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Ultrasonic cavitation in microspace

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Ultrasound was irradiated to a micro-1D and -2D space having a characteristic length of 200 μm, and the presence of cavitation was confirmed from video images, and the generation of OH radicals, which was quantitatively evaluated with fluorometry.

Microspace chemistry, *e.g.* microreactor[1] and μ-TAS (total analysis system),[2] has been recognized as an innovative technology which enables combinatorial approaches with the acceleration of reaction, analysis and measurement. In addition to chemical industries, the medical, pharmaceutical, biotechnology and food industries have enthusiasm for using such a technology. Generation of cavitation phenomena in liquids by the application of ultrasound is also an area which is widely studied due to its potential advantages and its applications. One of the so far unexplored strategies in this technique is whether it is possible or not to generate cavitation and hence sonochemical effects in such microspace reactors. Because, once cavitation phenomena can be induced in a microchannel with ultrasound, then it becomes possible to open a novel way of utilizing sonochemistry with microchips. In addition, one can exploit the cavitation bubbles generated as a micro-mixer or a pump, which are one of the key technologies for microspace chemistry. Also, microchannels are widely found in human tissues such as blood vessels, brain and kidney, where ultrasonic diagnosis is widely applied. Due to these applications, it becomes important to ensure that cavitation phenomena will not damage the living tissues in the conditions used during these diagnosis. In the medical field, shock-wave lithotripsy (SWL) has also been used routinely for the treatment of urolithiasis and 'cavitation' in the tissue has been sometimes discussed.[3,4] However, the pressure peak up to 50 MPa in SWL gives rise to totally different cavitation *i.e.* inertial cavitation, induced by the tensile stress of a lithotripter shock wave pulse.[5] Thus, less is known about the cavitation effects in microspace. This has prompted us to make an investigation in the present study as to whether ultrasound does or does not bring about cavitation phenomena in such a constrained microspace, in particular, in 1D and 2D systems. In these investigations, the resultant cavitation effects caused by the application of relatively mild ultrasound with sound pressure less than 0.5 MPa, which is commonly applied in a standing wave type sonoreactor, has been studied. In this study, ultrasound was irradiated to a microchannel (1D) and to a thin layer (2D), with their characteristic lengths of the order of a few hundred microns. The flow in the channel and in the thin layer was observed as video images by using a microscope. Furthermore, the resultant sonochemical effects in the microspace were quantified using a fluorescent probe as a function of ultrasound power density. The threshold value for the cavitation and their sonochemical efficiencies to produce OH radicals were compared with a conventional sonochemical reactor (3D).

1D- and 2D-microreactors and a small 3D-reactor as a reference were constructed as shown in Fig. 1. Each reactor was fabricated with a PZT oscillator plate (50 × 32 × 3 mm), aluminium plate (5 mm thick) and a plexiglas plate cover (5 mm thick for the 1D- and 2D-reactors) or a glass tube (20 mm height and 25 mm diameter for the 3D reactor). The components were tightly glued with each other using epoxy resin. During the operation, the reactor was settled on a large aluminium plate (200 × 120 × 10 mm) to release the heat from the PZT oscillator. The oscillator was driven by a continuous sinusoidal wave produced by a function generator (HP, 33120A) and the wave was amplified by a high speed bipolar amplifier (NF, HSA4012). The operating frequencies of 1D, 2D and 3D reactors were 162, 166 and 158 kHz, respectively. The input power of the reactor was monitored by the current and voltage meters equipped with the amplifier. The cavitation from the 1D- and 2D-reactors was observed under a microscope (Olympus, BX60) attached with a CCD video camera (MOSWELL, MS-560A). By virtue of the microreactor, cavitation bubbles generated are confined in a specified space. Therefore, the observation of the dynamic bubbles motion was easy even under a microscope with shallow focal depth. The generation of OH radicals produced by ultrasonic cavitation was monitored by their reaction with terephthalate anion to produce fluorescent hydroxyterephthalate (HTPA) ions.[6] Terephthalic acid was purified by recrystallization as a disodium salt in order to reduce the background fluorescence. The chemical dosimetry solutions were prepared as 2.0×10^{-3} M disodium terephthalate. In the microchannel (1D) and thin layer (2D) reactors, the dosimetry solution was fed by a syringe pump (Harverd Apparatus, H11-E) at a flow rate of 0.5 mL min^{-1} for 10 min and the sonicated solution was collected in a beaker. For the 3D reactor, a 5 mL solution in the reactor was sonicated for 10 min. The total number of HTPA molecules was determined by the fluorescence measurement of each solution using a spectrofluorometer (Shimazu RF-1500) with an excitation wavelength of 315 nm and an emission wavelength of 425 nm. The calibration was carried out with a dilute solution of HTPA, which was synthesized according to the literature method.[6] The detection limits of the terephthalate dosimeter were 2.1×10^{-13} mol ml^{-1} (1.2×10^{11} molecules ml^{-1}) in our experimental setup.[7]

Fig. 2(a) shows the amount of HTPA produced per s in a 1D microchannel as a function of power density. The threshold value for the cavitation was estimated to be about 0.7 W cm^{-2}. Additionally, small bubbles also emerged above this power density. Fig. 3 shows one shot of the video image of the bubbles in the microchannel. The bubbles formed were sometimes stuck to the channel wall, but after a few seconds the bubbles were carried away with the flow of the solution. The flow rate was 0.5 ml min^{-1} and thus the linear velocity which could be calculated was 21 cm min^{-1} in a microchannel having a 200 × 200 μm cross-section. The generation of small bubbles with diameter of a few microns has been observed and they moved around and grew up rapidly to a few tens of microns by coalescing with other bubbles. The

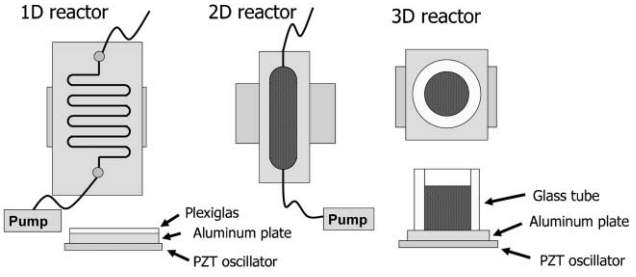

Fig. 1 Microspace sonochemical reactors.

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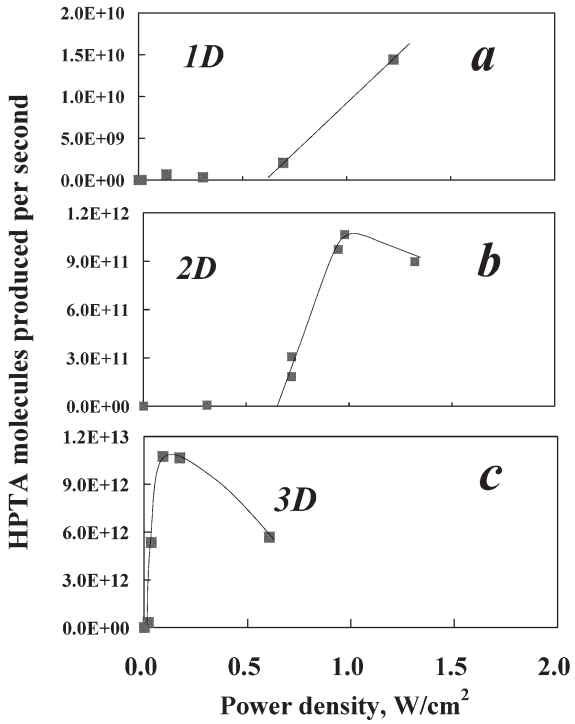

Fig. 2 Sonochemical production rate of HTPA in 1D, 2D and 3D microspace reactors.

generation rate of HTPA increased up to 1.5×10^{10} s^{-1} with an increase in ultrasonic power density. Fig. 2(b) shows the amount of HTPA produced per s in a 2D thin layer channel as a function of power density. The threshold value for the onset of cavitation in this case was estimated to be about 0.7 W cm^{-2}, which is almost the same as for the 1D microchannel. However, the production rate of HTPA was increased up to 1.0×10^{12} s^{-1}. For the 3D case, as shown in Fig. 2(c), the threshold value for the onset of cavitation was obviously decreased, as compared to the 1D and 2D cases, to 0.02 W cm^{-2}. The production rate of HTPA was increased up to 1.0×10^{13} s^{-1}. Moreover, an interesting and important phenomenon that has been observed in this investigation is the change in the threshold power density among these reactors which follows as, 1D $\cong$ 2D $>$ 3D. The requirement of a high threshold power density in case of microspace reactors is mainly due to the suppressant nature of the emergence of cavitation bubbles which may be due to the following two reasons. At first, the level of sound pressure and the mode of sound may be totally different among 1D, 2D channels and the 3D reactor. The surface wave mode should play an important role in 1D and 2D cases; however, to the best of our knowledge, sound modes in such a microspace have not been investigated so far. The probable second reason is that the bubble dynamics in constrained media is different from that in a free media. Zhong *et al.*[5] reported that the expansion of the bubbles inside a vessel phantom was significantly constrained, leading to asymmetric elongation of the bubbles along the vessel axis and much weakened collapse. In addition, the cavitation threshold value changed with the characteristics of the surface, consisting of channels (1D and 2D) or the reactor (3D). When the channels were made of glass, the cavitation bubbles were difficult to observe in 1D and 2D cases. For the 3D reactor, the threshold value increased from 0.02 W cm^{-2} for an aluminium metal surface to 0.7 W cm^{-2} for a glass surface. Coleman *et al.*[4] have reported that the cavitation

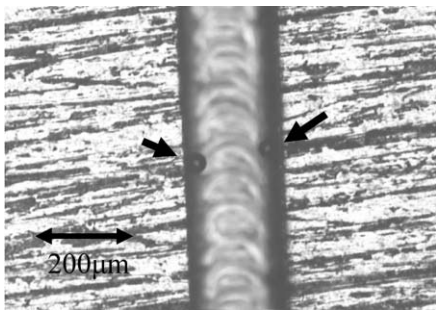

Fig. 3 Cavitation bubbles in a microchannel induced by ultrasonic irradiation.

threshold of human tissues lies between 1.5 and 3.5 MPa. These values are several times higher than that found in common sonochemical reactors. The above observations indicate that using a rather rough surface seems to be necessary to induce cavitation in microspace at low power density. The production rate of HTPA that has been observed in the three cases could also be related to the increase in the reaction volume. The reaction rate was increased from 1.5×10^{10} for 1D, 1.0×10^{12} for 2D, and to 1.0×10^{13} HTPA molecules s^{-1} in the case of the 3D reactor. On the other hand, the reaction volume has changed from $0.2 \times 0.2 \times 20 \times 3 = 2.4$ mm^3 for 1D, $0.25 \times 14 \times 20 = 70$ mm^3 for 2D, and to $20 \times 20 \times 10 = 4000$ mm^3 for 3D. The active oscillating zone was estimated from the cavitation bubble formation as the 20×20 mm center area of the piezoelectric oscillator. It can be observed that in going from 1D to 2D, the reaction rate has increased by 67 times while the volume has increased only by 29 times. An apparent increase in the reaction rate over the volume change could be related to the relaxation of space confinement when changing from 1D to 2D geometry. On the other hand, from 2D to 3D, the reaction rate increased by 10 times while the volume increased by 57 times. This result indicates that the total volume of 3D reactor is not so efficiently utilized as the 2D thin layered channel. In other words, the cavitation bubbles are somehow localized in the 3D reactor. Also, a decrease in the production rate of HTPA at higher input power density has been observed in 2D and 3D cases, and the estimation of the same was not possible in the 1D channel. These phenomena could be attributed to the generation of heat at the oscillator and the resultant increase in the temperature of the reactor. A cooling system should be incorporated or the heat design will be important when the ultrasound device is integrated in a microchip reactor.

In summary, the present investigation confirm the presence of cavitation in microspace. The understanding from the results provides guidelines for the new design of microreactors.

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