SINGLE-BUBBLE SONOCHEMILUMINESCENCE IN LUMINOL SOLUTIONS

Shin-ichi Hatanaka[1]; Hideto Mitome[2]; Kyuichi Yasui[2]; Teruyuki Kozuka[2]; Shigeo Hayashi[1]

Department of Applied Physics and Chemistry, The University of Electro-Communications[1];

National Institute of Advanced Industrial Science and Technology (AIST)[2]

1-5-1 Chofugaoka, Chofu, 182-8585, Japan[1];

Shimoshidami, Moriyama-ku, Nagoya 463-8560, Japan[2]

Tel: +81-424-43-5794

Fax: +81-424-43-5794

E-mail: hatanaka@pc.uec.ac.jp

ABSTRACT

Sonochemiluminescence (SCL) of luminol due to a single bubble is studied through spectral measurement. No SCL was observed from a stable single bubble that emitted high-intensity sonoluminescence (SL). In contrast, SCL was observed under conditions of unstable dancing single bubble, where a bubble grows and ejects tiny bubbles, making it "dance" by counteraction. Furthermore, SCL was observed from dancing bubbles even when SL was not observed, provided that the gas which should promote OH radical formation was dissolved. The instability of bubble collapse is the key parameter governing SCL.

INTRODUCTION

Ultrasonic irradiation of liquids provides a unique environment where high-energy chemical reactions occur.[1] The chemical effects originate from acoustic cavitation bubbles, which generate extremely high temperatures and pressures at collapse.[2] The extreme conditions in the

interior of bubble also lead to the emission of light, referred to as sonoluminescence (SL), which is manifested in two forms: multibubble (MB) SL and single-bubble (SB) SL.[3] The light intensity in the MB case increases significantly upon adding a small amount of luminol to aqueous alkaline solutions. This emission is called sonochemiluminescence (SCL) and is distinguished from SL,[4] because the emission is identical to *chemiluminescence* in the bulk liquid region, which results from the chemical reaction of luminol molecules with OH radicals produced within bubbles.[5] No counterpart has been reported for SCL in the SB case despite the well-known emission in the MB case.[6] Recently, Ashokkumar and Grieser reported the third type of emission referred to as sonophotoluminescence (SPL), where SL is absorbed to excite dissolved fluorescent solutes, leading to the emission of fluorescence associated with *photoluminescence*.[7] Their study of SPL covers both of MB and SB cases.[8]

The missing case, SCL for SB, is important in sonochemistry, because many sonochemical reactions involve radicals produced within bubbles, and we have successfully observed the SBSCL in aqueous luminol solutions through spectral measurement. The most important point is that no SCL is observed from a stable single bubble that emits high-intensity SL. Instead, SCL is observed from an unstable dancing single bubble, which grows and ejects tiny bubbles, making it "dance" by counteraction.

EXPERIMENT

The Experimental setup is shown in Fig. 1. A continuous sinusoidal signal generated by a function generator (NF Electronic Instruments, 1946) was amplified by a 50-dB power amplifier (ENI, 240L) and fed to a bolted Langevin-type transducer of 45 mm diameter (Honda Electronics). The transducer was fixed to a stainless steel plate at the bottom of a rectangular cell, which was 56×56×80 mm^3 internal dimensions and made of quartz glass of 2 mm thickness. Distilled water of 220 mL volume, which was partially degassed under air, was filled to 70 mm liquid depth in the cell. A bubble was inserted with a syringe and trapped at a pressure antinode in a standing wave field at a resonant frequency of 24.5 kHz. By adjusting pressure amplitude, SBSL was obtained at 20°C in liquid temperature and 2.0 mg/L (saturated value: 8.8 mg/L) in dissolved oxygen (DO), which was measured with a DO-pH meter (HORIBA, D-25). A calibrated hydrophone
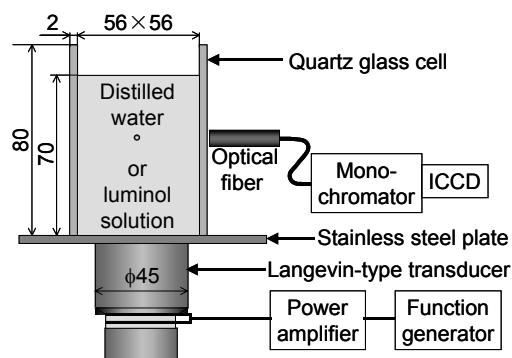

Fig. 1. Experimental setup.

(RESON, TC4038) was used to measure approximate pressure amplitude at the position of the bubble. SBSL spectra were collected using a monochromator (Bunkoukeiki, M25-T) through a quartz optical fiber with an intensified charge-coupled device (ICCD) detector (ANDOR Technology, ICCD 501-18F) with 0.1 s exposure for 300-cycle accumulation in the range of 250–710 nm. Aqueous sodium carbonate-luminol solutions were substituted for 1 mL distilled water in the cell, whose resultant pH value was 11.3. Sequent measurement of spectra was performed within 1 minute under the same conditions. The absorbance of luminol was measured with a UV-VIS spectrophotometer (HITACHI, U-2000).

RESULTS AND DISCUSSION

Figure 2 shows uncorrected spectra from a single bubble in distilled water and in 0.01, 0.05 and 0.10 mM luminol solutions. The insert shows the absorption and fluorescence spectra of the same luminol solutions. It is found that the spectrum of the distilled water is absorbed by the addition of luminol, and the absorption increases with the concentration of luminol. The spectral modification can be explained entirely by subtracting the luminol absorption spectrum from the water SBSL spectrum. On the other hand, the fluorescence of luminol photoexcitation is proportional to the luminol absorption, as shown in the insert. Since SPL results from direct photoexcitation,[7,8] the SPL intensity of luminol corresponds to the increasing luminol emission intensity with increasing luminol concentration. Therefore, the failure to observe the increasing intensity at 420 nm excludes the possibility that SPL contributions are significant.
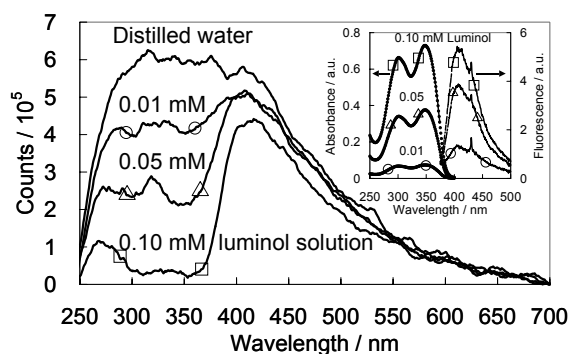

Fig. 2. Single-bubble sonoluminescence spectra in distilled water and in 0.01, 0.05, and 0.10 mM aqueous luminol solutions. The insert shows the absorption and fluorescence (photoexitation= 355 nm) spectra of the luminol solutions.

In order to examine the ratio of SCL to SL in the spectrum for luminol solutions, we added ethanol to quench SBSL. The quenching effect of alcohol on SBSL in water was reported by Ashokkumar et al.[9] Furthermore, Yasui[10] showed, based on simulation, that a methanol additive quenches SBSL but
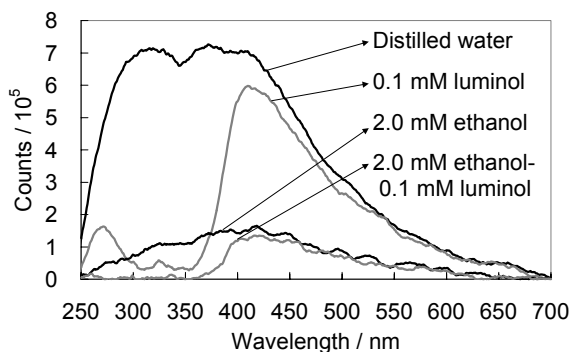

Fig. 3. Effect of 2.0 mM ethanol additive on the spectra from a stable single bubble in distilled water and 0.1 mM aqueous luminol solution.

hardly reduce the number of OH radicals produced within a bubble. This is also valid for ethanol. Thus, the ethanol additive should quench SL but hardly SCL. Figure 3 shows the effect of 2.0 mM ethanol additive (26 μL) on single bubble spectra in distilled water and 0.1 mM luminol solution. The SBSL spectrum in the ethanol solution is quenched preferentially at shorter wavelengths; the maximum intensity is about 20%, which is consistent with Ref. 9. Note that the spectrum in the presence of luminol is also quenched similarly to that in the absence of luminol at 420 nm. If SCL contributions were significant, the intensity of luminol emission would become substantially independent of ethanol when the solution contains luminol. Therefore, SCL also cannot contribute significantly to the observed single stable bubble emission spectra, because adding ethanol produces the same fractional reduction in 420 nm emission intensity in both the presence and absence of luminol.

Although the intensity ratio of SCL to SL is tens or hundreds in MB cases,[11] we could not distinguish SCL in the stable SB case. Unstable bubble collapse seems to promote the emission of SCL. Then, we performed further experiments under the condition of the unstable single bubble that is "a dancing bubble." A dancing single bubble grows in size with every acoustic cycle and emits tiny bubbles, "daughter bubbles," repeatedly, making it "dance" around the pressure antinode by counteraction.[12] We obtained dancing bubbles by Ar-gas bubbling (100 mL/min×3 min) in the cell of the same water above. Figure 4 shows the radius-time curves during one acoustic cycle in both the cases of a stable and a dancing single bubble. The experimental technique by which we have obtained these data can be found elsewhere.[13] In this figure, the measured acoustic pressure is also shown. The solid lines denote the 32-averaged data by light-scattering technique and the open circles denote the data by stroboscopic image-processing technique, which is shown only in the stable bubble case. Figure 5 shows the selected three stroboscopic images of each of the bubbles. The dancing bubble condition is a shape-unstable one. Although daughter bubbles are, in a manner of speaking, multibubble, the bubbles cannot be generated without an injection of bubble for the cavitation inception in contrast to the MBSL case. Figure 6 shows the spectra from dancing bubbles in distilled water and 0.1 mM luminol solutions in the absence and presence of 2.0 mM ethanol. Note that the spectral intensity in the
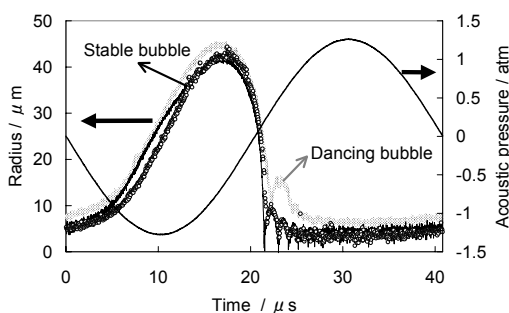

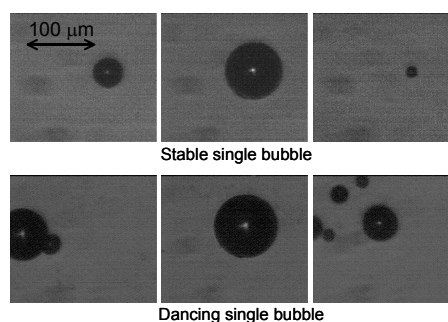Fig. 4. Radius-Time curves of a stable and a dancing single bubble.

Fig. 5. Stroboscopic images of a stable (top) and a dancing (bottom) single bubble.

luminol solution exceeds that in distilled water at 420 nm, and is independent of ethanol despite the quenching in distilled water. These results confirm that the luminol SCL contributes evidently to the observed dancing single bubble emission spectra.
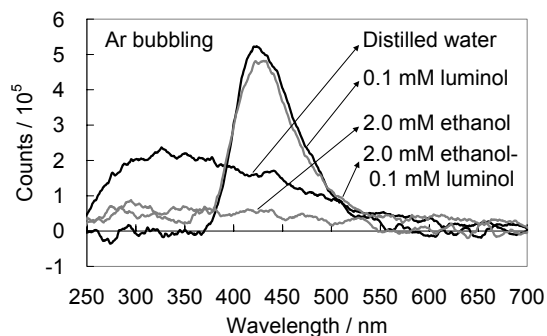

Fig. 6. Effect of 2.0 mM ethanol additive on the spectra from dancing single bubbles in distilled water and in 0.1 mM aqueous luminol solution with Ar-bubbling pretreatment.

It is clear that unstable bubble collapse is a key factor in SCL, *i.e.*, sonochemistry associated with OH radicals. Lepoint *et al.*[14] reported similar results in Weissler's reaction, where they observed I_3^- formation from a dancing single bubble but noted that this product was virtually eliminated if the bubble was stabilized. Didenko *et al.*[15] also noted that the emission from an unstable "moving bubble" gave rise to CN emission in methylformamide but that this feature disappeared when the bubble was made stable. They argued that the stable single bubble produced so high core temperatures that molecular species were dissociated. In theory, Storey and Szeri[16] showed that most OH radicals produced within a stable single bubble are confined to the bubble interior by the bubble wall. They discussed that the bubble that is unstable on collapse and breaks apart is much more productive in sonochemistry. We consider that OH radicals may be produced much more in the dancing single bubble and transported into liquid together with daughter bubbles.

Figure 7 shows the spectra from dancing bubbles in 0.1 mM luminol solutions for the various gas bubbling of O_2, N_2 and 1% Xe in N_2 instead of Ar. In these solutions, the air including Ar was partially dissolved. Under these conditions, no spectra are collected in distilled water. Nevertheless, luminol SCL is seen in the cases of O_2 and 1% Xe in N_2. This SB result is consistent with the MB one.[11] Non-sonoluminescing bubbles are chemically active. Again, the same result was shown in Ref. 14. Indeed, the dancing SBSCL intensity is increased by the presence of O_2 and/or Xe, because these gases promote H_2O_2 formation[17] and hence production of the superoxide radical anion required for luminol chemiluminescence.[5]
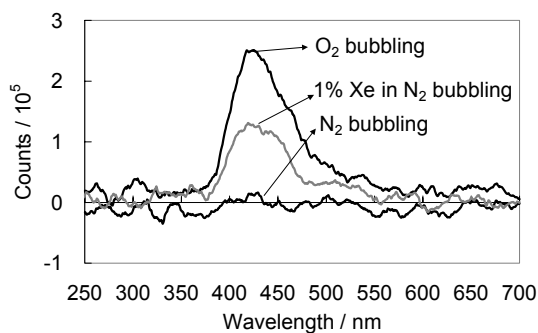

Fig. 7. Influence of gas contents on sonochemi-luminescence (SCL) spectra from non-sonoluminescing dancing bubbles in 0.1 mM aqueous luminol solutions.

CONCLUSIONS

The SCL of luminol was observed not from stable single bubbles but from dancing single bubbles. The SCL was observed from dancing single bubbles even when SL was not observed, depending on gas content. One of the key parameters in SCL is the instability of bubble collapse, in addition to the chemical reactions within the collapsing bubble.

REFERENCES

1. (a) Suslick, K. S. *Science* 1990, **247**, 1439. (b) Henglein, A. *Ultrasonics* 1987, **25**, 6. (c) Suslick, K. S.; Crum, L. A. In *Encyclopedia of Acoustics*; Crocker, M. J., Ed.; John Wiley & Sons: New York, 1997; **1**, 271. (d) Mason, T. J. *Sonochemistry*; Oxford University Press: New York, 1999.

2. (a) Flint, E. B.; Suslick, K. S. *Science* 1991, **253**, 1397. (b) McNamara III, W. B.; Didenko, Y. T.; Suslick, K. S. *Nature* 1999, **401**, 772.

3. Crum, L. A. *Phys. Today* 1994, **47**, 22.

4. Harvey, E. N. *J. Am. Chem. Soc* 1939, **61**, 2392.

5. McMurray, H. N.; Wilson, B. P. *J. Phys. Chem. A* 1999, **103**, 3955.

6. Henglein, A.; Ulrich, R.; Lilie, J. *J. Am. Chem. Soc.* 1974, **111**, 1989.

7. (a) Ashokkumar, M.; Grieser, F. *Chem. Commun.* 1998, 561. (b) Ashokkumar, M.; Grieser, F. *Ultrason. Sonochem.* 1999, **6**, 1.

8. Ashokkumar, M.; Grieser, F. *J. Am. Chem. Soc.* 2000, **122**, 12001.

9. Ashokkumar, M.; Crum, L. A.; Frensley, C. A.; Grieser, F.; Matula, T. J.; McNamara III, W. B.; Suslick, K. S. *J. Phys. Chem. A* 2000, **104**, 8462.

10. Yasui, K. *J. Chem. Phys.* 2002, **116**, 2945.

11. Hatanaka, S.; Yasui, K.; Tuziuti, T.; Mitome, H. *Jpn. J. Appl. Phys.* 2000, **39**, 2962.

12. Barber, B. P.; Weninger, K.; Lofstedt, R.; Putterman, S. Phys. Rev. Lett. 1995, 74, 5276.

13. (a) Kozuka, T.; Hatanaka, S.; Tuziuti, T.; Yasui, K.; Mitome, H. *Jpn. J. Appl. Phys.* 2000, **39**, 2967. (b) Kozuka, T.; Hatanaka, S.; Yasui, K.; Tuziuti, T.; Mitome, H. *Jpn. J. Appl. Phys.* 2002, **41**, (in printing).

14. Lepoint, T.; Lepoint-Mullie, F.; Henglein, A. In *Sonochemistry and Sonoluminescence*; Crum, L. A., Mason, T. J., Reisse, J. L., Suslick, K. S., Eds.; NATO ASI Series C 524; Kluwer Academic Publishers: Dordrecht, 1999; 285.

15. Didenko, Y. T.; McNamara III, W. B.; Suslick, K. S. *Nature* 2000, **407**, 877.

16. Storey, B. D.; Szeri, A. J. *Proc. R. Soc. Lond. A* 2000, **456**, 1685.

17. Mead, E. L.; Sutherland, R. G.; Verrall, R. E. *Can. J. Chem.* 1976, **54**, 1114.