Effect of ultrasonic wave on the syntheses of Au and ZnO nanoparticles by laser ablation in water

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Abstract We synthesized Au and ZnO nanoparticles by laser ablation in distilled water with the superposition of an ultrasonic wave. The effect of the ultrasonic wave was examined on the optical absorbance of colloidal solution and the crystallinity of synthesized nanoparticles. The absorbance of colloidal solution was enhanced by the ultrasonic wave, indicating more efficient production rate of nanoparticles. In addition, the ultrasonic wave enhanced the crystallinity of synthesized nanoparticles. These enhancements are attributed to the fact that the ultrasonic wave drives the repetitive formations and collapses of cavitation bubbles.

1 Introduction

Nanoparticles of various materials are applicable to various fields such as optical devices and medicines. The physical and chemical properties of nanoparticles are correlated with their structures and sizes. High crystallinity and uniform size distribution of nanoparticles are important characteristics.

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Recently, liquid-phase laser ablation attracted much attention as a novel method for synthesizing crystalline nanoparticles [1–8]. There are two types of reaction fields in liquid-phase laser ablation: laser ablation plasma and cavitation bubble. A remarkable feature of liquid-phase laser ablation is the fact that these reaction fields have high temperatures and high pressures. The high pressure and the high temperature of the laser ablation plasma are owing to the tight confinement of particles ejected from the target by ambient liquid [4, 9]. The cavitation bubble induced by liquid-phase laser ablation expands and shrinks with time [10], and another high-temperature, high-pressure state is realized at the collapse of the cavitation bubble [11]. The formation and the collapse of the cavitation bubble are unique phenomena of liquid-phase laser ablation, and are never realized in gasphase laser ablation.

In general, atomic and molecular species ejected from the target grow into nanoparticles inside the reactions fields and at the interface with ambient liquid [6, 12]. In particular, in a recent work, we have observed the growth of nanoparticles inside the cavitation bubble by laser-light scattering [13]. Therefore, it is expected that controlling the dynamics of the laser ablation plasma and the cavitation bubble is helpful to control the structure and the size of nanoparticles synthesized by liquid-phase laser ablation. We have proposed adding acoustic pressure by an exciting ultrasonic wave in ambient liquid as a method for controlling the dynamics of the reaction fields. In a previous paper [14], we have reported enhanced optical emission intensity of a laser ablation plasma and repetitive formations and collapses of cavitation bubbles in the presence of an ultrasonic wave in ambient water. By combining the above knowledge, i.e., the growth of nanoparticles inside the cavitation bubble and the control of the dynamics of the cavitation bubble, we can ex-

pect useful effects of the ultrasonic wave on the synthesis of nanoparticles.

In this work, we synthesized Au and ZnO nanoparticles by laser ablation in water with the superposition of an ultrasonic wave. Au and ZnO nanoparticles have unique properties for applications to biosensors and ultraviolet-light emitters [15, 16]. We examined the effect of the ultrasonic wave on the morphology, the optical absorbance, and the crystallinity of Au and ZnO nanoparticles.

2 Experiment

The experimental apparatus is schematically shown in Fig. 1. We prepared a rectangular container which was filled with distilled water. The inner size of the container was $70 \times 70 \times 120$ mm. A glass cell of $10 \times 50 \times 40$ mm was placed in the container to collect synthesized nanoparticles efficiently. The inner glass cell was also filled with distilled water, and an Au or Zn target was installed in the cell. The heights of water in the inner cell and the container were the same. A piezoelectric ultrasonic transducer was mounted at the bottom of the container, and an electrical power of 50 W at a frequency of 32 kHz was applied to the transducer to excite ultrasonic wave. The ultrasonic wave propagated toward the top of the container. The target was irradiated by YAG laser pulses with a wavelength of 1064 nm and a pulse duration of 10 ns from the normal direction. The laser beam was focused using a lens, and the laser energy was 1.5 mJ. The repetition frequency and the irradiation duration of the YAG laser pulses were 10 Hz and 20 minutes, respectively. The colloidal solution obtained inside the inner cell was analyzed by optical absorption spectroscopy. We dropped the colloidal solution onto a Si substrate for examinations using SEM and XRD. A carbon-coated copper grid was used for TEM analysis.
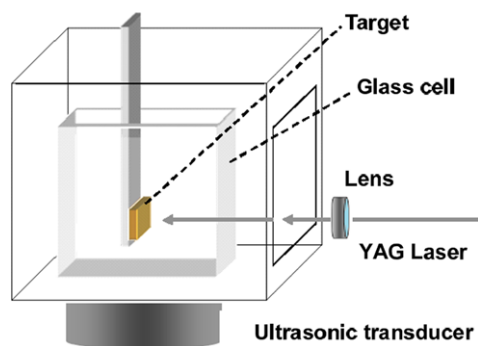

Fig. 1 Schematic drawing of experimental apparatus for synthesizing Au and ZnO nanoparticles by laser ablation in water with an ultrasonic wave

3 Results

3.1 Au nanoparticles

Optical absorbance spectra of colloidal solutions prepared by laser ablation of an Au target are shown in Fig. 2. The color of the colloidal solution prepared without ultrasonic wave was light pink as shown by the left bottle in the inset of Fig. 2(b). The color of the colloidal solution prepared with the ultrasonic wave was darker pink. A comparison between the optical absorbance spectra of these colloidal solutions is shown in Fig. 2(a). The spectra had characteristic absorption peaks at 520 nm, which were due to the surface plasmon band of Au nanoparticles [1]. A stronger absorbance at the surface plasmon peak was observed for the colloidal solution prepared with the ultrasonic wave, indicating the
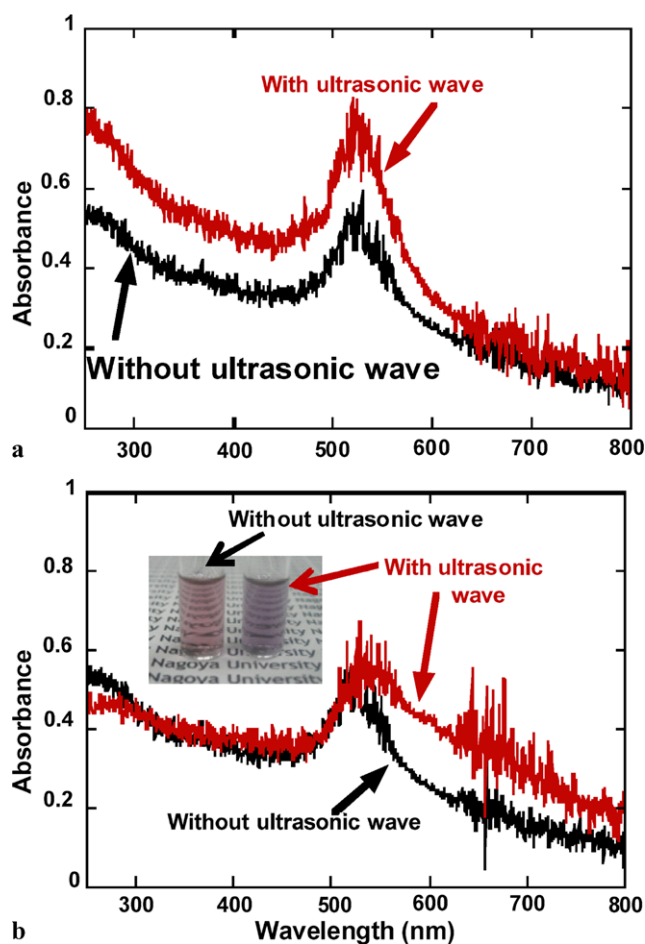

Fig. 2 Optical absorbance spectra of colloidal solutions of Au nanoparticles prepared with and without an ultrasonic wave. (**a**) Optical absorbance spectrum of colloidal solution prepared with an ultrasonic wave at the normal excitation mode is compared with absorbance spectrum with no ultrasonic wave. (**b**) Optical absorbance spectrum of colloidal solution prepared with an ultrasonic wave at the resonant excitation mode is compared with the absorbance spectrum with no ultrasonic wave. Pictures of colloidal solutions prepared with and without an ultrasonic wave are shown in the inset of (**b**)

increase in the density of nanoparticles stored in it. We examined the volume of the ablation crater formed on the surface of the target. As a result, we found that the volume of the ablation crater formed with the ultrasonic wave was 1.4 times greater than that without the ultrasonic wave, indicating more efficient erosion of the target in the presence of the ultrasonic wave.

We had another excitation mode of ultrasonic wave. When we adjusted the position of the inner glass cell in the vertical direction precisely, we observed the formation of mist from the water surface. This may be related to capillary wave and cavitation at the water surface [17]. The formation of mist means an increase in the pressure change at the water surface, and hence, we can reasonably expect an increase in the ultrasonic pressure in water. We call this condition as "resonant excitation" in this paper. The colloidal solution shown by the right bottle in the inset of Fig. 2(b) was prepared at the resonant excitation. The color of the colloidal solution prepared at the resonant excitation was not pink but purple. Figure 2(b) shows a comparison between the absorbance spectra of the purple colloidal solution and a colloidal solution prepared with no ultrasonic wave. The absorbance spectra of the purple colloidal solution had broadband absorbance at a wavelength range of 530–800 nm. In addition, the wavelength of the peak absorbance of the purple colloidal solution was 530 nm, which was shifted from the wavelength of the surface plasmon band of Au nanoparticles.

Figure 3(a) shows a TEM picture of nanoparticles prepared with no ultrasonic wave, while a TEM picture of nanoparticles prepared at the resonant excitation is shown in Fig. 3(b). As shown in Fig. 3(a), we observed relatively dispersed nanoparticles when we applied no ultrasonic wave. In contrast, we observed aggregated nanoparticles in the sample prepared at the resonant excitation, as shown in Fig. 3(b). On the other hand, we observed negligible change in the size distribution of nanoparticles by applying the ultrasonic wave, in spite of the difference in the degree of dispersion.

We examined the crystallinity of nanoparticles by XRD. Figure 3(c) shows XRD spectra of nanoparticles prepared with and without the ultrasonic wave. The ultrasonic wave was applied at the resonant excitation mode. The diffraction peaks at $2\theta = 38.3°$ and $44.2°$ correspond to the Au(111) and Au(200) planes, respectively. As shown in Fig. 3(c), nanoparticles prepared at the resonant excitation had higher diffraction peaks. In addition, the crystalline sizes evaluated from the Au(111) and Au(200) peaks were 20.1 and 19.4 nm for nanoparticles prepared at the resonant excitation, respectively, while they were 12.9 and 8.7 nm for nanoparticles prepared with no ultrasonic wave. Hence the excitation of ultrasonic wave at the resonant mode enhanced the crystallinity of Au nanoparticles.
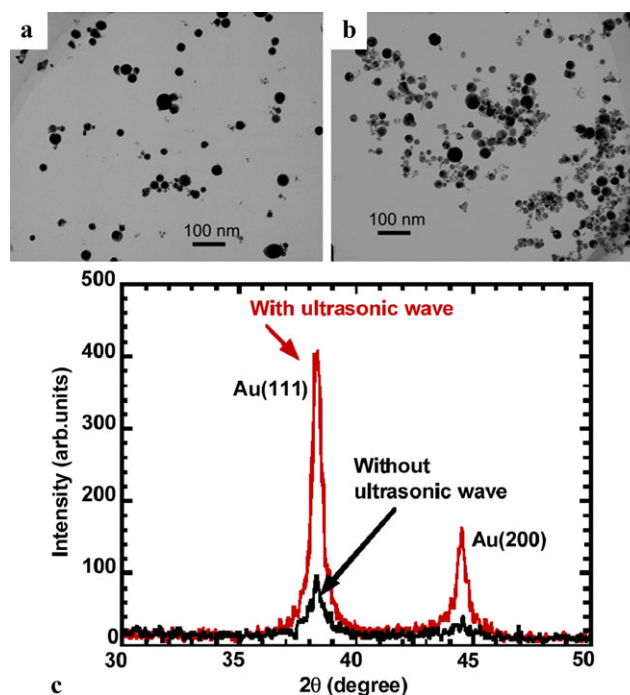

Fig. 3 TEM images and XRD spectra of Au nanoparticles. (**a**) TEM image of Au nanoparticles prepared with no ultrasonic wave, (**b**) TEM image of Au nanoparticles prepared with an ultrasonic wave at the resonant excitation mode, (**c**) comparison between XRD spectra of Au nanoparticles prepared with and without an ultrasonic wave. The ultrasonic wave was excited at the resonant mode

3.2 ZnO nanoparticles

Optical absorbance spectra of the colloidal solutions of ZnO nanoparticles prepared with and without an ultrasonic wave were compared. The normal mode was used for the excitation of the ultrasonic wave. We observed a stronger absorbance for the colloidal solution prepared with the ultrasonic wave, which was the same result as the case of Au nanoparticles.

The SEM and TEM images of ZnO nanoparticles prepared with the ultrasonic wave are shown in Figs. 4(a) and (c), respectively, and the SEM and TEM images of ZnO nanoparticles prepared with no ultrasonic wave are shown in Figs. 4(b) and (d), respectively. The morphologies of nanoparticles were significantly different between the two samples. As shown in Figs. 4(b) and (d), we observed almost no spherical nanoparticles when we applied no ultrasonic wave. The electron diffraction pattern shown in the inset of Fig. 4(d) indicates that nanoparticles prepared with no ultrasonic wave have an amorphous structure. On the other hand, we observed aggregated spherical nanoparticles, as shown in Figs. 4(a) and (c), when we applied the ultrasonic wave. The electron diffraction pattern shown in the inset of Fig. 4(c) indicates that nanoparticles prepared with the ultrasonic wave had a crystalline structure.
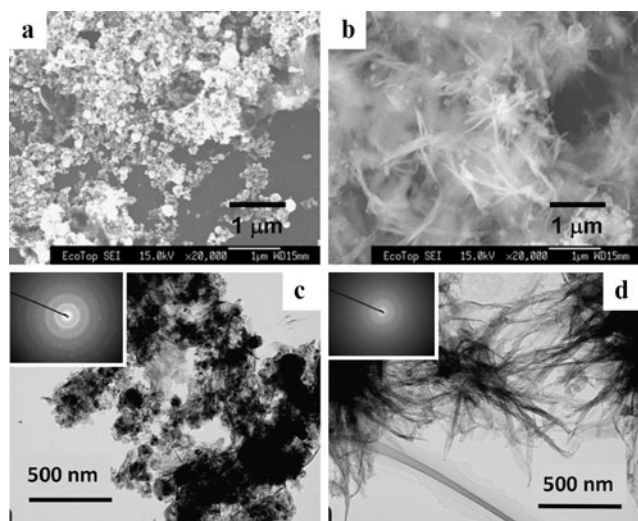
Fig. 4 SEM and TEM images of ZnO nanoparticles. (**a**) and (**b**) are SEM images of ZnO nanoparticles prepared with and without an ultrasonic wave, respectively, and (**c**) and (**d**) are TEM images of ZnO nanoparticles prepared with and without an ultrasonic wave, respectively

4 Discussion

As described in the previous section, we observed some remarkable effects of the ultrasonic wave on the synthesis of nanoparticles by liquid-phase laser ablation. An effect of the ultrasonic wave was the enhancement of the density of nanoparticles in the colloidal solution, as shown in Fig. 2(a). In a previous paper [14], we reported repetitive formations and collapses of cavitation bubbles in the presence of the ultrasonic wave in liquid-phase laser ablation. The cavitation bubbles at a long delay time after laser ablation were driven by the ultrasonic wave. On the other hand, in the absence of the ultrasonic wave, the formations and the collapses of laser-induced cavitation bubbles continued for several times, resulting in a static bubble at a long delay time after laser ablation [11]. In addition, in another previous paper [18], we pointed out additional etching of the target by the collapses of cavitation bubbles. Hence the enhancement of the density of nanoparticles in the colloidal solution can be attributed to the additional erosion of the target due to repetitive collapses of cavitation bubbles. The additional erosion was confirmed by the larger volume of the ablation crater in the presence of the ultrasonic wave. The superposition of the ultrasonic wave is helpful to obtain an efficient synthesis rate of nanoparticles.

Another effect of the ultrasonic wave was the enhancement of the crystallinity of nanoparticles. As shown in Figs. 3(c) and 4(c), we observed higher crystallinity of nanoparticles in the presence of the ultrasonic wave. The repetitive formations and collapses of cavitation bubbles may also contribute to the enhancement of the crystallinity. This is because, in a previous paper [13], we have shown

by laser-light scattering that the growth of nanoparticles occurs inside the cavitation bubble. It has been also shown that nanoparticles are stored inside the cavitation bubble until its collapse [13]. This means that nanoparticles are located in the high-temperature, high-pressure reaction field at the collapse of the cavitation bubble. If the high-temperature, high-pressure reaction field has positive contribution to the crystallization, the enhancement of the crystallinity of nanoparticles in the presence of the ultrasonic wave is attributed to the repetitive collapses of cavitation bubbles. Zhang et al. reported the enhancement of the crystallinity of ZnO nanoparticles by employing intense laser pulses for ablation [19]. A mechanism for the enhancement of the crystallinity by the intense laser pulses may be the enhanced temperature and pressure at the collapse of the cavitation bubble. However, the intense laser pulses resulted in the increase in the size of ZnO nanoparticles [19]. Therefore, the superposition of the ultrasonic wave is a useful method to obtain crystalline nanoparticles using low-energy laser pulses.

5 Conclusions

We have shown that the excitation of the ultrasonic wave in ambient liquid of liquid-phase laser ablation is a useful method for enhancing the density of nanoparticles in colloidal solution and the crystallinity of nanoparticles. These enhancements are considered to be obtained via repetitive formations and collapses of cavitation bubbles in the presence of the ultrasonic wave.

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