

Fabrication of Spherical-Shaped Submicron Particles of ZnO Using Laser-induced Melting of Submicron-sized Source Materials

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Recently, laser irradiation (LI) using non-focused laser beam at moderate fluence for colloidal nanoparticles concentrates much attention as a promising technique to produce spherical submicron-sized particles (SSMPs). In this study, we apply this technique on submicron-sized source particles of ZnO, differing from the previous studies in which nano-sized source particles were used. By using submicron-sized source particles, SSMPs were produced with no additional treatment to remove remaining source nanoparticles. In addition, it was revealed that SSMPs are not produced via simple melting of single source particle, but from agglomerates of the source particles that were formed prior to LI. It was also revealed that additional agglomeration of the SSMPs occurs during LI, resulting in the size increase of SSMPs with increasing laser fluence.

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1. Introduction

Laser irradiation (LI) for colloidal particles is a convenient method to control particle size. Recently, the laser-induced melting in liquids (LIML) technique receives much attention as an alternative laser irradiation method [1-7]. Differing from general laser irradiation method, in which focused laser irradiation at high fluence is used to induce evaporation of particles [8,9], non-focused laser irradiation at moderate fluence is used in LIML. In such laser irradiation conditions, the melting and fusion of source particles are efficiently brought about, although evaporation is suppressed, leading to the formation of spherical submicron-sized particles (SSMPs). Due to their smooth surface and narrow size distribution, SSMPs produced by the LIML method are a good candidate of cell markers and light scattering medium. They have applied this technique to prepare SSMPs of various materials such as B₄C [1], Fe [2], Cu [2], Ag [6], Si [5] CuO [2,7], WO [2], ZnO [2,3], and TiO₂ [4].

Recent works have shed light on the formation mechanism of SSMPs [10,11]. It has been revealed that SSMPs are not formed via the collision of melted NPs, but are formed via the fusion of agglomerated source NPs. In other words, it is necessary to induce the agglomeration of the source NPs prior to LI to produce SSMPs. In addition, this finding also reveals a difficult point of the LIML method. As the above works have shown, in some cases, the control of the agglomeration conditions of the source NPs is difficult. For example [10], no SSMP is produced from gold NPs stabilized by 1 mM sodium citrate, because sodium citrate inhibits the agglomeration of the NPs.

SSMPs are produced from gold NPs in pure water, because no protective reagent is contained. However, gold NPs in pure water is so instable that significant amount of the NPs are precipitated without absorbing LI and remain after LI. In general, the source NPs remaining after LI should be removed by means of centrifugation, leading to the decrease in the productivity of SSMPs.

In this study, we have employed an alternative approach to improve the productivity of SSMPs in the LIML method. We have used submicron-sized source particles instead of NPs. Using submicron-sized source particles, it can be expected that a SSMP will be formed via simple melting of single source particle, i.e. no agglomeration and fusion of NPs will occur. Therefore, no centrifugation treatment will be necessary after LI.

2. Experiments

The source material used in the present study was commercially available ZnO particles with two different sizes (average diameter: 100, 500 nm). These source particles were dispersed in distilled water. The concentration of the source particles was 0.2 mg/mL. LI using non-focused laser beam at 355 nm of a nanosecond-pulsed Nd:YAG laser was carried out for the colloidal solutions. The duration and repetition rate of laser pulse were, respectively 6 ns and 10 Hz. The diameter of the laser beam was 5 mm. The colloidal solutions were stirred during LI.

3. Results and Discussions

Fig. 1a shows a SEM image of 100 nm source particles of ZnO. The source particles have polygonal-crystalline-shapes. It was confirmed that the size of the most of the

particles were ca. 100 nm, although larger particles were contained. After the LI at 100 mJ/cm², these particles were transformed to SSMPs with the average diameter of 230 nm (Fig. 1b). As expected, no NPs were contained without using centrifugation treatment that is necessary to remove remaining NPs when nano-sized source particles are used. Recently, we have utilized these SSMPs as a random-laser medium [12].

Similar result was obtained from LI for the 500 nm source particles. As shown in Fig. 2a and 2b, SSMPs with the average diameter of 610 nm were produced from the polygonal-crystalline-shaped source particles (the diameter of the most of the particles was ca. 500 nm) after LI at 300 mJ/cm² for 90 min. From the fact that the average diameter of the SSMPs produced from the 500 nm source particles is larger than that of the SSMPs produced from the 100 nm source particles, one might consider that each SSMP must be produced via simple melting of single source particle. However, it should be noted that the size of the SSMPs produced from both the 100 and 500 nm source particles is significantly larger than that of the source particles, indicating that some size increasing processes are involved in this system.

The results of the experiments and theoretical calculations in the previous studies showed that the size of SSMPs produced by LI for NPs increases with increasing laser fluence [1-3,5], because the maximum volume of a particle which LI can melt increases with increasing laser energy absorbed by a particle. In addition, when such size increase of SSMPs occurs, involving of surrounding NPs by SSMPs during LI should occur. Taking such processes into account

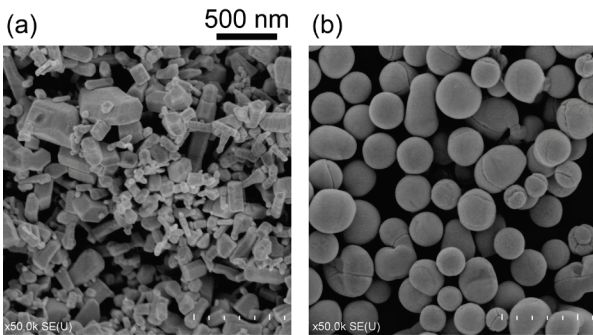


Fig. 1 SEM images of (a) 100 nm ZnO source particles and (b) SSMPs obtained by LI at 100 mJ/cm² for 90 min. The average diameter of the SSMPs was 230 nm.

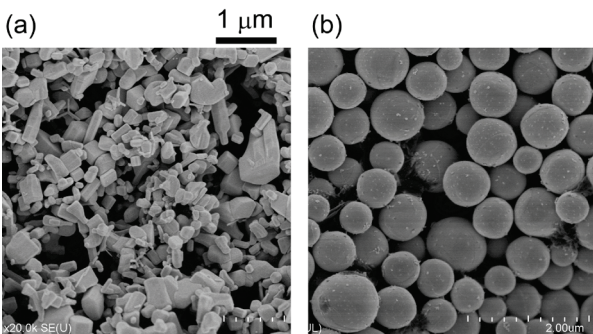


Fig. 2 SEM images of (a) 500 nm ZnO source particles and (b) SSMPs obtained by LI at 300 mJ/cm² for 90 min. The average diameter of the SSMPs was 610 nm.

for the present result, the fact that the size of the SSMPs is larger than that of the source particles suggested that the laser fluence would be higher than that enough to melt single source particle and the secondary fusion of SSMPs would occur. To investigate such process, shape change of ZnO particles at lower laser fluence was observed. As shown in Fig. 3a, for the 100 nm source particles, significant amount of the source particles remained when laser fluence was decreased to 90 mJ/cm², although the size decrease of SSMPs was not clear. For the 500 nm source particles, melted particles with non-spherical shapes were observed when laser fluence was decreased to 150 mJ/cm² (Fig. 3b). Carefully observed, such non-spherical particles were formed in the produces from the 100 nm source particles (Fig. 3a). One assumes that these non-spherical parti-

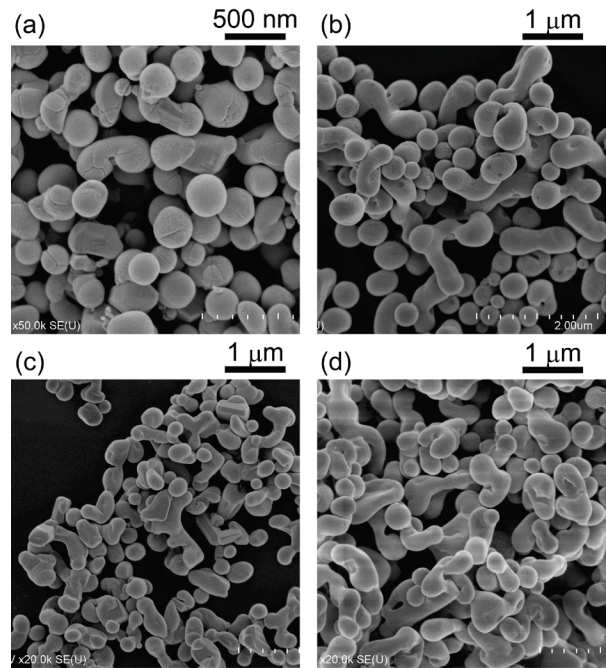


Fig. 3 SEM images of ZnO particles produced by LI for (a) 100 nm particles at 90 mJ/cm², (b) 500 nm particles at 150 mJ/cm², (c) 500 nm particles at 100 mJ/cm², and (d) 500 nm particles dispersed in a 20 mM sodium dodecyl sulfate aqueous solution at 140 mJ/cm². The LI duration was 90 min.

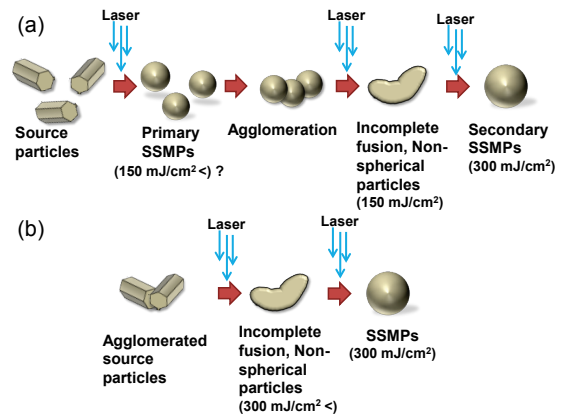


Fig. 4 Possible formation processes of SSMPs and the non-spherical particles from the submicron-sized source particles. Laser fluence used in LI for 500 nm particles are indicated.

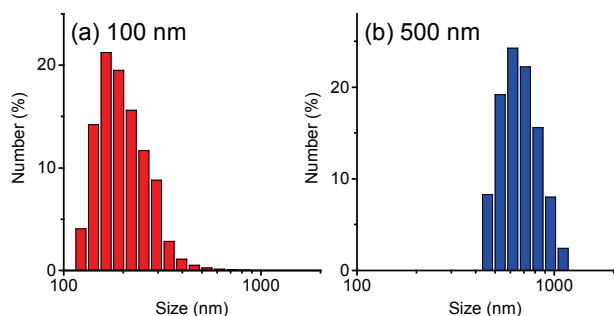


Fig. 5 Size distribution of the (a) 100 nm and (b) 500 nm source ZnO particles measured by means of the DLS method. The average size is (a) 210 and (b) 590 nm.

cles were formed via the incomplete secondary fusion of smaller SSMPs which can be produced at lower fluence (Fig. 4a). However, as shown in Fig. 3c, the non-spherical particles were still formed at 100 mJ/cm² at which significant amount of the source particles remained, suggesting that the non-spherical particles were formed from the source particles directly, not via the secondary fusion of SSMPs. In other words, these results suggested that the source particles form anisotropic-shaped agglomerates prior to LI, and the non-spherical particles are formed via the melting of such anisotropic-shaped agglomerates. At 100 mJ/cm² for 100 nm source particles and at 300 mJ/cm² for 500 nm source particles, the anisotropic-shaped agglomerates are melted completely and form SSMPs (Figs. 2b and 4b).

To confirm the agglomeration of the source particles, we carried out dynamic light scattering (DLS) measurements. As shown in Fig. 5, the average size of the 100 and 500 nm source particles obtained by means of the DLS measurements was respectively 210 and 590 nm. These values are higher than the size of the single source particles, and are similar to the average size of the SSMPs produced from these source particles. From these results, it is concluded that the source particles used in this study formed agglomerates prior to LI, and the SSMPs obtained from the submicron-sized source particles were formed from the agglomerates of the source particles.

We have tried to disperse the agglomerating source particles. However, when the source particles (500 nm) were dispersed in solutions containing surfactants (20 mM sodium dodecyl sulfite) and mixed by means of a vortex mixer, the major products formed at 140 mJ/cm² were still the non-spherical particles (Fig. 3d). Thus, it is suggested that

the agglomerates would be formed in the manufacturing process of the source particles such as calcination.

The result of the above experiments indicates that the minimum size of the SSMPs produced from the submicron-sized source particles is determined by size of the agglomerates of the source particles formed prior to LI. Next, the laser fluence dependence of SSMPs' size at higher laser fluence was investigated. Fig. 6a and 6b respectively shows the SSMPs produce from the 100 nm source particles by LI at 125 and 150 mJ/cm². The average size of these SSMPs was 270 nm (125 mJ/cm²) and 310 nm (150 mJ/cm²). From Fig. 1b (SSMPs produced by LI at 100 mJ/cm²) and these data, it was found that the size of SSMPs increases with increasing laser fluence. In addition, the relation between the laser fluence and the size of SSMPs is almost similar to that observed in the LIML study using nano-sized source particles [3].

In the formation process of SSMPs from nano-sized source particles, SSMPs grow involving surrounding NPs during LI [4]. Similarly, the fact that SSMPs formed at the higher fluence were larger than the source agglomerates indicates that SSMPs produced in the present system can also grow involving surrounding source particles and SSMPs during LI. In other words, the secondary fusion of SSMPs occurred when laser fluence was increased to 125 mJ/cm² and higher. To observe the secondary fusion of SSMPs more clearly, we carried out additional LI at 150 mJ/cm² for SSMPs that were produced by LI at 100 mJ/cm². As shown in Fig. 6c, the average size of the SSMPs was increased from 230 to 330 nm by the additional LI. In addition, this size is similar to that of SSMPs produced by LI for the source particles at 150 mJ/cm² directly (Fig. 6b). This result strongly supports that the increase in the SSMPs' size observed at 125 and 150 mJ/cm² is due to the secondary fusion of SSMPs.

It must be noted that the agglomeration (not fusion) of SSMPs during LI can also occur at 100 mJ/cm². However, larger SSMPs cannot be formed because the laser fluence is insufficient to melt the SSMPs' agglomerates.

4. Conclusion and remarks

The LIML method was carried out using submicron-sized source particles of ZnO, instead of nano-sized source particles. SSMPs that can be utilized as random laser medium were successfully obtained with no purification treatment that is necessary to remove remaining NPs when nano-sized source particles are used. It was found that the

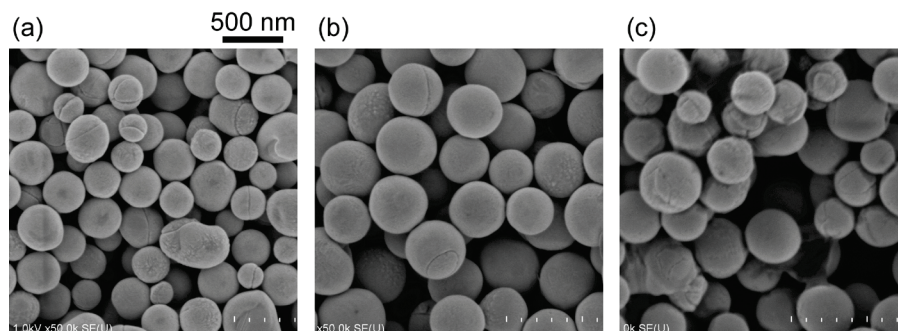


Fig. 6 SSMPs produced by LI for 100 nm ZnO source particles at (a) 125 mJ/cm² and (b) 150 mJ/cm². (c) SSMPs produced by additional LI 150 mJ/cm² for SSMPs produced by LI at 100 mJ/cm² for 100 nm particles. The duration of each LI duration was 90 min. The average diameter of the SSMPs was (a) 270, (b) 310, and (c) 330 nm.

SSMPs were not formed from the single source particle but from the agglomerates of the source particles. Therefore, the minimum size of SSMPs and the minimum laser fluence necessary to obtain SSMPs were determined by the size of the source agglomerates. On the other hand, at higher laser fluence, the increase in the SSMPs' size as a result of the secondary fusion of SSMPs became significant.

It must be noted that such roles of the agglomeration and fusion are essentially the same as those in the formation process of SSMPs from nano-sized source particles. However, these roles can be observed more clearly when submicron-sized source particles are used, because the unit (size of single particle) of the size changes is clearer. Another important point derived from the present study is that the minimum size and the size distribution of the SSMPs strongly depend on the agglomeration conditions of the source particles. Therefore, pre-treatment of the source particles such as milling will be useful to control the size and size distribution of SSMPs more precisely.

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