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On the Sonochemiluminescence from a Microspace
マイクロ流路からの音響化学発光

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1. Introduction

Many studies have been performed on the application of ultrasound to chemical reaction processes in micro-fluidic devices.[1-3] The chemical effects of ultrasound[4] are based on the formation of radicals and oxidants, such as hydroxyl radicals, ozone and hydrogen peroxide, by dissociation of water vapor subjected to extreme conditions. These conditions involve temperatures of several thousand degrees Kelvin and pressures of several hundred atmospheres within a nonlinearly pulsating cavitation bubble. The chemical reactions involving active species generated by ultrasound are referred to as sonochemical reactions and it has been found that both the mass transfer and mixing induced by streaming around bubbles undergoing pulsating motions assist in accelerating multiphase reactions.

The present study deals with the power dependence of the intensity of luminol-based sonochemiluminescence (SCL) in both a one-dimentional (1D) microspace and a 3D millimeter-sized space, with the aim of determining the optimal dissolved oxygen degree of saturation (DOS) values associated with high yields during sonochemical reactions.[5] Based on the results, a mechanism explaining the varying relationships of SCL intensity with DOS values in a 1D microspace and a 3D millimeter-sized space is proposed.

2. Experiment

The experimental apparatus used to measure the intensity of SCL resulting from luminol (3-aminophthalhydrazide) is shown in Figure 1. Luminol reacts with OH radicals generated in cavitation bubbles during intense ultrasound irradiation to yield aminophthalate anions which subsequently undergo the emission of blue fluorescence.[6] A solution consisting of 10.0 mM NaOH and 56.4 μM luminol was prepared in distilled water and the concentration of dissolved air in this solution was adjusted by bubbling air through the solution as well as by temperature control. Luminol solutions having different DOS values were loaded into a syringe (20 mL) and pressurized by the motion of its piston (20.2 mm in diameter) under the impetus of a syringe pump. Solutions at five different DOS values were prepared just prior to loading the syringe (DOS =

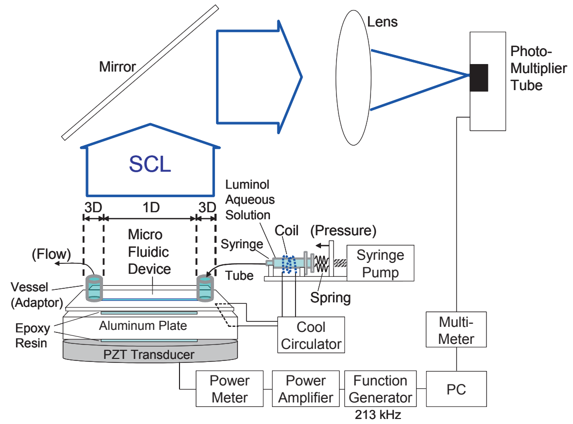

Figure 1. Experimental apparatus. (reproduced from ref. 5 by permission of © 2013 American Chemical Society)

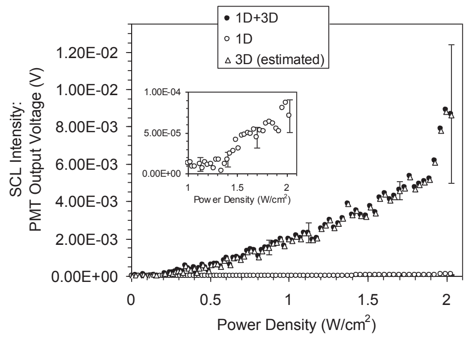

Figure 2. Variations in SCL intensity with power density at a DOS value of 0.500. The inset presents a magnified view of data from the 1D space. The vertical bars represent average relative errors. (from ref. 5 by permission of © 2013 American Chemical Society)

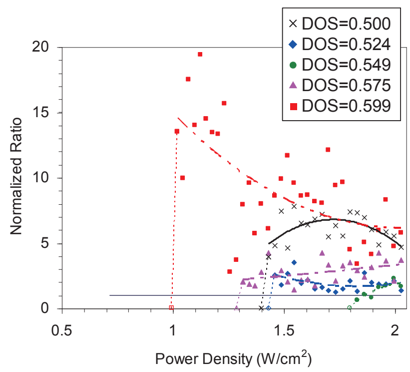

Figure 3. Variations in the 1D/3D SCL intensity ratio with power density, normalized by the 1D/3D volume ratio. Dotted lines extending from the horizontal axis indicate the power density threshold at each DOS. The solid line parallel to the horizontal axis is the 1D/3D volume ratio, defined as 1. Continuous, broken, dotted, dot and dash and two-dot fitted lines indicate normalized SCL intensity ratios at DOS values of 0.500, 0.524, 0.549, 0.575 and 0.599, respectively. (from ref. 5 by permission of © 2013 American Chemical Society)

1.001, 1.048, 1.097, 1.150 and 1.200 at atmospheric pressure). The DOS values of these same solutions when pressurized to 2.02 atm in the syringe were estimated to be 0.500, 0.524, 0.549, 0.575 and 0.599. The 1D space had a 100 μm × 100 μm cross-section and was contained in a glass plate (25.4 × 50.8 mm, 1 mm thickness). The SCL intensity of emissions from the 1D space was monitored along a 22 mm section of the longer side of the plate. The 3D space consisted of two tubular vessels, each 3.0 mm in internal diameter and 8.8 mm in internal height. The volumes of the 1D and 3D spaces were 0.22 and 124.4 mm^3, respectively. One of the 3D vessels connected to the syringe through a transfer tube played an adaptor to 1D space. The second 3D vessel was used to allow the solution to flow out of the 1D space.

Using a 55 dB power amplifier, a CW sinusoidal 213 kHz signal from a function generator was amplified. The input power was measured using a power meter. The combined sonochemiluminescent light emissions from the solutions in the 1D and both 3D spaces was detected with a photomultiplier tube and, in addition, light emitted solely from the 1D space was measured by temporarily shielding the 3D space emission with aluminum foil. The output voltage from the photomultiplier was received by a multimeter and the resulting data were acquired by computer. Each SCL intensity measurement was repeated three times. The SCL intensity component resulting from the 3D space was estimated by subtracting the measured emission from the 1D space from the combined emission detected from the 1D and both 3D spaces.

3. Results and Discussion

An example of the estimated SCL intensities obtained from the 3D space alone is shown in Figure 2, along with the combined and 1D emission at a DOS value of 0.500. The inset of the figure presents a magnified plot of the SCL intensity from the 1D space over the range of power density where the 1D SCL intensity begins to increase, and shows that the power-density threshold associated with the onset of 1D emission is significantly above that for 3D emission. Figure 3 shows the power dependence of the 1D/3D SCL intensity ratio, normalized by the volume ratio, at various values of DOS. In this figure, the dotted lines extending from the horizontal axis indicate the power density threshold associated with each level of DOS while the flat line parallel to the horizontal axis is the 1D/3D volume ratio, defined as 1. The fitted curves indicated by continuous, broken, dotted, dot and dash, and two-dot patterns correspond to the normalized SCL intensity ratios at DOS = 0.500, 0.524, 0.549, 0.575 and 0.599, respectively. A normalized ratio above 1 indicates that the 1D space provides a more effective volume for the sonochemical reaction than the 3D space. In this context, an effective volume means that there is only a small region in which the sonochemical reaction does not occur. Figure 3 shows that, in all cases except at a DOS value of 0.549 in conjunction with relatively low power density, the normalized SCL ratio is greater than the volume ratio. It is interesting to observe that the highest DOS value of 0.599, when applied with a reduced level of power density of approximately 1 W/cm^2, results in the highest SCL intensity ratio. This ratio is about 15 times greater than the volume ratio indicated on the corresponding fitted curve.

Since the increased quantity of bubbles in the 3D space lowers the acoustic amplitude in the solution, the trend observed for the normalized ratio at the highest DOS value of 0.599 occurs. This in turn tends to prevent the violent collapse of bubbles required to promote SCL at relatively low levels of power density. In contrast, the 1D space contains fewer bubbles throughout its volume, but most of these are capable of actively facilitating the sonochemical reaction. For this reason, the normalized ratio at the highest DOS value exhibits its maximum at a relatively low power density. Within a limited range of power density, the number of active bubbles in the 3D space increases with increasing power to a greater extent than in the 1D space, since there are more bubbles in the 3D space which have the potential to be active. Accordingly, the normalized ratio decreases with increasing power density.

The present study clarified that, using air-saturated solutions prepared at atmospheric condition, the sonochemical reaction in 1D microspace at pressurized condition can be more efficient than that in 3D. This implies that 1D microspace has more effective volume containing cavitation bubbles effective for sonochemical reaction than that in 3D when comparing the reaction efficiency per unit volume.

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