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RAPID COMMUNICATION

Formation and stability of ultrasonic generated bulk nanobubbles*

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Although various and unique properties of bulk nanobubbles have drawn researchers' attention over the last few years, their formation and stabilization mechanism has remained unsolved. In this paper, we use ultrasonic methods to produce bulk nanobubbles in the pure water and give a comprehensive study on the bulk nanobubbles properties and generation. The ultrasonic wave gives rise to constant oscillation in water where positive and negative pressure appears alternately. With the induced cavitation and presence of dissolved air, the bulk nanobubbles formed. "Nanosight" (which is a special instrument that combines dynamic light scattering with nanoparticle tracking analysis) was used to analyze the track and concentration of nanobubbles. Our results show that in our experiment, sufficient bulk nanobubbles were generated and we have proven they are not contaminations. We also found nanobubbles in the ultrasonic water change in both size and concentration with ultrasonic time.

Keywords: bulk nanobubble, ultrasonic, nanoparticle tracking analysis, dissolved oxygen

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1. Introduction

Bulk nanobubbles have drawn researchers' attention in the last few years. Bulk nanobubbles are spherical gas bubbles with a mean diameter no more than 1000 nanometers. Possibly the earliest direct evidence of bulk nanobubbles with diameters of less than 1 μm was reported by Johnson and Cooke in 1981.[1] Following this work, little was published on bulk nanobubbles until the 1990s, when Bunkin *et al.*[2,3] reported the existence of stable microbubbles in dilute solutions of electrolytes. These microbubbles were thought to be stabilized by repulsive interactions between ions adsorbed to the interface and provide nuclei for optical cavitation. The new millennium brought a burst of publications on bulk nanobubbles.[4–7] However, these experiments are correctly criticized for a lack of direct evidence that the nanoparticles being observed actually consist of gas while the surface nanobubbles are directly imaged via atomic force microscopy (AFM)[8,9] in 2000 and bulk nanobubbles' unique properties such as long-life time and very high pressure inside according to Yong-Laplace equation have led to reports nanobubbles being treated with great caution because no thermodynamic stability is possible in classic theory.[10] Perhaps the most direct evidence that bulk nanobubbles that consist of gas was presented by Kobayashi *et al.*[11] in 2014. Bunkin *et al.* used a modulation interference microscope to image nanobubbles in sodium chloride solutions.[12] In summary, evidence that bulk nanobubbles are indeed gas-filled comes from a wide range of experiments.

Despite the limited amount of research into bulk nanobubbles, bulk nanobubbles have already been shown to have potential in many applications, including oxygenation using nanobubbles is also being applied to the bioremediation of groundwater pollution and water treatment.[13,14] Nanobubbles are currently being assessed for application to mineral separations using froth flotation.[15] Another possible application is in depletion flocculation for the dewatering of mineral tailings.[16] Bulk nanobubbles have been demonstrated to effectively clean proteins from surfaces.[17] The absence of added surfactants means that chemical residues are not an issue and that the cleaning process is likely to be more environmentally friendly. Nanosized bubbles are preferred in some applications because they can be used to target the capillaries outside the pulmonary bed.[18] Nanobubbles or related entities have also been implicated in oxygenated medical saline for the treatment of asthma and other autoimmune diseases with remarkable efficacy.[19–22]

From the experimental perspective, nanobubbles generation methods include ethanol–Water exchange (E–

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W exchange),[9,23,24] direct immersion,[8] temperature change,[25,26] electrochemical reactions,[27] cold water adding,[28] and so on. However, these methods mostly generate surface nanobubbles and, to some extent, are very complicated and costly to operate or might bring in contaminations. A method to produce sufficient bulk nanobubble still remains to be discovered and the ultrasound method could be theoretically possible.

In this work, we focus on the unique cavitation property of ultrasonic wave in a liquid solution. Ultrasonic waves consist of a series of horizontal and vertical mechanical waves which spread evenly in the liquid solution. The molecules in the solution constantly oscillate in solution where positive and negative pressure appears alternately, when wave density reaches a point higher than the cavitation threshold, under the negative ultrasonic wave pressure, a cavitation nucleus forms between liquid molecules then dilate or shrink with the change of ultrasonic wave.[29–31] The pioneering research about ultrasound-induced bubbles can be traced back to 1962, which concluded that high-energy neutrons could contribute to bulk water cavitation caused by ultrasound.[32] Scientists in 2000 and 2005 reported the generation of bulk nanoparticles by sonication (42 kHz, 70 W) in the presence of a palladium-coated surface in different solution,[4,33] although in these studies nanobubbles might be attached to palladium-coated electrode forming surface nanobubbles. The ultrasound mechanism is indeed feasible to generate nanobubbles. In addition, ultrasound is a very mature technique and relatively simple to control the parameter, which means under certain conditions, we can produce sufficient bulk nanobubbles for measurement.

In this paper, we introduce a method to use cavitation induced by an ultrasonic wave to produce bulk nanobubbles and give a comprehensive study on this method. First, we demonstrated that the nanoparticles that we generated and measured are indeed bulk nanobubbles. By comparing the concentration of nanobubbles before and after degassing and decrease of dissolved oxygen, we confirm our assumption is correct. Then, we studied further into this phenomenon to measure the nanobubbles' change in the bulk solution. We found nanobubbles first reached a maximum value then decreased in amount but increased in size, where nanobubbles are distributed approximately even in the bulk solution. Finally, we explained the mechanism of bulk nanobubble generation with ultrasonic methods. Consequently, we look forward to seeing if our method could have broad application in various fields.

2. Experimental section

2.1. Materials

Deionized pure water (room temperature) was prepared with an ELGA PURELAB Classic water purification system to obtain a conductivity of 18.2 Ω·cm. To eliminate the influence of pollutants, the glass container and syringes used in the experiment were immersed in chromic acid for 12 hours to remove possible organics, they were then flushed by ultrasound and dried at 150 °C in the vacuum chamber (keelrein Instrument Co., Ltd) before use. The ultrasonic generator and its accessory equipment (SB-5200 DTDN) was purchased from Ningbo Scientz Biotechnology Co. Ltd. The deeply degassed water was prepared by putting deionized water in a clean sealed glass container for 72 hours under 0.1 atm.

2.2. Nanobubbles produced by the ultrasonic method

The basic principle of nanobubble generation methods is to create a locally oversaturated state for gas to induce the nucleation of gas molecules for the next formation of nanobubbles.[34] There is one important factor, gas saturation.[35] The saturated concentration of gas in water is related to the pressure and a high gas concentration may not be necessary. According to Henry's law $P_g = HC$, in which P_g is the partial pressure of gas, H is Henry's law constant, and C is the gas solubility, when the gas pressure (P_g) decreases to a certain degree, the gas unsaturated aqueous solution at normal temperature and pressure would turn into a gas oversaturated state, and extra gas molecules might be released and aggregate into bubbles. While our method concentrating on the nucleation: ultrasonic cavitation. When the ultrasonic wave contains higher intensity than the "cavitation threshold", tiny nuclei form internally, with their diverse behaviors in the opposite/negative pressure zone, the nuclei shrink or dilate, and if the nuclei dilate to a certain magnitude, then the gas molecules dissolved in the solution transfer into a nucleus to grow up to a nanobubble.

Based on these principles, we put a glass container (diameter 75 mm, height of water 80 mm) in the ultrasonic water which was covered by a porous membrane to separate contamination from the air but maintain the normal pressure, the container was vibrated under the ultrasonic wave at a frequency of 40 kHz and the 300 W power of the generator. The temperature is set to 25 °C.

2.3. Nanoparticle tracking analysis

Nanoparticle tracking analysis (NTA) (NS300, Malvern instrument) was used with a blue laser light source (65 mW, $\lambda = 405$ nm) to measure the size and concentration of nanobubbles. It was equipped with a 20-magnification microscope and a high-speed camera. When the laser light struck on the particle, scattering faculae formed. The track of scattering faculae was recorded by the high-speed camera. Each result was gathered from the average of five measurements, and the movie was last for 60 seconds, captured at 25 frame/s. The camera level was usually set at 10, the threshold was set at 3 and the solution viscosity was 1 CP. Optical field of view was fixed (approximately 100 μm by 80 μm) and the depth

of the illuminating beam was approximately 10 μm. Here, the size of individual particle (nanobubble) could be calculated with its diffusion from Brownian motion. The number of particles (nanobubbles) was counted by NTA, thus the particle (nanobubble) concentration could be obtained by dividing the volume of the field of view. Every experiment was repeated five times independently. Considering the positions to take the water solution in the bottle might influence the results, we take samples in a different position in the solution and found no obvious distinction. This part will be discussed in more detail later on.

2.4. Dissolved oxygen measurement

The dissolved oxygen measurement device includes Versa Star Pro meter (VSTAR91, Thermo Fisher Scientific) and Dissolved Oxygen Probes (083010MD, Thermo Fisher Scientific). Before measurement, we unscrew the membrane cap from the probe and fill the membrane cap about 3/4 full with new electrolyte solution. We then assemble the probe into the meter and press the f1 key to perform the DO calibration. After a successful calibration, our samples can be tested.

We rinse the DO probe with deionized water, blot dry with lint-free tissue. We then place the DO probe and optional stirrer in the sample, press measure key to perform AutoRead mode, the reading will automatically be stored when the "AR" appears. We repeat the experiment three times, noticing that the sample must be immediately measured once ultrasonic ends or it may cause errors to the experimental results.

3. Results and discussion

3.1. The formation of nanobubbles produced by the ultrasonic method

First, we used NTA to measure the formed nanobubbles and obtained the concentration and size distribution. Figure 1(a) shows a typical snapshot of produced nanoparticles measured by NTA after 1 min ultrasonic. Some white spots can be seen in the image which means that the same nanoparticles were formed. It should be noted that those white spots were not real nanoparticles.

To prove formed "nanoparticles" are gas nanobubbles, we compared three systems: pure water, the water after 1 min ultrasonic and then degassed water. The concentrations of "nanoparticles" measured by NTA in those systems are presented in Fig. 1(b). The results show that the concentration of formed "nanoparticles" would increase considerably after ultrasonic disposal compared with the pure water system. However, it will decrease quickly if degassing the ultrasonic water. Those results indicated that the formed "nanoparticles" are gas nanobubbles. There are also some bulk nanobubbles in pure water without ultrasonic as compared to the concentration of nanobubbles in pure water and degassing system.

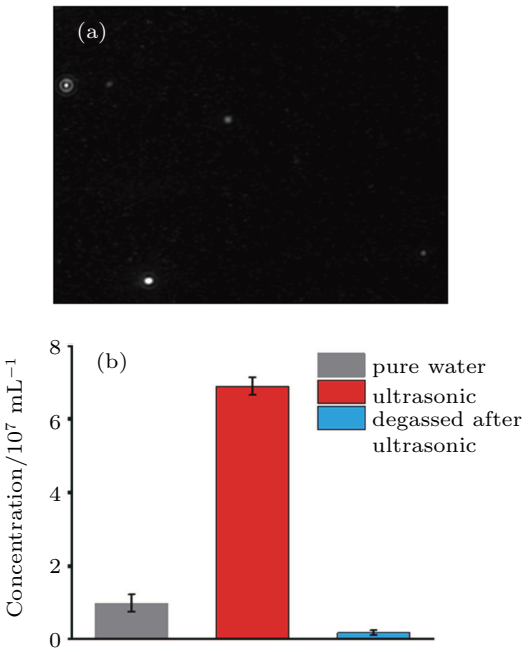


Fig. 1. (color online) (a) A typical snapshot of produced nanoparticles measured by measurement by NTA after 1 min ultrasonic (40 kHz, 25 °C); (b) concentrations of generated nanobubbles in pure water, after 1 min ultrasonic and degassed after ultrasonic (40 kHz, 25 °C).

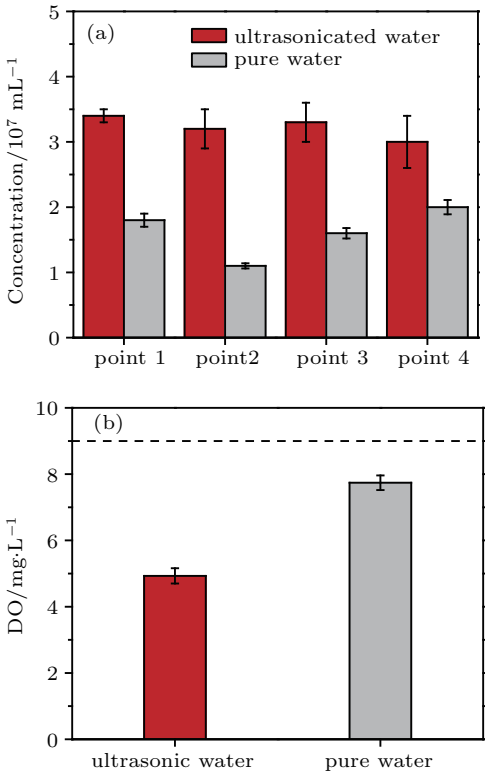


Fig. 2. (color online) (a) Concentration of nanobubbles obtained at 4 different collecting points in pure water before and after ultrasonic 5 minutes ultrasonic (40 kHz, 25 °C). (b) Dissolved oxygen in pure water before and after ultrasonic 5 minutes (dotted line means standard DO value in saturated oxygen dissolved pure water under 25 °C, 1 atm atmosphere).

We further explore whether bulk nanobubbles exist in all regions of the water uniformly after ultrasonic. Therefore, we collected four samples using glass syringes randomly in the glass container after ultrasonic 5 min. The pure water collected in the 4 positions before ultrasonic was studied as a

control. As shown in Fig. 2(a), the concentration of formed nanobubbles are nearly equal at four different places after ultrasonic but higher than the control pure water system. At the same time, we also measured the concentration of dissolved oxygen in pure water before and after ultrasonic (see Fig. 2(b)). More interestingly, the DO value obtained in ultrasonic water is lower than that in pure water. These results prove that bulk nanobubbles may from the dissolved air and stable in the undersaturated gas state once they formed.

3.2. Dependence of produced nanobubbles on the ultrasonic time

We further study the influence of ultrasonic time on the formation of nanobubbles. We changed different ultrasonic time, such as 0.5 min, 1 min, 2 min, 3 min, 5 min, 10 min, and compared the sizes and concentration of formed bulk nanobubbles. At the same time, the pure water was as the control and set as 0 min. Each sample was measured repeatedly five times by NTA. The typical results were shown in Fig. 3. From Fig. 3(a), it can be found that the nanobubbles concentration in the bulk solution firstly increase and reach a maximum at approximately 1 min and then decrease gradually. The average diameter of formed nanobubbles slightly increases with the increased ultrasonic time as shown in Fig. 3(b), which corresponds to the decrease in the concentration of nanobubbles. The size distributions of nanobubbles at 0 min, 1 min, 3 min, and 10 min were shown in Fig. 3(c). All the sizes of bulk nanobubbles were below 300 nm. At 1 min, the 100 nm nanobubbles reach maximum and then decreased with the ultrasonic time. Comparing with the pure water system, it can be seen that the concentration of formed nanobubbles in pure water without ultrasonic was lower than that of after ultrasonic. The average diameters of bulk nanobubbles in pure water were in the range from 100 nm to 200 nm, and had no large difference with the systems after ultrasonic.

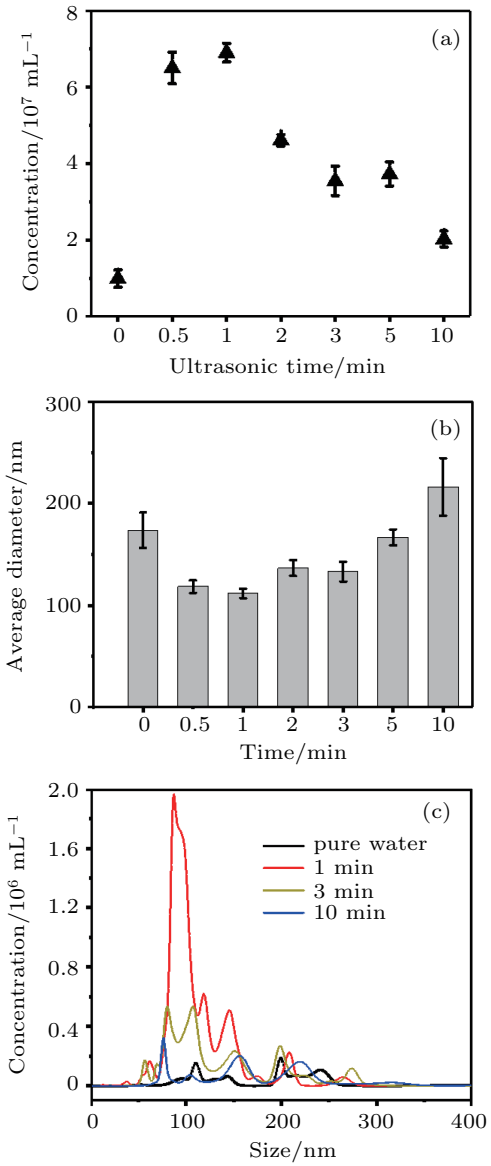


Fig. 3. (color online) (a) Statistics of the nanobubbles' average diameters with different ultrasonic time in the ultrasonic water. (b) The nanobubbles concentration with different ultrasonic time in the ultrasonic water. (c) The detailed size distribution with different ultrasonic time in the ultrasonic water.

These results might be explained in Fig. 4. The dissolved gases first form tiny bubbles during the ultrasonic by receiving the oscillation energy, causing the lower concentration of dissolved oxygen. Then with the ultrasonic time, small bubbles may start to coalescence to bigger ones, which decrease the concentration of the bulk nanobubbles. The possible mechanism of bulk nanobubbles still remains to be discovered and we think they may stabilize by the charge of bulk nanobubbles or special properties, such as high interior density.[36]

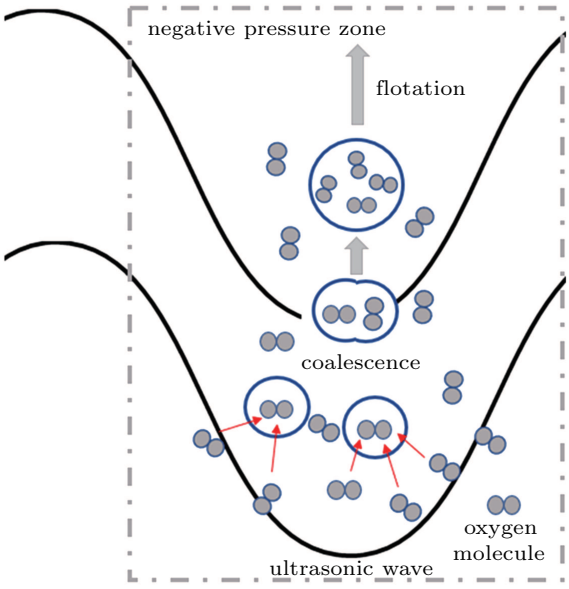


Fig. 4. (color online) Mechanism of bulk nanobubbles generation by ultrasonic method.

The results obtained are significant because, among all the nanobubbles' applications, if we can produce nanobubbles using a method that causes little damage on our body and cells,

then it would be very helpful in medical applications. Appropriate ultrasound suits this need perfectly, while the effectiveness and simplification of ultrasound is highly noticeable. We can assume that by using ultrasound to produce nanobubbles of proper amount and size by controlling the power, time, and so on. we will be able to study further into nanobubble's applications in various important fields.

4. Conclusion

In our experiment, we produce bulk nanobubble by direct ultrasonic methods and we then study their properties and generation mechanism using DLS with NTA and a DO measurement device. Summarizing our results and comparing concentration before and after degassing, we prove that most of the nanoparticles that are generated are indeed bulk nanobubbles. Based on this and the nanobubbles' even distribution in a bulk solution, we found that during ultrasonic oscillation, in the bulk solution, as ultrasonic time increases, the bulk nanobubbles first reach a maximum concentration and then gradually decrease while their sizes increase. Our results would be very helpful to generate bulk nanobubbles for further studies on nanobubbles' properties and applications. They may also be a helpful evidence that indicates the existence of bulk nanobubbles. Furthermore, the ultrasonic method has proven to be a mature technique in many fields. Therefore, we can expect broader applications of nanobubbles using the ultrasonic method.

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