Suppression of Sonochemiluminescence Reduction at High Acoustic Amplitudes by the Addition of Particles

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Received: September 12, 2007

The effect of particle addition to a liquid or liquid surface on the sonochemiluminescence (SCL) was investigated using a luminol aqueous solution under ultrasonic treatment at 154 kHz. The acoustic-amplitude dependence of the SCL intensity was measured, in addition to capturing images of luminescent spatial patterns. At higher acoustic amplitudes, the cavitation efficiency dramatically reduces. This behavior is suppressed in the presence of particles. Particle addition provides nucleation sites for cavitation bubbles, lowering the cavitation threshold, and weakening the liquid surface vibration as the pressure amplitude decreases. It is shown that the reduction in SCL is suppressed under the addition of alumina particles into luminol aqueous solution. As the amount of alumina particles increases, the range of acoustic amplitude for suppressing the reduction in SCL is enlarged toward high amplitude, and the intensity of the SCL increases. Simultaneous addition of alumina particles into the solution and hydrophobic polytetrafluoroethylene (Teflon) particles onto the liquid surface is also effective. Examination of SCL images revealed that alumina particles added to the liquid at high acoustic amplitude caused the entire region of the reaction volume to be homogeneously luminous. If hydrophobic particles cover the solution surface, the surface vibration at high acoustic amplitude is fixed and the sound field becomes stable. This is responsible for suppression of the reduction in SCL and leads to a high rate of sonochemical reaction, even at high acoustic amplitude.

1. Introduction

A violent collapse of ultrasonic cavitation bubbles in an aqueous solution, from an acoustic amplitude of more than the cavitation threshold,[1] causes extreme temperatures of several thousand Kelvin, several hundred atmospheric pressure, and heating and cooling rates greater than 10^9 K/s.[2] A collapsing cavitation bubble in liquid water produces oxidants, such as hydroxyl radicals, oxygen atoms, hydrogen peroxide, etc., by the decomposition of water.[2,3] Chemical reactions with these oxidants caused by an acoustic cavitation bubble are referred to as sonochemical reactions.[2−4] Upon the violent collapse of cavitation bubbles, light, called sonoluminescence,[5] is emitted from the inside of the bubbles. If the aqueous solution contains dissolved chemicals such as luminol, reaction with oxidants from the cavitation bubbles causes the solution to emit light, called sonochemiluminescence (SCL).

At excess acoustic amplitude, the SCL reduces or the sonochemical reaction rate reduces when the amplitude increases.[6−8] Negishi showed that at first the SCL increased with increasing sound intensity but then reduced (or nearly vanished) rather suddenly at high sound intensity.[6] Regarding the rate of hydrogen peroxide production in a vessel with a free liquid surface, Lindström[7] reported a similar tendency to that shown by Negishi.[6]

It is possible to suppress the reduction in SCL if vibration of the liquid surface is inhibited. Lindström suppressed the reduction in the sonochemical reaction rate by setting a plate on the liquid surface.[7] According to Lindström, in the absence of the plate a fountain is generated at the liquid surface, which prevents the formation of a standing wave field and lowers the pressure amplitude, leading to a reduction in chemical yield. Similarly, Henglein et al.[8] mentioned the effect of setting a sheet on a liquid surface. According to Henglein et al.,[8] a sheet prevents the formation of a fountain at the liquid surface, and the quality of cavitation at low ultrasound intensities, which is favorable for chemical action, is at least partly maintained at higher intensities when the sheet is present. However, there has been no attempt to use particle addition to enhance the sonochemical reaction rate by suppressing the reduction in the rate at excess pressure amplitude. The addition of particles lowers the pressure amplitude,[9] and the vibration of the liquid surface is softened. Also, the addition of particles into the liquid provides nucleation sites for initiation of cavitation bubbles and decreases the cavitation threshold.[10] This has the potential to enhance the sonochemical reaction rate. The mechanism for sonochemical-rate enhancement by particle addition is as follows. The gas pocket[11] is stabilized due to an action of surface tension in a concave shape at the gas−liquid interface in a

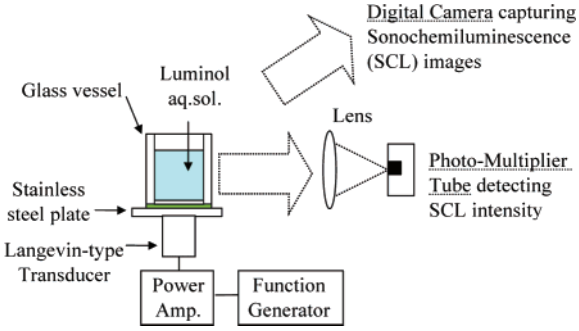

Figure 1. Experimental apparatus.

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10.1021/jp077319r CCC: $37.00
Published on Web 11/09/2007

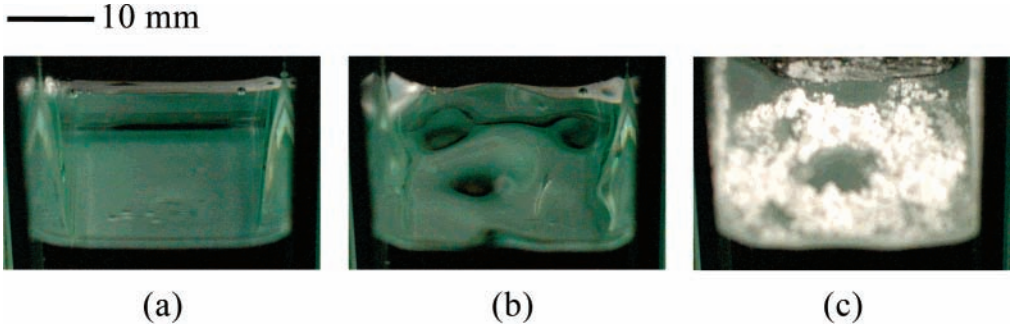

Figure 2. Change in the liquid surface due to ultrasound: (a) ultrasound-off in the absence of particles; (b) ultrasound-on in the absence of particles; (c) ultrasound-on in the presence of hydrophobic particles on the liquid surface. Note that these images are focused on the liquid surface and are captured from an inclined angle.

crevice on a particle surface surrounded by liquid when external pressure such as ultrasound is not applied. The volume of gas increases under reduced pressure at a cycle of rarefaction phase when an ultrasound is applied. The expanded gas becomes convex to release a free and tiny cavitation bubble from the crevice. Such a tiny cavitation bubble is not only provided repeatedly during sonication from the particle surface but also has a potential to pulsate. There are effective amounts and sizes for particle addition that attain sonochemical-rate enhancement. Accordingly, the increase in the number of cavitation bubbles by appropriate addition of particle results in an increase in sonochemical reaction rate. Recently, the authors have revealed the mechanism of rate enhancement in sonochemical reaction by particle addition through the measurement of acoustic cavitation noise and liquid temperature.[12] It was shown that the addition of alumina particles of appropriate amount and size results in an increase in the sonochemical reaction rate when both the acoustic noise and temperature rise due to cavitation bubbles also increase, compared with that in the absence of the particles. This suggests that the reaction-rate enhancement by the addition of particles of appropriate amount and size comes from an increase in the number of cavitation bubbles.

It is expected that if the liquid surface is covered by a hydrophobic material such as polytetrafluoroethylene, then the surface vibrations are damped by surface tension.

In this study, the effect of particle addition to a liquid or liquid surface on SCL is investigated by measuring the dependence of the SCL intensity on the acoustic amplitude, in addition to capturing images of luminescent spatial patterns.

It should be noted that the SCL reduction at high amplitude presented here is different to that caused by the addition of organic acids.[13]

2. Experimental Section

Figure 1 shows a schematic of the experimental apparatus and setup. In the experiment, a continuous wave sinusoidal signal of 154 kHz, generated by a function generator (NF Electronic Instruments, 1942), was amplified by a 55 dB power amplifier (ENI, 1140 LA) to drive a Langevin type transducer (Honda Electronics, 45 mm in diameter) attached to a transducer plate (1 mm thick and 110 mm in diameter). The range of the function-generator output related with acoustic amplitude was 0−700 mVpp. A glass vessel with inner dimensions of 30 × 30 × 145 mm^3 was filled with 62 mL of luminol (3-aminophthalhydrazide) aqueous solution, where the solution was prepared by mixing 1 mL of 250 mM $NaCO_3$−2.5 mM luminol and 61 mL of distilled water. The thickness of the glass vessel was 5 mm. The sonication used was indirect ultrasound irradiation. Oil was inserted between the bottom of the vessel and the transducer plate for transmission of the ultrasound into the liquid inside the vessel. The calorimetric power was 9.2 W in the absence of particles at a function-generator output of 340 mVpp.

Luminol reacts with OH radicals generated in the cavitation bubbles to give aminophthalate anions and a blue fluorescence when intense ultrasound propagates through the luminol solution;[14] that is, the luminol exhibits SCL. Air was dissolved in the solution and the concentration of dissolved air was adjusted to saturation by bubbling air. The temperature of the solution in the vessel was set at 20 °C.

Alumina particles (Adomafine) of 10 μm in mean diameter were added to the solution. Teflon (polytetrafluoroethylene) (Sanplatec, TFW-1000, mean diameter: 10 μm) particles were added to the solution surface. Figure 2 shows images of the liquid surface captured from an inclined angle under conditions of the ultrasound on or off and with or without hydrophobic particles on the liquid surface. Deformation of the liquid surface occurs for both cases, and with the ultrasound on, as shown in Figure 2b,c. It seems that in Figure 2c, at around the center of the liquid surface, most of the Teflon particles move aside and away from the raised liquid surface; however, a thin layer of Teflon particles remain on the surface. Note that the function-generator output related with the acoustic amplitude was the same for Figure 2b,c. The function-generator output, 500 mVpp, was enough to cause a reduction in SCL, as shown later.

The SCL image was captured with a digital camera (Nikon, D70) and the intensity was measured using a photomultiplier tube (Hamamatsu Photonics, R928) in the presence or the absence of the addition of particles as the function-generator output was changing. A converging lens was set between the vessel and the photomultiplier tube to ensure that all the luminescent positions were detectable. The duration of sonication was 1 min in each case.

The sound pressure amplitude in the absence or presence of alumina particles was measured every 2 mm along the sound beam axis in the sonicated liquid using a hydrophone (Brüel & Kjær, 8103).

3. Results and Discussion

3.1. Distribution of Sound Pressure Amplitude in the Vertical Direction. Figure 3 shows the distribution of sound pressure amplitude measured along the sound beam axis under different conditions of function-generator output and addition of alumina particles. In each case, the amplitude changes periodically with the distance from the surface. The sound pressure amplitude at 340 mVpp was lower by 8% on average in the presence of alumina particles (0.5 g) compared to that in the absence of particles (open triangles and circles, respectively).

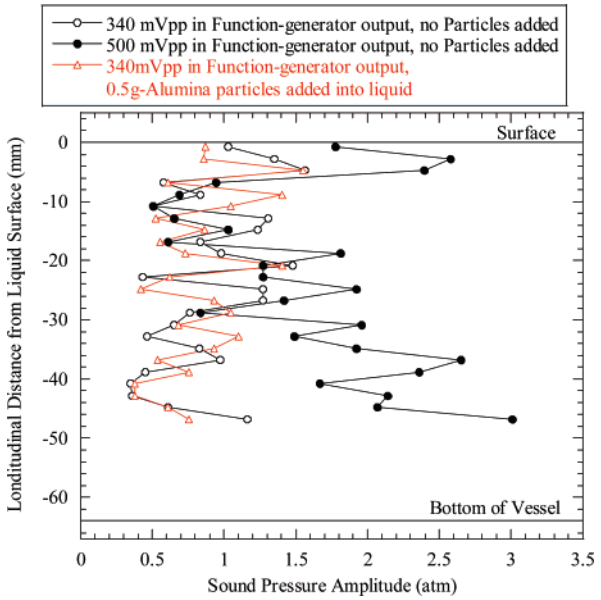

Figure 3. Sound pressure amplitude measured along the sound beam axis in the absence/presence of alumina particles.

Note that the data in Figure 3 are time-averaged and do not reflect the vibrations of the liquid surface.

A time-averaged sound field is composed of two pressure−amplitude components of standing wave and progressive wave. In Figure 3, the standing wave component is the variation in the sound pressure amplitude with position, and the progressive wave component is the averaged level of the sound pressure amplitude from zero. It seems that the ratio of the progressive wave component to the standing wave component is relatively larger at 500 mVpp (filled circles) than the ratio for both cases at 340 mVpp (open circles and triangles). This is apparent at the position nearer to the bottom on the side of the transducer. In the case where the progressive wave component is dominant, cavitation bubbles are unable to position and pulsate stably at around the pressure antinode, which leads to the reduction in SCL.

3.2. Change of SCL Intensity Due to the Addition of Alumina Particles. Figure 4 shows the dependence of the SCL intensity on the function-generator output in the presence or absence of alumina particles in the solution. All intensities are normalized using the maximum intensity value in the absence of particles. The SCL intensity was close to zero at 0 mVpp in Figure 2. The alumina particles used are chemically inactive and are not responsible for the luminol chemiluminescence without application of ultrasound. At relatively low acoustic amplitude (up to 320 mVpp), the presence of a small amount of particles (0.24 or 0.50 g) results in high intensity compared with that in the absence of particles, whereas a larger amount of particles (1.25−1.49 g) results in low intensity. This is because the pressure amplitude decreases as the amount of the particles increases.[9] When an appropriate amount of particles was added, the SCL intensity was 2 times higher than that in the absence of particles at the same function-generator output (360 mVpp) where the intensity in the absence of particles showed a peak. These results are consistent with those we previously reported for KI oxidation under sonication in the presence of alumina particles.[12]

As for the scattering of SCL by particles, it is important to consider an appropriate balance between the two counteracting effects due to the presence of solids, i.e., greater reflection from the surface and attenuation effects. This is left to future study.

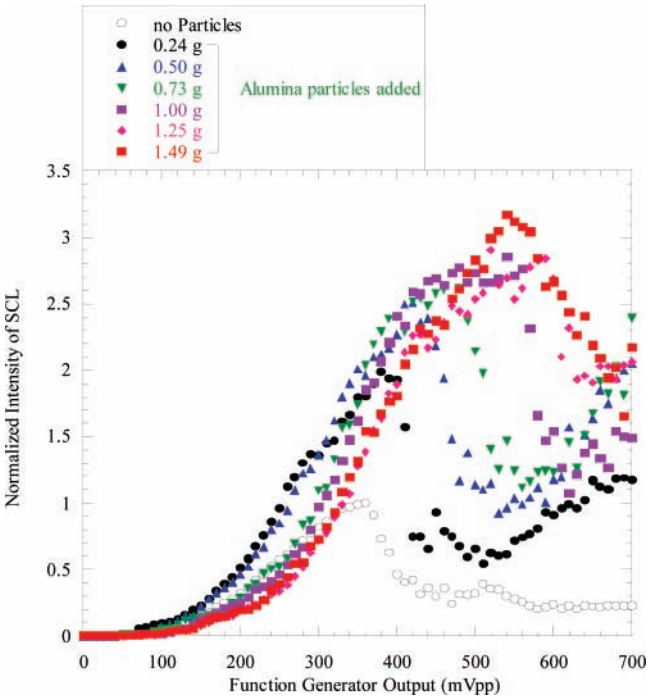

Figure 4. Dependence of the SCL intensity on function-generator output related to acoustic amplitude in the presence or absence of alumina particles added to the solution. All intensities are normalized using the maximum intensity value in the absence of particles.

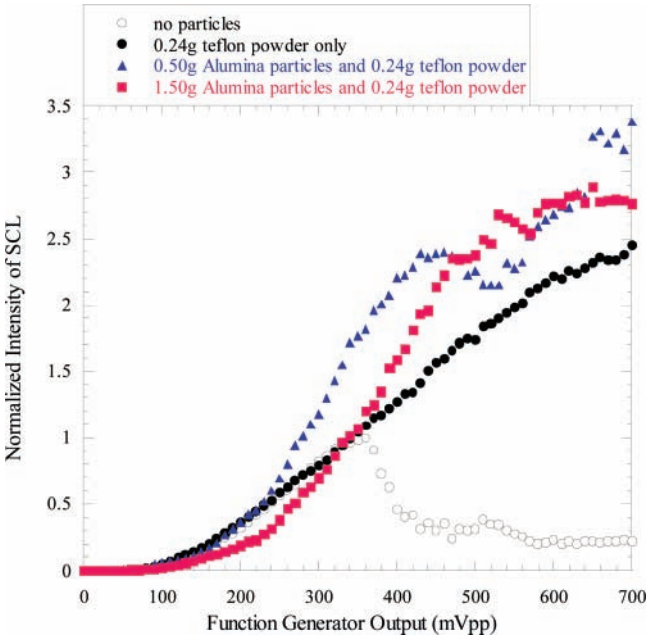

Figure 5. Dependence of the SCL intensity on the function-generator output related to acoustic amplitude in the presence or absence of Teflon or alumina particles added to the solution. All intensities are normalized using the maximum intensity value in the absence of the particles.

In the range from 340 to 700 mVpp, as the amount of alumina particle addition is increased, the intensity increases. The maximum intensity obtained for addition of 1.49 g of particles was more than 3 times higher than that in the absence of particles. It seems that the peak shifts toward the region of higher acoustic amplitude as the amount of particle addition is increased. Therefore, high-rate sonochemical reaction is expected by the addition of particles that prevents the reduction in SCL up to higher acoustic amplitude.

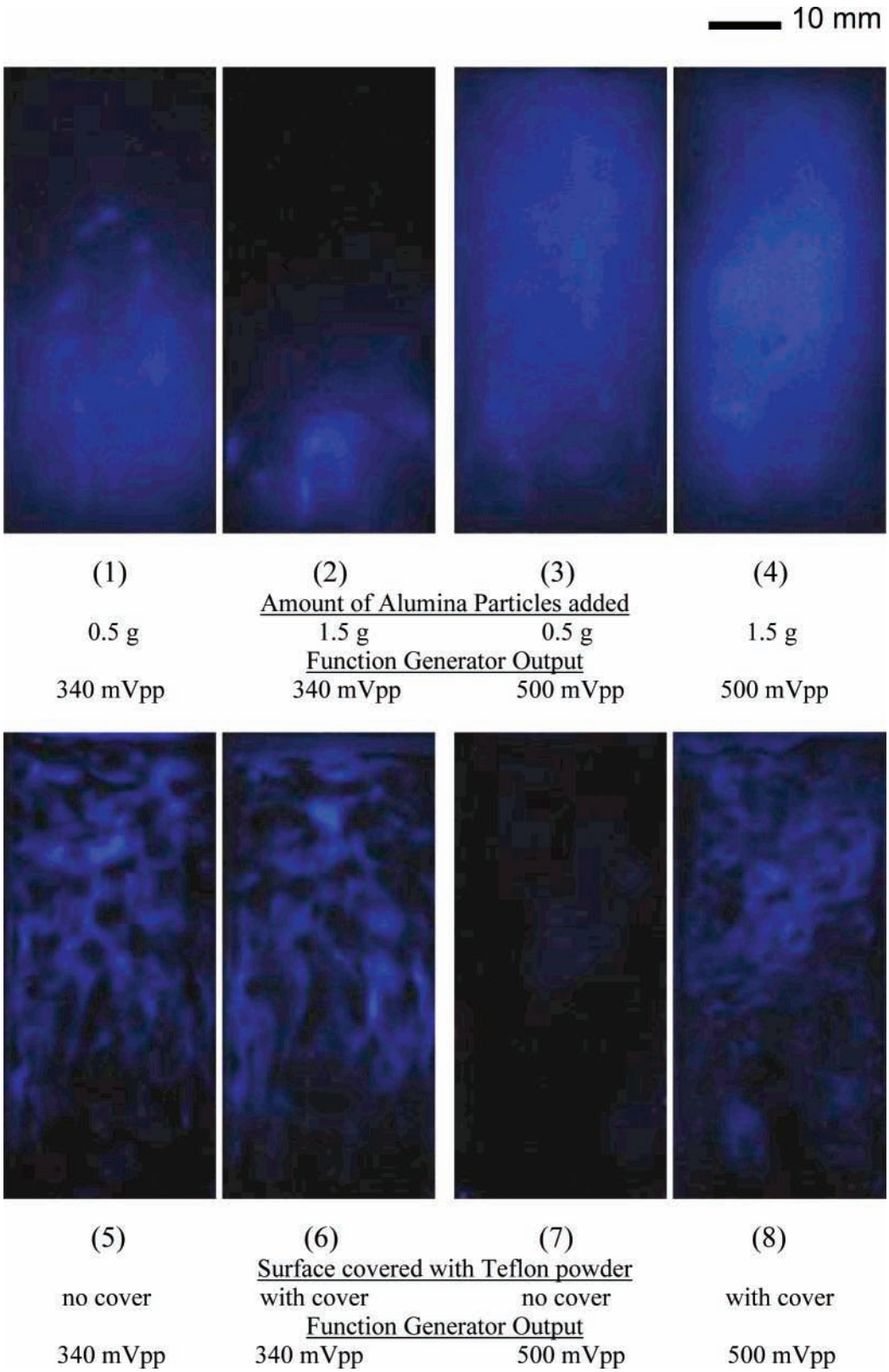

Figure 6. Photographs of sonochemiluminescence in the presence or absence of alumina particles or Teflon particles in or on the solution.

3.3. Change of SCL Intensity Due to the Addition of Alumina Particles and Teflon Particles. Figure 5 shows the dependence of the SCL intensity on the function-generator output in the presence or absence of Teflon particles or alumina particles in the solution. All intensities are normalized using the maximum intensity value in the absence of particles. It is remarkable that in the case of Teflon particle addition alone (filled circles) the intensity increases monotonically as the acoustic amplitude increases. The Teflon particles cover and fix the liquid surface, causing the surface vibration to stop. This is effective for the formation of a stable resonant standing wave. Therefore, high-intensity SCL is obtained due to fixation of the liquid surface by covering with hydrophobic particles, even at high acoustic amplitudes.

With the addition of both alumina and Teflon particles to the solution, a further increase in SCL intensity is obtained at

high amplitude (in the range from 360 to 700 mVpp), compared with that for Teflon only. In the case of 1.50 g of alumina particles and 0.24 g of Teflon particles, the intensity at relatively low acoustic amplitude (up to 320 mVpp) was lower than that for the solution with no particles added. This is similar to the case of larger addition of particles (1.25−1.49 g) as in Figure 4; the amount of particle addition is in excess to that required to lower the pressure amplitude, which leads to low intensity.

3.4. Change of SCL Spatial Patterns Due to the Addition of Alumina or Teflon Particles. Figure 6 shows photographs of SCL taken with a digital camera at different conditions of particle addition and function-generator output. In each image, the bottom of the glass vessel set on the transducer is located below the bottom of each image and liquid surface is at the upper portion of the figure.

Comparing (1) and (2) in Figure 6, where both solutions are under relatively low acoustic amplitude, the bright region is wider for a smaller amount of particle addition. For the larger amount of particle addition, the bright region is limited to near the vessel bottom. Alumina particles are denser than the liquid and tend to sink, because the ultrasonic dispersion of particles is ineffective due to the low acoustic amplitude. As a result, most particles stay near the vessel bottom, so that there are few nucleation sites for cavitation bubbles provided by particles in the upper region that would lead to SCL. This is more obvious at larger particle addition that decreases the acoustic amplitude.

In the case of high acoustic amplitude (Figure 6(3),(4)), it is expected that the ultrasonic dispersion of particles is effective for transporting particles over the entire region in the vessel. It is noteworthy that, in the presence of particles added into the solution under high acoustic amplitude, the whole region inside the vessel becomes a homogeneous reaction site, as seen in Figure 6(3),(4). This is useful for the establishment of a highly efficient sonochemical reactor. Note that an appropriate amount of particles added should be set, because an excess amount of particles leads to the lowering of the acoustic amplitude and a decrease in the sonochemical reaction efficiency.

The SCL images show little difference between the absence and the presence of Teflon particles covering the liquid surface under low acoustic amplitude (Figure 6(5),(6)). Under high acoustic amplitude it is confirmed that the absence of Teflon particles permits a reduction in SCL (Figure 6(7)), and the presence of Teflon particles suppresses the reduction (Figure 6(8)). Note that there are bright and dark patches of SCL in Figure 6(5),(6),(8) as there are no alumina particles added to the solution. The luminescent patches of Figure 6(8) are the finest among the three cases of Figure 6(5),(6),(8). This may be due to high acoustic amplitude with wider distribution and may be close to the phenomenon seen for a low concentration of dissolved gas.[15] This means that the region where the acoustic amplitude is greater than the cavitation threshold is wide. Thus, a fine luminescent region that reflects a wide reaction site is obtained when the reduction in SCL is suppressed due to fixation of surface vibrations by the addition of hydrophobic particles on the liquid surface.

In Figure 6(5),(6), the expected lateral stripes typical of a standing wave field[16] were not observed. In the present experiment, the liquid volume is relatively small and the pressure amplitude is sufficiently high for the traveling wave component to cause the motion of bubbles toward the liquid surface that pulsate and emit SCL. At this time, the luminescent pattern in the longitudinal direction emerges, and the lateral stripe is faint. The luminescent pattern may also be influenced by the side wall.[17]

3.5. Mechanism for the Reduction in SCL. The mechanism proposed here for the reduction in SCL is as follows. The position of tiny cavitation bubbles, which can contribute to sonochemical reaction in the antinodal plane of a standing wave field, shift from the sound beam axis toward the side wall of a vessel by the action of primary Bjerknes force as the acoustic amplitude increases.[16,18,19] Note that there is a sound pressure field where the pressure amplitude decreases as the distance from the sound beam axis increases. The primary Bjerknes force changes from an attractive to a repulsive force depending on the pressure amplitude and bubble radius, and assisted by coalescence of bubbles due to the secondary Bjerknes force. At excess amplitude, there are few tiny bubbles except near the side wall, and the liquid surface is easily vibrated by radiation forces, because little absorption and scattering of sound by the bubbles is expected. The vibration causes the sound field to become unstable and ineffective for the formation of a standing wave field. At this time, cavitation bubbles are difficult to generate. In the present experiment at high acoustic amplitude, Teflon particles fixate some vibration of the liquid surface, while maintaining some deformation of the surface, as shown in Figure 2c. Note that, as the Teflon particles locate on the liquid surface where the position is a pressure node, the Teflon particles do not act as nucleation sites. Surface vibration of the liquid, rather than surface static deformation, is responsible for the reduction in SCL. Accordingly, at excess amplitude, it is difficult for many cavitation bubbles to pulsate and lead to sonochemical reaction or SCL, unless the vibration of the liquid surface is fixed.

4. Conclusion

In conclusion, as the acoustic amplitude increases, the SCL intensity increases monotonically up to higher acoustic amplitude by the addition of larger amounts of alumina particles into luminol aqueous solution, and the SCL reduces at high acoustic amplitude under no addition of alumina particles. Simultaneous addition of alumina particles into the solution, and hydrophobic Teflon particles onto the liquid surface, is also effective. Through the study of SCL images, it was found that in the presence of alumina particles in the liquid at high acoustic amplitude, the whole region of the reaction volume is homogeneously luminous. If hydrophobic particles cover the solution surface, the surface vibration at high acoustic amplitude is fixed and the sound field becomes stable. This is responsible for the suppression of SCL reduction and leads to a high rate in sonochemical reaction even at high acoustic amplitude.

Acknowledgment. Part of this study was supported by funding from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

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