Study on Formation of Plasma Nanobubbles in Water

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Abstract. Nanobubbles of less than 400 nm in diameter were formed by plasma in pure water. Pre-breakdown plasma termed streamer discharges, generated gas channels shaped like fine dendritic coral leading to the formation of small bubbles. Nanobubbles were visualized by an optical microscope and measured by dynamic laser scattering. However, it is necessary to verify that these nanobubbles are gas bubbles, not solid, because contamination such as platinum particles and organic compounds from electrode and residue in ultrapure water were also observed.

3. Introduction

Micro- and nano-bubbles have potential applications in many fields such as medical treatment, medicine, food, cosmetic, health care and machines. For example, they have been applied as contrast media for ultrasound diagnosis, media of targeted drug delivery, bubble washing for beauty treatment, homogeneous cream for improvement of taste, micro pore material for creation of new materials, a power source for micro machines and reduction of drag force around submerged objects in water. For these applications, size control and stability of bubbles are required [1].

Generally, bubbles grow in supersaturated liquid and shrink in unsaturated liquid due to diffusion through the bubble interface. It is known that nanobubbles of 100 nm in radius disappear within micro second, the disappearance time becoming shorter with smaller bubbles. However, it has been reported that nanobubbles in water exist for several hours, the plausible mechanism of the reduction of the surface tension being due to the existence of nano particles, OH ions and surface-active agents. This reduction of surface tension causes reduction of internal pressure of nanobubbles, leading to long lifetime. In the field of a lot of researches on interfacial water, the existence and lifetime of nanobubbles are still under discussion [2].
Regarding interfacial phenomena of microbubbles, it has also been reported that the interface of the microbubbles have a positive in the case of a pH less than 3 though they have a negative in the case of a pH greater than 3 [3]. The nanobubbles become stable in a high pH solution but unstable in a saline solution with a high concentration. It is considered that the negative charge prevents aggregation and combination of nanobubbles and that nanobubbles become more stable which leads to a longer lifetime.

Methods using electrolysis, a supersonic wave [4], and pore materials [5] have been reported to produce nanobubbles in solution in large quantities. In the case of electrolysis, the size of nanobubbles is influenced by the concentration of the solution, pH, polarity and potential of the electrode. It decreases with an increase of the current density and flow velocity around the electrode. In the case of ultrasonic waves, the size increases with the increase of the power of the ultrasonic waves and with the concentration of the solution, and decreases with the addition of a surface-active agent and an increase in the length of its chain. In the case of porous materials, the size of nanobubbles is influenced by the pore sizes and hydrophilicity of the material surface. However, these methods require electrolyte solutions to achieve longer lifetime and the nanobubbles in pure water disappear in a short time.

We herein have proposed a new method of nanobubble formation using plasma to achieve greater stability in pure water without any electrolyte solution. The formation processes and visualization methods of “plasma nanobubbles” were investigated to develop a new method of nanobubble formation and to understand the physical features of nanobubbles.

4. Experimental methods

4.1. Experimental setup

Figure 1 shows the experimental setup. Plasma was generated at a tip of a platinum wire electrode of 0.3 mm, which, except for the end force of the electrode, was covered with silicone. A ring-shaped grounded platinum wire electrode was installed at the bottom of ultrapure water. The water was exposed to air for 40 min, leading to electrical conductivity of 2.5 MΩ·cm. Applied voltage was -5.5 kV at maximum and -3.5 kV at minimum with a frequency of 10 kHz.

4.2. Measurement methods

Underwater plasma generates streamer discharges known as pre-breakdown phenomena, and gas channels are formed along the streamer discharges due to Joule heating. The process of the formation and collapse of the gas channels was visualized with a high-speed camera (Nac Image Technology, MEMRECAM). Nanobubbles in a droplet of several mm in diameter on a clean glass plate were visualized by a digital microscope (Keyence, VX-9700). The digital microscope was capable of magnifying images up to 5000 times with a working distance of 4 mm. Visualization was performed in a clean bench to avoid contamination.

Fig. 1 Experimental setup and photograph of the plasma emission.
Size distributions of nanobubbles were analyzed by dynamic light scattering devices (Otsuka Electronic, DLS-6500 and Sympatec, NANOFOX). To analyze substances in plasma-generated water, a scanning electron microscope (SEM) and a transmission electron microscope (TEM) were used for visualization, and X-ray analysis and ICP-MS were used for analysis of the elements.

5. Results and discussion

5.1. Visualization of plasma-generated gas channels

Figure 2 shows the formation and collapse process of gas channels shown as shadows and Fig. 3 shows a magnified snapshot of the gas channels. The gas channels, shaped like fine dendritic coral, were generated by streamer discharges due to Joule heating. These narrow gas channels collapsed while combining with each other at each position. After collapse, small bubbles were generated and remained. These results imply that plasma in water is capable of generating fine bubbles.

Fig. 2 Formation process of gas channels by plasma generation at the tip of the electrode. Residual fine bubbles were also observed after collapse of the gas channels. The process is not a series. The scale bar is 1 mm.

Fig. 3 Magnified snapshot of gas channels at the tip of the electrode. Many fine gas channels were generated by streamer discharges. The scale bar is 100 µm.

5.2. Visualization of plasma-generated nanobubbles

Figure 4 shows the plasma-generated nanobubbles (a) and spherical polymer particles of 200 nm in diameter (b) visualized by the optical microscope. The nanobubbles were observed along the edge of the droplet. This could be caused by the fact that most nanobubbles were located in the focal point of the microscope because the depth of the water became shallow near the edge and the limitation of nanobubbles movement by Brownian motion occurred at the edge. The size of nanobubbles was less than several hundred nanometers. Although the outlines of nanobubbles of less than 200 nm were not clear, many such nanobubbles were observed. Here, spherical polymer particles of 200 nm in diameter were visualized using the optical microscope, as shown in Fig. 4 (b). Although their outlines were also not clear, they were observed. These nanobubbles were located along the entire outline of the droplet and were not observed in the ultrapure water without the generation of plasma. Furthermore, these nanobubbles were also observed even after 3 days.
5.3. Size distribution of plasma-generated nanobubbles

Figure 5 shows the size distribution of the plasma-generated nanobubbles. The size was distributed from 50 nm to 400 nm and the peak frequency was around 120 nm. These results mean that nanobubbles of less than 400 nm in diameter can probably be generated by plasma in water [3]. Here, the generated bubbles of greater than micro meter size moved up and were released into air.

6. Conclusion

In this study, a new method of nanobubble formation using plasma in water was developed. “Plasma nanobubbles” of less than 400 nm were visualized and measured experimentally and it was shown that those nanobubbles were quite stable in pure water. It is necessary to verify that these nanobubbles are gas bubbles, not solid, because contamination such as platinum particles and organic compounds from the electrode and residue in ultrapure water were also observed by SEM, TEM and ICP-MS.

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