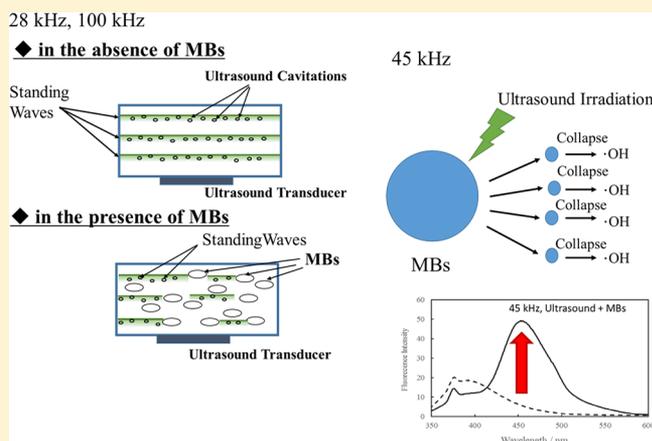


Influence of Microbubbles on Free Radical Generation by Ultrasound in Aqueous Solution: Dependence of Ultrasound Frequency

Nanae Masuda,[†] Aya Maruyama,[†] Toshihiko Eguchi,[‡] Tsutomu Hirakawa,[§] and Yoshinori Murakami^{*,†}[†]Department of Materials Engineering, Nagaoka National College of Technology, Nishi-Katakai, Nagaoka, 940-2188, Japan[‡]Aura-tec Co., Ltd. 1725-2 Tsubuku-honmachi, Kurume, Fukuoka 830-0047, Japan[§]Environment Management Research Institute, AIST, Tsukuba, Ibaraki 305-8569, Japan

ABSTRACT: The influence of microbubbles on sonochemical efficiencies has been investigated under 28, 45, and 100 kHz ultrasound irradiation. For the 28 and 100 kHz ultrasound frequencies, microbubbles suppressed the I_3^- formation from KI solution as well as the 7-hydroxycoumarin formation from coumarin solution caused by the ultrasonic irradiation. On the other hand, for the 45 kHz ultrasound frequency, microbubbles enhanced the I_3^- formation from KI solution as well as 7-hydroxycoumarin formation from coumarin solution caused by the ultrasonic irradiation. Detection of H_2O_2 after the irradiation of ultrasound in the presence or absence of microbubbles was also performed, and it was found that H_2O_2 formation was enhanced only when microbubbles were introduced under the 45 kHz ultrasonic irradiation, which was in good agreement with the results of KI oxidation dosimetry measurements and of coumarin fluorescent probe measurements. Based on these present results, plausible mechanisms that explain the dependence of the ultrasound frequency on the enhancement and suppression of free radical formation in the presence of MBs were proposed.



1. INTRODUCTION

In a recent years, the application of sonochemical processes as an advanced oxidation process have intrigued by a lot of engineers because of the high efficiencies as well as the easy operations.^{1–3} Ultrasonic irradiation into a liquid is known to generate acoustic cavitation, and then the collapse of these cavitation bubbles results in a hot spot, which has an extremely high temperature and pressure.⁴ As a consequence of the high temperature and pressure in a hot spot, water in a solution was thermally decomposed to form reactive hydroxyl radicals, followed by the sonochemical reactions as well as sonoluminescence via the free radical reaction mechanism.

It has been reported that the addition of alcohol to an aqueous solution greatly reduces sonoluminescence relative to that in pure water.^{5–8} They suggested that alcohol adsorbs on the surface of bubbles and stabilizes the pulsation of bubbles. On the other hand, Sunartio et al.⁹ reported that, at relatively low ultrasonic powers, adding a certain concentration of alcohol increased the sonoluminescence intensity relative to that for pure water. Tuziuti et al.¹⁰ also observed a higher sonoluminescent intensity with relative lower power in a solution of lower ethanol concentration. They attributed the reason for the increase of the sonoluminescent intensity as a decrease of bubble–bubble coalescence under low solubility. Thus, the important roles of the stability of cavitation bubbles on the intensity of sonoluminescence have been suggested from

these works. It can also be expected that the stability of cavitation bubbles has an influence not only on the sonoluminescence intensity but also on the overall reaction rates of sonochemical reactions.

Recently, microbubbles (MBs) with diameters of 10–50 μm have been explored for various applications for water treatment.¹¹ MBs are so tiny, that they are stable in an aqueous solution for longer periods of time than normal macrobubbles. Therefore, MBs are well-known to have excellent gas dissolution ability, and thus various applications of MBs are available now.¹² It has also been reported that ζ -potentials of MBs in aqueous solutions were negative for a wide range of pH conditions¹³ and that hydroxyl radicals were also formed by collapsing MBs under acidic conditions less than $\text{pH} < 3$.^{14,15} Although numerical works have been done for the investigation of the physical and chemical properties of MBs, relatively fewer works have been done for the investigation on the interaction of ultrasound with MBs. Kobayashi et al.¹⁶ reported agglomeration and rapid ascent of microbubbles using ultrasound with frequency of 2.4 MHz and concluded that aggregation of microbubbles was caused by the secondary Bjerknes force¹⁷ on the bubble in the liquid phase. They also

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reported that addition of surfactants to the MBs in a solution decreased the aggregation efficiencies using ultrasound.¹⁸ Since ultrasound accelerates the aggregation process of the microbubbles in an aqueous solution, there might be some effects on the behaviors and stabilities of the cavitation bubbles formed by the irradiation of ultrasound to a solution. Because stabilities of the cavitation bubbles are strongly related to the efficiencies of the free radical formation by the thermal decomposition of water in a hot spot, the free radical formation by ultrasound might be influenced by the existence of MBs in a solution. However, as far as we know, there are no reports that the amount of free radicals formed by ultrasound cavitation is influenced by the MBs introduced into an aqueous solution.

In the present work, we have investigated the influence of existence of MBs on generation of free radical by ultrasound irradiation using several analytical techniques such as KI method, coumarin fluorescence probe method, and a titanium sulfonate reagent titration method to detect H₂O₂ formed by the recombination reaction of OH + OH. With three different ultrasound frequencies (25, 64, and 100 kHz), the different effects of the free radical formation on MBs were investigated.

2. EXPERIMENTAL METHODS

Figure 1 shows a schematic of the experimental setup. As shown in Figure 1, the ultrasonic transducer (W-115T, Honda

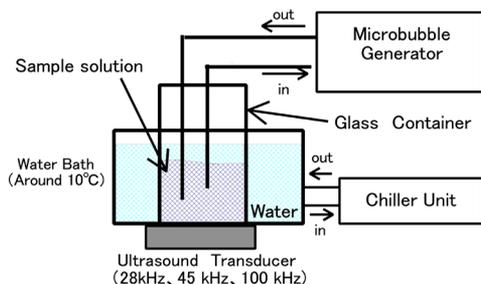


Figure 1. Schematic figure of the experimental setup.

Electronics), which has a maximum output of 300 W, was attached to the bottom of the water tank, and the temperature of the water tank was kept to around 10 °C by circulating the water of the tank to the cooling bath (LTC-S300C, AS ONE Inc.). A 500 mL glass container with external diameter of about 80 mm and a flat thin bottom of about a few millimeters was placed in the center of the water bath and was exposed to ultrasound continuously for a certain time from the ultrasound transducer attached at the bottom of the water bath after 300 mL of sample solution was filled into a glass container in the water tank. During the ultrasonic irradiation, the temperature of the sample solution was carefully checked to be constant via a thermometer in a sample solution. The ultrasound transducer can generate three different ultrasound frequencies of 28, 45, and 100 kHz, and then the sonochemical efficiency of each frequency was checked by the KI oxidation dosimetry method, which was previously reported by Koda et al.¹⁹ as the best method to calibrate sonochemical efficiencies compared with the other methods.

To introduce MBs into the sample solution, the microbubble generator (OM4-MDG-045, AURA Tec Co.Ltd.) was connected to the sample solution. The microbubble generator circulates the sample solution with the flow speed of 1.3–1.7 L/min and produces very uniform microbubbles by dissolving

the air into the sample solution using a high pressure system and then by reducing the pressure abruptly at the exit nozzles. Figure 2 shows the bubble diameter distributions measured via

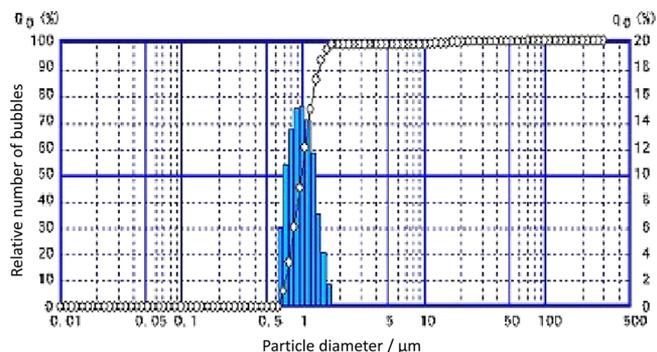


Figure 2. Bubble diameter distributions of the microbubble generator (OM4-MDG-045, AURA Tec, Co. Ltd.) measured via the laser particle size analyzer.

the laser diffraction particle size analyzer (SALD-7000, Shimadzu). For these bubble size measurements, the measurements were performed using the flowing system with flow rate of 1 L/min to avoid the influence of the coalescence of microbubbles during the bubble size measurements. The diameter and length of the connecting tube between the microbubble generator and the laser diffraction particle size analyzer were about 4 mm and 50 cm, respectively. As shown in Figure 2, it is clearly seen that relatively uniform bubble size distributions having diameters between 0.6–1.2 μm with the maximum of 1 μm (full width of half-maximum is within 0.4 μm) were obtained for this microbubble generator. The number of microbubbles generated in the microbubble generator is estimated to be around 1.0×10^9 bubbles $\text{cm}^{-3} \text{s}^{-1}$ based on the assumption that all of the gas introduced into the MB generator becomes microbubbles with 1 μm diameter ($5 \times 10^{-19} \text{ m}^3$ in volume).

3. RESULTS AND DISCUSSIONS

3.1. Measurement of I₃⁻ Absorption Formed by Ultrasound Irradiation to KI Solution in the Presence and Absence of MBs. It has been reported by Koda et al.¹⁹ that KI oxidation dosimetry using 0.1 mol dm⁻³ KI solution was the simple and the easiest method to calibrate the sonochemical efficiency. Therefore, we have first attempted to use the same KI oxidation dosimetry techniques to investigate the effects of microbubbles on the sonochemical efficiencies. Since cavitation formed by the different ultrasound frequencies might possibly interact with the microbubbles in a different way, we have performed the KI oxidation dosimetry experiments with three different ultrasound frequencies (28, 45, and 100 kHz) in both the presence and absence of microbubbles.

Figure 3 illustrates examples of the absorption spectra in the presence and absence of microbubbles after 30 min ultrasound irradiation. All of the results measured at three different ultrasound frequencies (28, 45, and 100 kHz) were also given. Figure 3 clearly shows that the influence of microbubbles on the sonochemical efficiencies differed with three different ultrasound frequencies. That is, I₃⁻ absorption at 350 nm was enhanced by the presence of microbubbles under the 45 kHz ultrasonic irradiation, while I₃⁻ absorption was suppressed by the presence of microbubbles under irradiation of 28 and 100

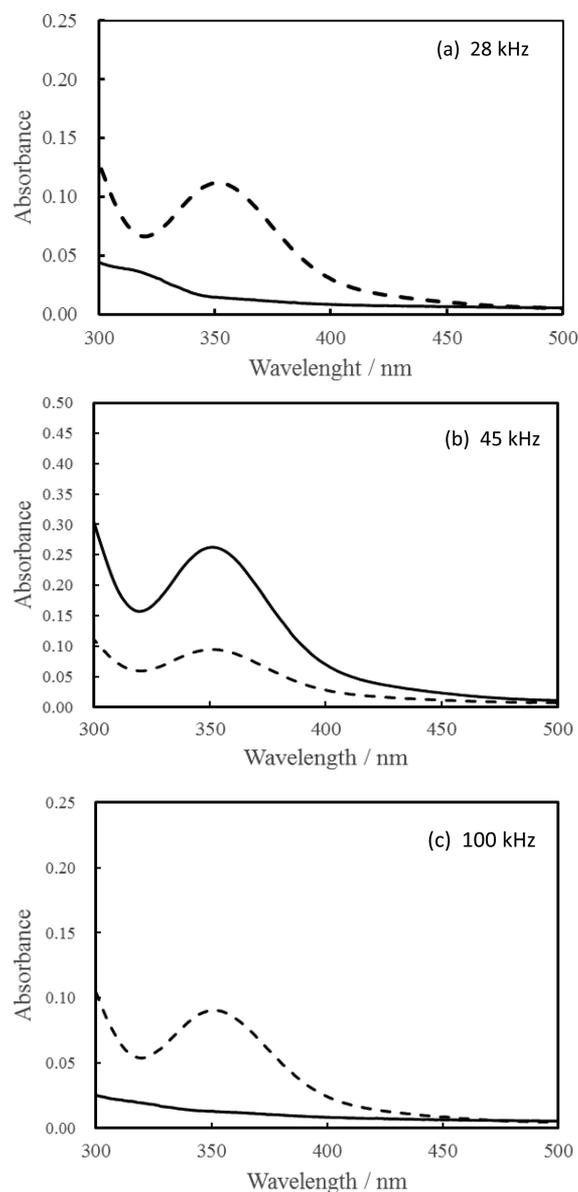
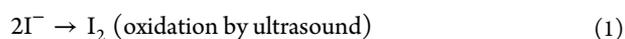


Figure 3. Absorption spectra of I_3^- after the 30 min irradiation of ultrasound to 0.1 M KI solution in the presence (solid line) and absence (dashed line) of MBs with frequency of (a) 28 kHz, (b) 45 kHz, and (c) 100 kHz.

kHz ultrasounds. It was also confirmed that I_3^- absorbance at 350 nm after 30 min ultrasonic irradiation in the absence of microbubbles was nearly the same value of around 0.10 irreversible to the ultrasound frequencies, suggesting that the sonochemical efficiencies were nearly the same with three different ultrasound frequencies in our experimental setups. Since I_3^- was formed by the oxidation of I^- ion followed by the subsequent reaction with the excess I^- ,



the present results indicated that microbubbles had positive or negative effects on the oxidation reaction 1, depending on the ultrasound frequencies. Oxidation of I^- ion by the ultrasonic irradiation was due to OH radicals formed by the collapse of these cavitation bubbles in a hot spot, and therefore, it was

speculated that microbubbles influenced the formation of cavitation bubbles. To confirm that microbubbles have different effects on the I_3^- formation by the irradiation of three different ultrasound frequencies (28, 45, and 100 kHz) to 0.1 mol dm^{-3} KI solution, a different size of glass container (volume 1000 mL, external diameter of about 120 mm with a flat bottom) was used and 400 mL of sample solution was filled into the glass container for the KI oxidation dosimetry experiments. Figure 4

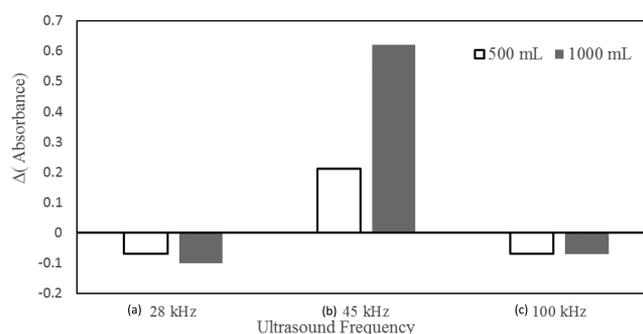
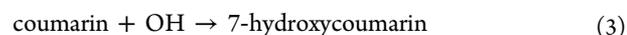


Figure 4. Comparison of the effect of MBs on the final absorbance for I_3^- at 350 nm formed by the 30 min ultrasound irradiation to 0.1 M KI solution. The ultrasound frequencies were (a) 28 kHz, (b) 45 kHz, and (c) 100 kHz.

shows the comparisons of the I_3^- absorbance between in the absence of MBs and in the presence of MBs after 30 min ultrasound irradiation for each ultrasound frequency. In Figure 4, the results of the 500 mL glass container are also given. All these experiments were repeated more than three times, and the average value is used in Figure 4. As shown in Figure 4, irreversible to the type of glass containers, microbubbles enhanced I_3^- formation by ultrasonic irradiation with the frequency of 45 kHz. On the other hand, microbubbles suppressed I_3^- formation by ultrasonic irradiation with the frequencies of 28 and 100 kHz. It was also found that the 1000 mL glass container had larger enhancements of I_3^- formation than the 500 mL container with the frequency of 45 kHz, but that the effect of the suppression for I_3^- formation with the frequencies of 28 and 100 kHz was almost similar between these two containers.

3.2. Measurement of the Fluorescence Spectra for 7-Hydroxycoumarin Formed by the Sonolysis of Coumarin in the Presence or Absence of MBs. It has been demonstrated in the previous section that influence of the microbubbles to the ultrasonic oxidation reactions of I^- ion in KI solution is strongly dependent on the ultrasound frequencies (28, 45, and 100 kHz). To confirm such ultrasound frequency dependence, coumarin fluorescence probe methods were also applied in the present study. Since coumarin is easily oxidized by OH radicals to form 7-hydroxycoumarin by the following reaction scheme



and 7-hydroxycoumarin is much more fluorescent than coumarin, the amount of OH radicals can be easily monitored via the fluorescence of 7-hydroxycoumarin around 450 nm formed by reaction 3 in a coumarin solution. So far, therefore, this coumarin probe method is now accepted as one of the standard methods used as the probe of OH radicals formed in various environments.^{20,21} Ultrasound irradiation is also known to form OH radicals by the collapse of the cavitation

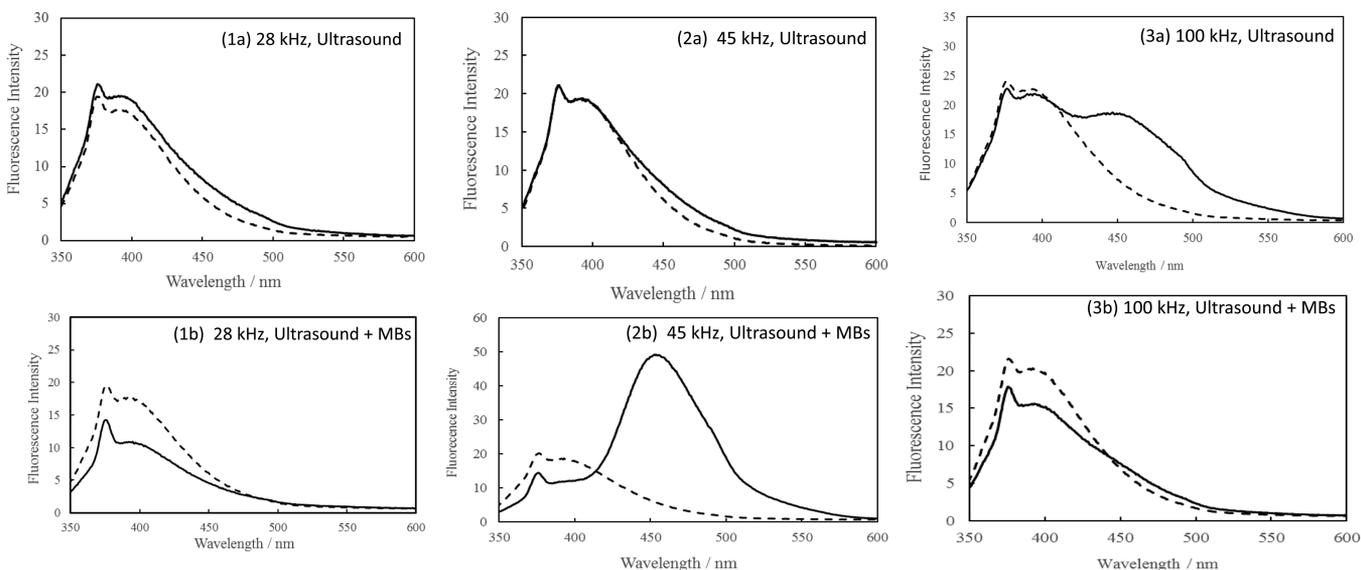


Figure 5. Fluorescent spectra of 0.1 mM coumarin solution after 30 min ultrasound irradiation in the (a) absence and (b) presence of MBs. The solid and dashed lines are the absorption spectra taken at 30 and 0 min after the ultrasound irradiation, respectively. Excitation wavelength was 332 nm, and the ultrasound frequencies were (1) 28 kHz, (2) 45 kHz, and (3) 100 kHz.

bubbles,^{22,23} and thus, the coumarin probe method is appropriate for monitoring the influence of microbubbles on the sonochemical reactions.

Figure 5 shows typical examples of the fluorescence spectra of 0.1 mM coumarin solution before and after the 30 min ultrasound irradiation in the absence and presence of MBs. In the absence of MBs, only the ultrasound with the frequency of 100 kHz gave a small shoulder around 450 nm, indicating that 7-hydroxycoumarin was formed by the irradiation of 100 kHz ultrasound in 0.1 mM coumarin solution. On the other hand, there was no clear evidence for the formation of 7-hydroxycoumarin when the ultrasound frequencies were 28 and 45 kHz. This is consistent with the previous study of Koda et al.⁶ that sonochemical efficiencies abruptly increase around 100 kHz. In other words, sonochemical reactions only occurred for the ultrasound frequency above 100 kHz, but fewer sonochemical reactions occurred for the ultrasound frequencies of below 100 kHz, such as 28 and 45 kHz.

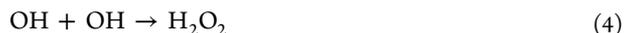
However, when MBs were introduced into the sonochemical reactors, a small shoulder peak around 450 nm, which appeared when the 100 kHz frequency of ultrasound was irradiated to 0.1 mM coumarin solution in the absence of MBs, was completely disappeared. On the other hand, a large fluorescence peak of 7-hydroxycoumarin around 450 nm appeared when the 45 kHz frequency of ultrasound was irradiated to 0.1 mM coumarin solution in the presence of MBs. Thus, we could conclude that microbubbles enhance 7-hydroxycoumarin formation only when ultrasound of 45 kHz frequencies were irradiated to the 0.1 mM coumarin solution and that formation of 7-hydroxycoumarin was suppressed when MBs were introduced into the solution with ultrasound irradiation of 28 or 100 kHz frequencies. These results are in good agreement with the results of KI oxidation dosimetry experiments as was described in the previous section. Decrease of the fluorescent intensity around 400 nm was also observed for the ultrasound of all frequencies (28, 45 and 100 kHz) when the MBs are introduced into the sonochemical reactors as shown in (1b), (2b), and (3b) of Figures 5. To understand the reason for such decrease of the fluorescence around 400 nm, we have measured

the temporal change of the fluorescence intensity at 400 nm during the circulation of the sample solution into the MB generator without irradiating ultrasound and it was found that the fluorescence intensity started decreased immediately after the circulation into MB generator and then the fluorescence intensity at 400 nm became nonzero constant value even after the long-term circulation, which was typical example of the temporal profile of the adsorption equilibrium. Thus, it was confirmed that the decrease was due to the adsorption to the wall of the MB generator or otherwise the interface between air and water of bubbles, not due to the reaction caused by MBs, which is consistent with the previous results with Takahashi et al. that at neutral pH condition no phenol decomposition was observed by the collapse of MBs.¹⁵ To confirm these results of the coumarin fluorescent probe experiments were not caused by the special condition caused by the 500 mL glass container, the 500 mL glass container with 300 mL of 0.1 mM coumarin solution was replaced with a 1000 mL glass container with 400 mL of 0.1 mM coumarin solution and the same coumarin fluorescence probe experiments were performed. Although different size of glass container was used, similar frequency dependence was also observed.

Increase of the sonochemical efficiencies by the introduction of MBs under the 45 kHz ultrasound irradiation was suggested from both KI oxidation dosimetry and coumarin fluorescent probe measurements in the present study. However, to confirm the important roles of MBs on the enhancement of the formation of ultrasonic cavitation bubbles, information about the absolute concentration of OH radicals increased by the introduction of MBs under the 45 kHz ultrasound irradiation was important. Since the reaction products and the yield of OH radical for the reaction of coumarin with OH radical has already been reported by Zhang et al.²¹ using the same fluorescence measurements, we can estimate the absolute concentration of OH radicals formed by the ultrasonic irradiation to the 0.1 mM coumarin solution. Absolute concentration of 7-hydroxycoumarin was determined by measuring the fluorescence intensity at 450 nm with various concentrations of 7-hydroxycoumarin. From these fluorescence calibration experiments, the amount of

7-hydroxycoumarin increased by the 30 min ultrasound irradiation of 45 kHz ultrasound frequency in the presence of MBs was estimated to be around 8.3×10^{13} molecules cm^{-3} . Since around 8.3×10^{13} molecules cm^{-3} of 7-hydroxycoumarin were formed by the 30 min ultrasound irradiation, the formation rate of 7-hydroxycoumarin was calculated to be around 1.5×10^8 molecules $\text{cm}^{-3} \text{ s}^{-1}$. Using literature value (6.1%)²¹ of the reaction yield of 7-hydroxycoumarin by the reaction of OH with coumarin, about 2.5×10^9 molecules $\text{cm}^{-3} \text{ s}^{-1}$ of OH radicals were increased by introducing MBs in the 500 mL glass container under the 45 kHz ultrasound irradiation.

3.3. Measurement of Hydroxyperoxide (H_2O_2) Formed by the Sonolysis of Water in the Presence and Absence of MBs. In both of the measurements of the KI method and the coumarin probe method, it was confirmed that microbubbles enhanced the OH radical formation with 45 kHz ultrasonic irradiation, while microbubbles suppressed the OH radical formation with 28 and 100 kHz ultrasonic irradiation. Since OH radicals formed by the sololysis of water are expected to recombine with each other to form H_2O_2 by the following reaction,



It is speculated that H_2O_2 formation will also be enhanced by MBs under 45 kHz ultrasound irradiation and that H_2O_2 formation will be suppressed by MBs under 28 and 100 kHz ultrasound irradiation. In the present study, H_2O_2 were titrated by adding 2 mL of titanium sulfate ($\text{Ti}_2(\text{SO}_4)_3$) reagent to the ultrasound irradiated water sample (400 mL) and measured the appearance of new absorption band around 400 nm.²⁴ For these H_2O_2 measurements after 3 h ultrasound irradiation to pure water, titanium sulfate reagent was added to titrate H_2O_2 formed by the ultrasound irradiation. As expected, new absorption band around 400 nm by reaction of H_2O_2 with $\text{Ti}(\text{SO}_4)_2$ was observed only with the experiments of the 45 kHz ultrasonic irradiation in the presence of MBs for 3 h. But when the ultrasound frequencies became 28 and 100 kHz, no H_2O_2 formation was observed using this $\text{Ti}_2(\text{SO}_4)_3$ titration reaction method. The results of the ultrasound frequency of 45 kHz are given in Figure 6. Calibrating the absorption band

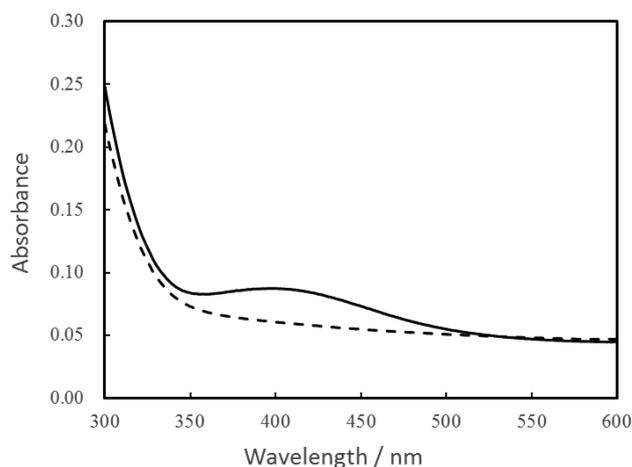


Figure 6. Absorption spectra between 300 and 600 nm after 3 h irradiation of ultrasound to water after adding 2 mL of $\text{Ti}_2(\text{SO}_4)_3$ in the presence (solid line) and absence (dashed line) of MBs with frequency of 45 kHz.

around 400 nm with H_2O_2 , the increased amount of H_2O_2 by introducing MBs under the 45 kHz ultrasound irradiation was determined to 2×10^{16} molecules cm^{-3} . Dividing the number of H_2O_2 molecules with time, the formation rate of H_2O_2 became 2×10^{12} molecules $\text{cm}^{-3} \text{ s}^{-1}$. This value is about 100 times larger than the estimated value of the rate of OH radical formation derived by the coumarin probe method. The reason is not yet well understood, but one plausible explanation is that, for coumarin fluorescent probe measurements, a large part of OH radicals were lost with other side reactions originating from the existence of coumarin in a solution.

3.4. Mechanism for the Enhancement and Suppression of Sonochemical Reactions with MBs. The present experiments support the conclusions that MBs play important roles on the sonochemical efficiencies. Ogi et al.²⁵ have already pointed out the important roles of the dissolved gas in sonochemical degradations. However, the effect of ultrasound frequencies on the free radical enhancement or suppression of MBs as presented in this paper have not been reported before. Since the sonochemical efficiencies were strongly related to the hot spots generated by the ultrasonic cavitation, it is speculated that microbubbles influenced the stabilities of ultrasonic cavitation. According to the previous experimental studies,²⁶ stable cavitation is produced in a standing wave field. Since air in microbubbles strongly reflects the ultrasound wave that have transversed in water due to the large difference of acoustic impedance between air and water, microbubbles disturb the standing wave formed by the ultrasonic transducer attached to the water tank. Thus, microbubbles reduces the hot spot created by the collapse of cavitation bubbles and then reduced the yield of OH radical formation. This might be the reason for the suppression of OH radical formation by microbubbles for the 28 and 100 kHz ultrasound irradiations.

For 45 kHz ultrasound irradiation, OH radical formation was enhanced by microbubbles. This phenomena could not be explained only by the disturbance of standing wave of ultrasound wave by microbubbles. Makuta et al.²⁷ have recently reported the bubble collapse by the ultrasonic irradiation followed by the microbubble generations. If 45 kHz ultrasound could interact with MBs with diameter of around $1 \mu\text{m}$ used in the present study and new small cavitation bubbles are formed from them, it is probable that OH radical formation under the irradiation of 45 kHz ultrasound was enhanced by microbubbles. The schematic figure of the mechanism was given in Figure 7.

Although the bubble collapse by the irradiation of ultrasound was experimentally confirmed by Makuta et al.,²⁷ fundamental understanding of the interaction between bubble and ultrasound is not well understood. It is well-known that primary and secondary Bjerknes forces are the main forces that act to a bubble in the acoustic field.⁴ However, these forces are dependent on the acoustic force field, and it is not probable that these primary and secondary Bjerknes forces are the reason why only the ultrasound frequency of 45 kHz has the ability to enhance the radical formation. According to the recent experimental studies of the direct observation of a single bubble under the ultrasound field,²⁸ the Minnaert bubble resonant frequency of bubble is the key factor on the collapse of bubbles under the ultrasound field. The Minnaert bubble resonance frequency f , which is given in the following expression²⁹

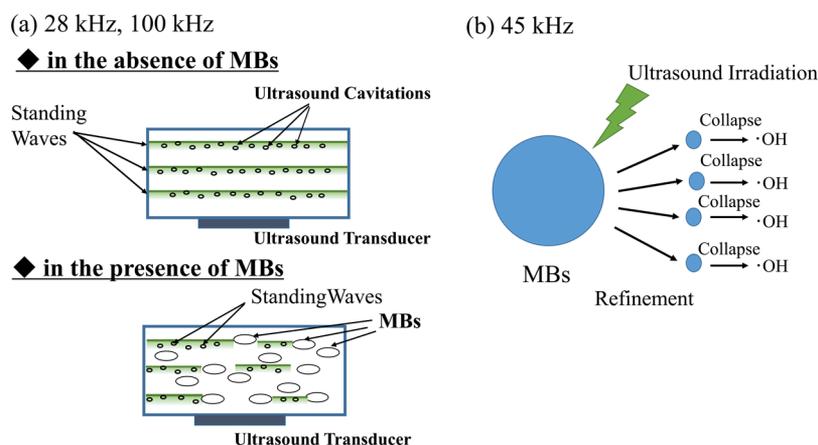


Figure 7. Schematic of the influence of the MBs on the formation to the cavitation bubbles.

$$f = \left(\frac{1}{2\pi R} \right) \left(\frac{3\gamma P_0}{\rho} \right)^{1/2}$$

where R is the bubble radius (m), γ is the specific heat ratio, ρ is the density of water (kg/m^3), and P_0 is the pressure of the bubble (Pa), was calculated for all of the ultrasound frequencies (28, 45, and 100 kHz) used in the present study. However, the calculated bubble radii R that were resonant to the ultrasound frequencies of 28, 45, and 100 kHz were around 120, 70, and 30 μm , respectively, and thus the resonant bubble radius is much larger than the bubble radius (around 1 μm) generated by the microbubbles used in the present study. According to the recent numerical simulation of sonochemical reactions for various ultrasonic frequencies and various acoustic amplitude inside an isolated spherical air bubble,³⁰ dissociation of H_2O_2 to form OH radical preferentially proceeds with lower ultrasound frequencies due to the longer duration of high temperature at the bubble collapse, although ultrasound with higher frequency has higher energy densities inside the bubble. Thus, the chemistry of the microbubble under the ultrasound irradiation are complicated phenomena. So far, the mechanism of enhanced radical formation by the 45 kHz ultrasound irradiation obtained in the present study is not clearly given. The direct visualization of the collapse of microbubbles as well as the measurements of the bubble size reduction with the irradiation of 45 kHz ultrasound is another way to make clear the radical-enhancement mechanism with the ultrasound of 45 kHz, but it was not successful because microbubbles disappeared immediately after the irradiation of ultrasound as was previously reported by Kobayashi et al.¹⁶ Further work is needed to clarify the reasons, and now studies are underway to clarify the mechanism.

AUTHOR INFORMATION

Corresponding Author

*E-mail: murakami_mb@nagaoka-ct.ac.jp.

Notes

The authors declare no competing financial interest.

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