number, and k is the heat conductivity of the surrounding liquid or vapor generated by liquid evaporation. On the submicrometer scale, the Nusselt number is constant at $Nu_d \approx 2$, because the convection around a submicrometer particle is negligible [27, 28]. When the particles are cooled by evaporated liquid, the heat transfer coefficient of particles 300 nm in diameter can be estimated as 0.29 MW m^{-2} K^{-1} from Eq. (2). In this case, particles heated to the melting point are cooled to the temperature of the surrounding liquid on a microsecond time scale. Therefore, a pulse interval of 2.5 ms is sufficient for particle cooling.

The heat energy accumulated in the particles E_p is the difference between particle heating by laser absorption and particle cooling by conductive heat transfer.

$$\frac{dE_p}{dt} = Q_{abs}^{\lambda} \cdot \frac{\pi d^2}{4} \cdot J(t) - \frac{dq_p}{dt} \quad (3)$$

Here, Q_{abs}^{λ} is the absorption efficiency, $\frac{\pi d^2}{4}$ is the particle geometric cross section, and $J(t)$ is the time-dependent laser fluence. The absorption efficiency of SMSPs is calculated from refractive index and extinction coefficient using Mie theory [25, 29].

The particle temperature T_p below the melting point, at the melting point, and above the melting point is defined by the following equations.

$$T_p(t) = T_0 + \frac{1}{\rho_p \cdot \frac{\pi d^3}{6} \cdot c_s} \cdot E(t) \quad (4)$$

$$T_p(t) = T_m \quad (5)$$

$$T_p(t) = T_{\mathrm{m}} + \frac{1}{\rho_p \cdot \frac{\pi d^3}{6} \cdot c_l} \cdot \left[E(t) - \rho_p \cdot \frac{\pi d^3}{6} \cdot \left(H_{T_m} - H_{T_0} + \Delta H_m\right)\right] \quad (6)$$

Here, ρ_p is the density of the particle, $\frac{\pi d^3}{6}$ is the particle volume, c_s is the particle specific heat in the solid state, T_m is the melting point of the material, $H_{T_m} - H_{T_0}$ is the relative enthalpy required for the start of melting, ΔH_m is the latent enthalpy of melting, and c_l is the particle specific heat in the liquid state.

Fig. 6 shows the calculated highest attained temperature of a ZnO spherical particle 250 nm in diameter irradiated with a nanosecond laser (pulse width 50 ns, laser fluence 182 mJ $pulse^{-1}$ cm^{-2}). The highest attained temperature is elevated by an increase in the temperature of the surrounding liquid because this increases the initial particle temperature. Moreover, the highest attained temperature of the particles constantly cooled by a liquid vapor film (red line) was higher than that of the particles cooled by a liquid undergoing a phase transition from liquid to vapor (black line). When using a laser with a pulse width of several tens of nanoseconds, the particles dissipate heat energy to the surrounding liquid because heated particles are cooled by a liquid with high heat conductivity during the initial stage of heating [26]. Therefore, a low-heat-conductive vapor film around the particles generated by heat accumulation reduces heat dissipation.

Calculations suggest that the highest attained temperature of a particle increases by a few hundred K through heat accumulation in the adjacent liquid. The actual attained temperature of particles irradiated with a pulsed laser at a laser fluence of 182 mJ $pulse^{-1}$ cm^{-2} would be near the boiling point because NSPs were formed at a laser fluence of 203 mJ $pulse^{-1}$ cm^{-2} (Fig. 1). Therefore, heat accumulation in the liquid adjacent to particles may cause heating of the particles to the boiling point, resulting in nanoparticle formation at a pulse frequency of above 400 Hz.

4. Conclusions

SMSPs were fabricated by irradiation with a KrF excimer laser (wavelength 248 nm, pulse width 50 ns) onto 6 ml of the suspension with a particle concentration of 200 ppm in a glass vessel. The total time of laser irradiation for the synthesis of SMSPs can be reduced using a high-frequency pulsed laser at a laser fluence of 182 mJ $pulse^{-1}$ cm^{-2} ($\leq$ 200 Hz). The size of the obtained SMSPs is similar in this frequency range. In contrast, NSPs and SMSPs are simultaneously formed using a pulsed laser with a frequency of 400 Hz or higher. This result suggests that the

laser energy is accumulated in particles and liquid by consecutive laser pulses, resulting in partial evaporation of the particles above the pulse frequency threshold (≥400 Hz). Through this vaporization process, the average diameter of the obtained SMSPs decreased. However, the time required to cool particles from the melting point to ambient temperature is much shorter than 2.5 ms (pulse interval for a pulse frequency of 400 Hz). Therefore, nanoparticle formation was attributed to an increase in the suspension temperature. The average suspension temperature was elevated during laser irradiation, especially at a high pulse frequency. The liquid temperature adjacent to the particles is higher than the average suspension temperature because the particles irradiated with laser pulses are the heat source for the suspension. Calculations suggest that the highest attained temperature of the particles increases by a few hundred K through heat accumulation in the adjacent liquid, resulting in nanoparticle formation at a high pulse frequency.

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Figure Captions

Fig. 1. SEM images of (a) raw ZnO particles and particles irradiated with a KrF excimer laser (100 Hz) at a laser fluence of (b) 182 mJ pulse^{-1} cm^{-2} and (c) 203 mJ pulse^{-1} cm^{-2}.
Fig. 2. SEM images of ZnO particles irradiated with a KrF excimer laser at a laser fluence of 182 mJ pulse^{-1} cm^{-2}. Pulse frequency of (a) 25 Hz, (b) 200 Hz, (c) 400 Hz, and (d) 800 Hz.
Fig. 3. SEM images of ZnO particle precipitates by natural sedimentation of the suspension irradiated with a KrF excimer laser irradiation at a laser fluence of 182 mJ pulse^{-1} cm^{-2}. Pulse frequency of (a) 25 Hz, (b) 200 Hz, (c) 400 Hz, and (d) 800 Hz. The corresponding particle diameter distributions of (a-d) are shown in (e-f), respectively.
Fig. 4. Pulse frequency dependence on (a) mass fraction of SMSPs in the products and (b) average particle diameter measured by counting only ZnO SMSPs in Fig. 3 and only NSPs in Fig. 2 obtained by nanosecond pulsed KrF excimer laser irradiation at a laser fluence of 182 mJ pulse^{-1} cm^{-2}.
Fig. 5. Increase in the suspension temperature during laser irradiation at various pulse frequencies measured by thermocouple immersed in the liquid.
Fig. 6. Highest attained temperature of SMSPs 250 nm in diameter irradiated with a nanosecond laser with pulse width of 50 ns at a laser fluence of 182 mJ pulse^{-1} cm^{-2}. Cooling by surrounding liquid undergoing phase transition from liquid to vapor (Black line), and cooling by surrounding vapor generated by liquid evaporation (Red line).

Highlights

- Submicrometer spherical particles were fabricated at various pulse frequencies.
- Production efficiency was improved by a high-frequency laser.
- Spherical nanoparticles were formed above the pulse frequency threshold.
- The effect of the liquid temperature on the pulsed laser heating was estimated.