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Generation and Characterization of Nanobubbles

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ABSTRACT

Many researchers have focused their research on nanobubbles due to their mysterious properties and potential applications. Nanobubbles are formed from two parts: an inner core (central gas) and an outer layer (stabilizing shells), each with its own physical and chemical properties. The core is a low-density compartment and constitutes the main part of the volume of a nanobubble. The shell, which is mostly composed of surfactants, polymers or proteins, forms a protective layer around the core and prevents gas diffusion. The efficient production of nanobubbles and the determination of their gaseous nature with existing methods are still challenging. So far, various methods such as hydrodynamic/acoustic cavitation, ceramic membrane filtration, depressurization of saturated solution, Solvent exchange, and electrochemical method have been used to produce nanobubbles. Different techniques such as nanoparticle tracking analysis, light scattering methods, electron microscopy, atomic force microscopy, resonance mass measurement, and spectroscopy techniques are employed to confirm nanobubbles formation. This review focuses on the production methods of nanobubbles as well as their characterization techniques.

INTRODUCTION

Nanobubbles are tiny pores (between tens and hundreds of nanometers) filled with gas, which have attracted the attention of scientists in the last two decades due to their extraordinary physicochemical properties such as large surface area to volume ratio, high internal pressure, rapid adhesion on hydrophobic surfaces and long-term stability, and their potential applications in fields such as biomedicine, environment, agriculture and energy systems have been studied [1-3].

Based on their morphology and location, nanobubbles are surface nanobubbles that form at the solid-liquid interface or bulk nanobubbles, which are nanoscopic gas spheres that form stable colloids in supersaturated solutions. Surface nanobubbles are cap-shaped structures formed at the interface between water and hydrophobic solids. These nanobubbles have been observed on various substrates, and various theoretical models have investigated their unusual stability. Based on available evidence, bulk nanobubbles suspended in water are actually filled with gas. Despite recent studies, some researchers speculate about the existence and stability of bulk nanobubbles. The Epstein-Plesset theory in 1950 investigated the lifetime of a single bubble as a function of bubble radius and saturation. Researchers have reported that bulk nanobubbles can be stable for days, weeks, and months. The long-term stability of bulky nanobubbles can be attributed to the small buoyancy force and the prevention of bulky nanobubbles from rising to the free surface, their Brownian motion, and their stability against dissolution [4-10].

Nanobubbles consist of two components: an inner core or central gas and an outer layer or stabilizing shells, each with its own characteristics. The core, as a low-density compartment, constitutes the main part of the volume of a nanobubble. A variety of applications of nanobubbles can be achieved by changing the gas inside the core. The shell, acting as a protective layer around the gas, prevents the gas from diffusing into the aqueous environment. The shell is mostly made of surfactants, polymers or proteins, and its material plays an important role in the rigidity of the bubbles and their resistance to rupture [11].

To date a number of different physical and chemical methods have been employed to generate bulk nanobubbles such as high-shear rotor-stator devices operating in batch or continuous mode, chemical reaction, microfluidics, water-solvent mixing, hydrodynamic cavitation, ultrasonic oscillation, nano-membranes, pressure induced supersaturation, and periodic pressure change method. Also, there are various methods to produced surface nanobubbles including ethanol–Water exchange temperature change electrochemical reactions, direct immersion, and cold water adding. Despite many studies, there is still a need to find new and efficient methods of producing nanobubbles so that they can be

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used in various industrial applications. Ideal production methods should be clean, cheap, controllable and able to produce nanobubbles at high concentrations and on large scales [2,6-9].

To date, many researchers have investigated various properties of nanobubbles such as hydraulic diameter, size and concentration distribution, size, shape, stability, and surface charge properties [12-14]. The methods used for nanobubble characterization mainly include image analysis [15], acoustic methods [16-19], electrical impedance [20,21], optical methods such as high-speed photography [22-23], nanoparticle tracking analysis (NTA) [24-26], dynamic light scattering (DLS) [27,28], laser particle size analyzer (LPSA) [29-31], zeta sizer [32-33], as well as direct measurement with optical microscopy and indirect measurement by inverse estimation of dissolved oxygen (DO) [34], laser pulse methods [35], X-ray techniques [36], fluid dynamics methods [37], image analysis [38], optical microscopy methods and photography [39]. The development of characterization methods with chemical sensitivity and high resolution is essential for better identification of nanobubbles.

Considering the potential application of nanobubbles in various scientific, industrial, environmental and agricultural fields, it is necessary to review recent advances in their production methods and detection methods. The purpose of this article is to provide a summary of scientific research conducted on various methods of production and characterization of nanobubbles.

Generation Methods of Nanobubbles

The generation of NBs is a complex physicochemical process that depends significantly on different parameters. Two pathways could be involved in the basic principles of NBs generation in solutions. The first pathway is the emergence of gas bubble phase as a new thermodynamic phase from the liquid phase that is normally at a metastable state. This method starts from a process called nucleation. Based on the classical nucleation theory, the rate of nucleation, R is obtained from the Gibbs free energy cost ΔG of generating the new phase in an exponential relationship as equation (1):

$$\sim \exp\left(-\frac{\Delta G}{k_B T}\right) \quad (1)$$

Here k_B and T are the Boltzmann constant and the temperature, respectively. In the homogeneous nucleation, ΔG of creating a spherical bubble nucleus in a gas oversaturated solution can be described as:

$$\Delta G = \frac{4}{3}\pi R^3 \Delta G_{lg} + 4\pi R^2 \gamma \quad (2)$$

where r and g are the nucleus radius and the surface tension of gas/liquid interface, respectively. ΔG_{lg} presents the difference of Gibbs free energy between the bulk liquid and the gas nuclei per unit volume at the same pressure. Since nucleation process normally takes place in a supersaturated condition, ΔG_{lg} is always negative. Clearly, the surface free energy term of $4\pi R^2\gamma$ dominates the bulk free energy term with R^3 in the case of a small radius r. This can cause a positive ΔG and generating an energy barrier for the bubble nucleus to grow homogeneously. Therefore, homogeneous nucleation rarely occurs and is very slow. Thus, the bubble generation in solution is greatly a heterogeneous nucleation process. Some impurities or a certain surface are often needed to decrease the surface area of nuclei far below $4\pi R^2$, and therefore, lower the surface free energy term within Gibbs free energy cost, and in turn, the heterogeneous nucleation is more probably, and the nucleation takes place much faster. In fact, the main physiochemical principle for formation of BNBs is the heterogeneous growth of bubble nuclei in a gas oversaturated liquid. Another pathway for production of nanobubbles includes the collapse or shrinkage of microbubbles, where the exact mechanism for formation of nanobubbles is not clear and still remains controversial. Spherical bubbles in liquids are not stable, and they will finally collapse by a process of either expansion or removal through buoyancy or shrinkage. The famous Rayleigh-Plesset equation perfectly describe the dynamics of bubbles, except the final stage of bubble collapse which called implosion and leads to very high temperature and pressure inside the bubble. When cavitation bubbles implode, light emission can be observed. The 'sound to light' phenomenon is called sonoluminescence and has been investigated since the 90s. During the bubble collapse process, there is another pathway for bubbles to shrink into NBs and stabilize them. This idea has recently been investigated by considering the radius-dependent surface tension on the highly curved gas/liquid surface of NBs, which implies the mechanical and thermodynamic stability of spherical NBs in water. The surface tension and the diffusion condition at the bubble interface can be changed by the hydrophobic impurities attached to the gas/liquid interface. This suggests another possibility to obtain stable BNBs from the microbubbles. The mechanism of microbubbles shrinking to stable NBs has not yet been well described, and disagreements about this hypothesis still exist. To date, many methods have been suggested to generate NBs. In this section, the reported methods of BNB creation in recent years are summarized and categorized into different branches based on their specific principles or mechanisms. The main techniques for production of nanobubbles include cavitation, ceramic membrane filtration, depressurization of saturated solution, gas-water circulation, electrochemical techniques, solvent exchange and application of electric/magnetic field [2,40].

Nanobubbles Generation by Cavitation

Thornycroft and Barnaby introduced the term cavitation in 1895, but the first investigation of cavitation was carried out in the 1710s [41]. Nucleation or formation of cavities is the first stage of cavitation. In nucleation process, the structure of liquid is ruptured for formation of a hole using external forces. Furthermore, rupture starts at a weak location where the intermolecular forces approach zero [42-43]. In fact, when rapid variations in pressure in a liquid occur in places with relatively low pressure, vapor-filled cavities are formed. This phenomenon is known as cavitation [2,44-46]. Nanobubbles can be frequently generated in solutions by creating cavities. Cavitation

mechanisms are caused by pressure reduction below the certain critical value. Based on the pressure reduction mechanism, cavitation can be classified into four categories [8,11,47-49] namely hydrodynamic, acoustic, optical and particle cavitation.

Hydrodynamic cavitation is one of the most critical techniques to generate NBs. During hydrodynamic cavitation creation and growth of gas bubbles in a liquid occurs due to the rupture of either a liquid–solid or a liquid–liquid interface by external forces [2]. Hydrodynamic cavitation is associated with variation in the pressure of liquid flux due to system geometry [8]. Indeed, hydrodynamic cavitation leads to vaporization and bubble formation as a result of variations in geometry of system because of the changes in pressure in a flowing fluid, like in a Venturi-type circulation. mechanical agitation, depressurized flow constriction and axial flow shearing can cause hydrodynamic cavitation as was developed by Favvas et al. in 2021 [50,51].

When the liquid passes through a constriction such as throttle valve, orifice, etc., the kinetic energy and consequently the speed of the liquid increases, leading to reduction of the pressure. If the throttling pressure falls below the vapor pressure of the medium at the operating temperature (cavitation threshold pressure), then millions of cavities can be created. This is known as hydraulic cavitation and well-described describes by Bernoulli's equation [52].

$$P+\frac{1}{2}\rho U^2 = C \qquad (3)$$

where P, ρ, and U are the pressure, the liquid density, and the water flow velocity at a point where the pressure is P, respectively, and C is a constant value.

If $U>\sqrt{\frac{2C}{\rho}}$, the pressure will be negative and this is the threshold for starting the cavitation phenomenon [11]. Cavitation process is influenced by different factors including operational conditions, geometric parameters, reagent concentrates, dissolved gas content, and the addition of solids. A venturi tube is usually used as a hydrodynamic cavitation device which helps for the NBs generation during hydrodynamic cavitation, and affect on the fluid flow by its rough/fractal surface characteristics and also can transform the system from a liquid/gas mixture to a colloidal phase. The liquid in the cylindrical throat has higher flow velocity and lower pressure than the liquid in the entrance cylinder, leading to cavitation. So far, various designs of cavitation tube have emerged and are commercially available for laboratory research works, commercial flotation operations, and flotation machines [2,11].

During the formation of nanobubbles using hydrodynamic cavitation, the aqueous solution becomes milky due to the existence of a large number of microbubbles. Shortly after cavitation stops, the solution turns clear again because bubbles rise buoyantly and burst at the top of the liquid [50]. A critical time for the system to reach equilibrium status has been suggested to be 30 min by Michailidi et al. [53]. The optimum processing time depends on the geometrical characteristics of the generator, such as the size of the orifices, the surface roughness, the effective surface area, the counter flow length, and the applied feed fluid pressure. This method for NBs generation has some advantages such as low pump power, generation of NBs with high-density and mean diameter smaller than 100 μm, and compact size. NBW generated with this method has been widely applied for mineral processing and wastewater treatment, because of its energy-efficient and economical [11].

Nanobubbles are usually hydrodynamically created using two techniques. One method includes dissolving gases in liquids by compressing gas flows in liquids, and then releasing those mixtures through nanosized nozzles to generate nanobubbles. In another method by injection of low pressure gases into liquids, gas breaks into bubbles by focusing, fluid oscillation, or mechanical vibration [8].

It is possible to create low pressure by ultrasonic waves passing the liquid, which known as acoustic cavitation and causes changes in local pressure and the consequent creation of bubbles [8,11,50]. Like hydrodynamic cavitation, acoustic cavitation involves the generation, expansion, growth, and adiabatic collapse of microscopic cavities or microbubbles. While it has been assumed that microbubbles always collapse and disappear, now we presume that the disappearance of those microbubbles leads to the formation of nanobubbles which went undetected before. However, another possibility is that such nanobubbles are created directly via cavitation [4]. Acoustic cavitation is relatively simple and applicable in large liquid samples [2]. In this method, the amount of dissolved gas has a significant influence on the number of produced nano-entities [11].

Ultrasound generators are compact, contamination-free, simple in operation, and have a short generation time. Another advantage of this method is that the number of bubbles can be controlled by tuning the ultrasonic frequency and power. Leroy and Norisuye [54] noticed that ultrasound is an ideal tool for studying the existence of bulk NBs for several reasons including its sensitivity to minute quantities of gas; determination the size distribution of bubble; and (iii) its unambiguous discrimination between gaseous and solid/liquid inclusions. Nevertheless, analyzing literature data show that there is not generally unified statement regarding the generation of NBs using acoustic cavitation. Such contradiction could be related to the utilization of different experimental apparatus, various experimental parameters, and different aims of the experimental setups. Chen et al. [55] classified the ultrasonically created bubbles based on the ultrasonication time and frequency, into different zones including low (20–50 kHz), medium (200–1000 kHz), and high (>1 MHz). They have reported that because of the transient cavitation effect, the NBs are unstable at low frequencies, while the medium range of frequency was chosen as the best range for acoustic-assisted flotation processes regarding the creation of stable NBs. They have found that power ultrasound (20–100 kHz) penetrates into the liquid and generates acoustic cavitation bubbles [56]. The pressure sharply reduces below the saturated vapor pressure and causes greatly dissolving of air and its conversion to bubbles. Miastkowska et al. [57] showed

that ultrasound's frequency, time, and power significantly impact the size of bubbles that generated acoustically [2].

Optical cavitation can create bubbles by passing a high-intensity light beam such as short-pulsed lasers focused into low absorption coefficient solutions. Particles such as protons, neutrinos, and high intensity light photons with high speed that pass through the liquid can also generate cavitation to creat bubbles. Obviously, only very few reports are available for this method so far because of their high energy consumption and technical limitations that is not conducive for practical application [8,11].

NBs generation by Ceramic Membrane Filtration

Bulk nanobubbles can be generated by forcing gas through a porous medium, such as a membrane, into a flowing liquid. It has been reported that it is possible to produce NBs using ceramic membranes with uniform nanopores. The NBW generation system is composed of a ceramic tubular filter, a pressurized gas cylinder, a gas flow meter and a gas pressure regulator. This generator can create NBs smaller than 100 nm when the pore size of the ceramic tube is 100 nm. This system allows to control the bubble size and uniformity. This method has several advantages including: (1) generation of NBs with strong resistance to corrosive chemicals, and extending the application of NBs to concentrated acids and high-pressure environments; (2) creation of NBs independent from liquid circulation, greatly decreasing the volume, operation cost and space requirement. However, there are some disadvantages for this method like its longer time and about 90 min continuous injection to generate NBs and reach their stabilization than other techniques [11,50].

NBs generation by Depressurization of Saturated Solution

Calgaroto et al. proposed that the depressurized air-saturated solution could form NBs through a needle valve [58]. NBs can be created simultaneously by gas mass transfer from the liquid to gas phases. In this method, the air-saturated water solution is decompressed at a high flow velocity into an empty column through a needle valve with NBW formed. Based on the Henry's Law, the amount of gas used to form gas nucleus depends on the saturation pressure. Thus, the low air/water interfacial tension helps to increase the concentration of NBs, and it is possible to maintain the high concentration NBs in NBW for at least two weeks. One of the advantages of generation of NBs with this method is high stability and longevity of NBs. Therefore, this technique can be successfully applied for heavy metals removal and mineral flotation [11].

NBs generation by gas-water circulation

This technique combines pressurized mechanical cyclic and spiral liquid flow (gas-water circulation) for creation of NBW. The process of NBW generation generally takes 20 min with a consumption of 1 L gas. After injection of some specific gas together with the liquid into the cylinder, normal bubbles broken down into NBs because of the created strong shear force. The freshly formed NBW is similar to a milky white liquid, owing to the existence of large number of visible microbubbles, which is relatively stable and very clear for 5–10 min after generation [11].

NBs generation by Electrochemical Method

An alternative method to produce NBs is electrolysis of water. Using this method, nanobubbles are formed through electrochemical processes on electrodes. In fact, gas bubbles initially produce on the surface of electrode and then develop until they finally separate and float [50]. In fact, if a direct electric current passes through an electrolyte solution, a reduction reaction occurrs at the cathode which leads to the release of H_2 gas molecules. Similarly, O_2 gas molecules form by oxidation of the hydroxyl group, OH^-. This technique seems to be a good candidate for generation of microbubbles and nanobubbles. In fact, both bulk and surface nanobubbles35 of hydrogen and oxygen gas can be produced by water electrolysis in an electrochemical cell [9]. In this method, oxygen and hydrogen bubbles form at the hydrophobic surface–water interface with producing oxygen and hydrogen gases at the surface which plays as a negative electrode. It is possible to control the formation, growth, and size of NBs by tuning the experimental parameters such as applied voltage and reaction time. It has been reported that the number of hydrogen bubbles generated was substantially larger than the oxygen ones, because the solubility of oxygen in water is almost two times the hydrogen solubility during the electrolysis process. Furthermore, oxygen bubbles are more stable than air bubbles [2].

The electrochemical nucleation of bubbles on the surfaces of solid nano-electrode has been studied by some researchers [59,60]. According to the reports, the reduction of protons in acidic solutions [59] and oxidation of N_2H_4 [60] and H_2O_2 [61] forms hydrogen, nitrogen, and oxygen gases. Based on the findings of another work, bulk nitrogen NBs with diameters of 200–300 nm can be generated by the chemical reaction between sodium nitrite and ammonium chloride [62]. The results of this study show these bubbles can form only if they are trapped between two carbon films [2]. These reports have not addressed the fundamental and operational aspects of the electrolysis process for production of BNB and are limited in both number and scope. Therefore, to optimize the number concentration and size of the nanobubbles it is necessary to systematically study the different parameters such as strength of electric field, ionic strength and type of electrode surface [9].

Solvent exchange

It has been reported some more methods for nanobubble generation in the literature. One of the practical, efficient, and easiest methods to generate ultrafine bubbles is solvent exchange, which applies an exchange of two solutions with different gas solubility such as ethanol and water. This method produce nanobubbles by replacing a gas/ oil-saturated solution such as ethanol with a poor solvent such as water, which provides the required condition of oversaturation for nucleation. In fact, mixing of solvents such as water and ethanol equilibrated with atmospheric gases causes the supersaturation of dissolved gases which

are less soluble in the mixture than in the individual components. This can leads to the nucleation of bulk nanobubbles [2,4]. Solvent exchange method which usually uses to create NBs on a laboratory scale includes a few steps. At first, a hydrophobic material must be in contact with water. Then, ethanol replaces water, and NBs are generated and cover the surface of substance. In this method, organic solvents such as ethanol, methanol, and 2-propanol can be applied for formation of NBs. Since air has a higher solubility in ethanol than water, the exchange process leads to gas supersaturation, resulting in NB nucleation of NB. In addition, other techniques such as exchanging cold water against hot water and ethanol solution against salt solution have been used to create NBs. According to the findings of some researchers the number of NBs enhances with increasing the concentration of alcohol up to 70%, and above this concentration, the nanobubbles will be disappeared [2].

Application of external electric/magnetic field.

Recently the generation of bulk NBs by applying external magnetic/electric fields has been developed which is quite novel and has not been noticed until recently. Based on this technique, bulk NBs can be formed by circulating deionized water through an alternating and oscillating magnetic/electric field. In this method, the formation of bulk NBs is attributed to the enhanced surface polarization at the gas/water interface caused by the external magnetic/electric field which leads to cavitation at the liquid interface [40,50].

All the above methods are ideal for theoretical laboratory studies. However, very few of these techniques can generate NBs at a high enough rate for industrial applications [50]. One of the very important points of using NBs is related to electrical expenses and energy consumption of their generation methods. Among these aforementioned methods, hydrodynamic cavitation is suggested as the most promising technique for large-scale mineral flotation applications because of its high throughput and simple design [2]. Hydrodynamic or acoustic cavitation are the most popular routs to create nanobubbles on a large scale for engineering applications such as wastewater treatment. Therefore, the investigation for NBs generation methods that are affordable, simple to scale up, have process control, and can produce bulk NBs with high concentrations is ongoing for industrial applications [50].

Characterization of NBs

As we know, the long-term existence of BNBs suspensions contradicts the prediction of short-lived nanobubbles in water by Epstein-Plesset theory. In order to resolve this paradox, it is important to develop reliable detection and characterization techniques for BNBs in liquids. The direct visualization of BNB in liquids by optical microscope is a difficult task because of large transparency of BNBs with the size of several nanometers to hundreds of nanometers in liquids. Another challenge is how we can distinguish the gas NBs in liquid from other colloidal dispersions containing solid nanoparticles such as biological vesicles [40]. The characterization and analysis of nanobubble mainly includes the hydraulic diameter, size distribution and concentration [63]. Furthermore, many researchers have investigated the NB size, shape, stability, surface charge properties, and kinetics [12-14].

To date, different methods have been reported for characterization of nanobubble solution. The analysis techniques such as light scattering and high resolution electron microscopies have poor chemical sensitivity. It is very important and urgent to develop the characterization methods with chemical sensitivity and high spatial resolution for BNBs research. Different test techniques may result in various reported results for the same solution. Based on the studies the size and distribution of NBs depend on the various operational conditions and system design. Furthermore, it is not easy to directly measure the pressure and gas density inside the bulk nanobubbles because of the limitations of existing characterization techniques. Therefore, it is unable to confirm whether the Laplace pressure theory is applicable to nano size bubbles. In the following the techniques applied for characterization of BNBs in solutions will be discussed [2,40,63].

The bubble size is one of the important physical properties that can be measured under different conditions with the gas hold-up and velocity. Several techniques are available to detect the size of bubble, including image analysis [15], acoustical methods [16-19], electrical impedance [20-21], as well as optical methods such as high-speed photography [22-23]. These common methods are not capable to measure the ultrafine bubbles with too-small diameters [34]. In recent years, several methods have been employed to measure the NB size distribution, including nanoparticle tracking analysis (NTA) [24-26], dynamic light scattering (DLS) [27-28], the laser particle-size analyzer (LPSA) [29-31], zeta sizer [32], zeta-phase light scattering (ZPALS) [33], as well as direct measurement by optical microscopy and indirect measurement by dissolved oxygen (DO) reverse estimation [34]. Over recent decades, different bubble size-measurement methods have been developed, including laser pulse methods [35], X-ray techniques [36], fluid dynamics methods [37], image analysis [38], optical microscopic and photographic methods [39]. Although these techniques have been widely applied for analysis and characterization of NBs, they have several disadvantages such as requirement for a low bubble concentration, time-consuming data processes, and a transparent barrier needed for image acquisition [64]. It has been reported that laser diffraction-based technologies, e.g., nanoparticle tracking analysis (NTA), dynamic light scattering (DLS) and laser particle size analyzer (LPSA), are the preferred methods to measure the bubble size [65].

The performances of nanobubbles strongly depends with their size distribution; therefore, it is very important to measure the size distribution of nanobubbles accurately. However, it is necessary to measure not only the wide size range from nm to μm but also the size of bubble in various conditions such as in a very dilute concentration of bubbles to a high concentration of bubbles. Thus, it is need to find

a simple automatic bubble size measurement technique [66].

Atomic Force Microscopy

The size, shape, surface tension, contact angle, and internal pressure within a nanobubble are of interest for both describing nanobubbles and addressing the stability of nanobubble [67]. The most direct evidence for the existence of nanobubbles is provided using atomic force microscopy (AFM). Lou et al. have reported the existence of NBs using AFM in 2000 [68], when the first image of NBs on the hydrophobic solid surface was observed [2]. The size of surface nanobubbles can be detected easily, compared to bulk nanobubbles, mainly using AFM technique. This technique has recently been employed to measure the bubble size on the solid surface. The incomparable 3D resolutions of surface NBs is known as one of the best advantages of this method. In particular, it is possible to extract the contact angle of NBs from the cross-sectional profile of NBs in the AFM image. However, there are several limitations and disadvantages for the AFM technique such as the inevitable perturbation of the sample by the probe. Therefore, the main concern was that the bubbles were not exist on the surface until the surface was perturbed using the AFM probe. After several complementary measurements, it was confirmed that the presence of surface nanobubbles is not the result of the tip perturbation [2,69,70]. Lou et al. [71] reported the presence of nanobubbles at the interface of mica and water by AFM. The AFM images of nanobubbles on the surface of silicon modified by octadecyl trichlorosilane were obtained by Ishida et al. [72] and this images strongly confirmed the existence of nanobubbles [73].

Light Scattering Methods

If we assume that BNBs move in liquids following Brownian motion and do not float quickly, they can be detected using laser scattering-based methods because of the high refractive index contrast between liquids and gas bubbles. It has been suggested that a simple and convenient method to discriminate between BNBs suspensions and clean solutions without any particles or bubbles inside (both are transparent in bare eyes) is using a laser beam to illuminate them. Due to the Tyndall effect, the laser beam can be scattered and viewed with bare eyes in BNBs suspensions while nothing is observable in the clean solution [40].

Light scattering methods are fundamental for nanobubble investigations as well as detection and characterization of colloidal particles. A simple light scattering method that often uses in practical settings for detection and analysis of nanobubbles, is to visually study the light scattered when a water sample illuminate with a common laser pointer [74]. Optical light scattering methods can detect nanobubbles size and concentration [10]. However, these techniques cannot observe a difference between gas bubbles and solid particles or droplets [74]. Measurement techniques based on light scattering such as Nanoparticle Tracking Analysis (NTA) and Dynamic Light Scattering (DLS) are known as the most commonly method for detection and analysis of the size and concentration of nanobubbles in water. Nanobubbles like other nanoparticles present Brownian motion and can scatter light. Both NTA and DLS techniques can measure Brownian motion and relate it to a hydrodynamic diameter equivalent, with the motion of smaller nanobubbles being more exaggerated [50]. The measurement size range is limited in each method [66].

NTA is a technique for the direct and real-time visualization and caracterization of NBs in liquid suspension. This method can measure concentration, fluorescence, zeta potential, size distribution and particle size ranging bout 10 nm to 1 μm in liquid and needs fast computer systems that can cope with the computationally intensive video analyses in suitable time frames. In order to estimate bubble diameters accurately a laser illumination unit and a combination of an ultra-microscope is necessary. There are more detailed information about measurement mechanism in literature [2,63,75-76].

Nanoparticle Tracking Analysis

In NTA, the liquid sample can be viewed in a regular microscope while illuminated at about 90^{o} angle to the line of view. Dispersed particles are viewed and recorded using a video as bright dots against a black background. The Brownian motion of each particle analyzes to determine their hydrodynamic size. Since a nanoparticle is tracked individually, a more detailed size distribution can be obtained in comparison with DLS method. NTA method captures the movement of each scattering object in the solution with a dark field microscopy and characterizes their trajectories to deprive their sizes respectively based on Stokese-Einstein relationship of Brownian motion. In this technique a CCD camera tracks the motion of each particle in the detection box in the x and y directions in a certain period of time after the particles scatter the laser light. According to the equation of diffusion theory, the Brownian motion velocity of the bubble can be obtained and then size of each particle is measured. In the other word, NTA measures Brownian motion by tracking the movement of each nanobubble using image analysis. This movement can be related to the size of nanobubbles. In fact, this method tracks particles inside a specified volume and the obtained size distribution which is a number distribution can be used to obtain the relative concentration of nanobubbles. In order to cover the whole submicron size range, it is necessary to make several recordings with various optical settings. The obtained size often have a considerable spread and the results are statistical due to the stochastic nature of Brownian movement. This method is sensitive to settings for recording and analysis [77]. NTA have been employed as one of the most popular techniques for characterization of NBs. The NTA method is very accurate and reliable for size measurement with a typical reliable particle size ~30 nm to 1 μm. As for the concentration, it should be mentioned that the fluid channel is usually very narrow, about 10 μm of depth, to allow the efficient illumination for the data acquisition by the camera. Therefore, in each image an extremely small volume of liquid can be measured. The perfect detectable range of concentration for NTA is about 10^{7}~10^{10}/mL, and good quality of data can be obtained in the range of

10^8~10^9 /mL with 8~100 objects in each frame of the captured video. There are several points that should be taking in account. Firstly, the Einstein equation is derived by treating the bubble as a solid ball without boundary slip and obviously the motion of the nanobubbles in liquids does not conform to this concept. Therefore, the obtained particle sizes could not be the nanobubble size, but their hydraulic diameter. Secondly, Data acquisition by NTA technique is sensitive to camera and image analysis settings. A poor focus can leave many particles untracked, and particles will drift in an unsteady flow condition. Thus, protocols for NTA experiments must be design carefully. Several suggestions are capture in a steady laminar flow, monitor for a long time, and repeat the measurement of both control and sample group multiple times. One of the fatal limitations of the light scattering-based methods is that they cannot distinguish bulk nanobubbles from insoluble droplets and solid nanoparticles. [2,40,50,63,74].

Dynamic Light Scattering

Dynamic light scattering (DLS) is a well-established method to measure the size of particles such as polymers, micelles, emulsions, proteins and bubble size distributions in colloidal suspensions in the sub-micron region by detecting the Brownian movement of particles. This technique have been applied for bulk and surface-attached NBs [2,52]. DLS method does not visualize the nanobubbles but can observe the time dependent variations in scattering intensity obtained from the relative Brownian movements of the nanobubbles within a sample. It is possible to calculate the average nanobubble size from time dependent variations in light intensity**.** The obtained intensity distribution can be transformed to a volume distribution. Since this conversion is based on a variety of assumptions the number distributions obtained using this method are often inaccurate [50]. In DLS method, a liquid sample in a cuvette of typically around 10 mm width is illuminated with a laser beam. A detector located at a certain angle relative to the illumination beam detects the light scattered by particles in the sample. The detected signal fluctuate faster or slower because of the Brownian motion of the particles, depending on the size of the dispersed particles [2,74]. The dynamic light scattering is based on the decays of the autocorrelation function of scattered light intensity. Smaller particles have a faster decorrelation of the scattered intensity compared to the larger ones, and thus, they can be used for size determination [40]. When the laser irradiates on the surface of small enough particles, the laser is not only absorbed and refracted, but also scattered, which is known as Rayleigh scattering [63]. The scattering signal can be either directly received by the detector or superposed by a reference beam [2]. Particle movement causes Doppler shift of the frequency of scattered light. These changes can help to obtain the second-order auto-correlation function of light intensity. The radius of the particle can be calculated using the Einstein equation of Brownian motion in diffusion theory [63]. DLS method has several advantages including: the experiment is almost fully automatized and fast, so that extensive experience is not needed for routine measurements; it is possible to measure several parameters of interest, such as molecular weight, diffusion constant, and a radius of gyration; also this technique has modest development costs [2]. Additionally, this technique is very sensitive and can detect particles in a wide size range, from less than one nanometer to several micrometers and analyzes all the illuminated particles as an ensemble [74]. However, DLS has also specific limitations that restrict its application. In this method the particles in the system must be distributed uniformly with low concentrations to obtain the average diameter of all the particles. The presence of large particles in the solution with unevenly distribution, the test result may contain a big error. Furthermore, the optical models typically rely on the assumption of spherical entities that is rarely observe in real-life analysis [2,63].

Laser Particle Size Analyzer

Among available methods for detecting NB size, laser particle size analyzer (LPSA) is known the most frequently used method. This technique can measure the size based on the Mie's theory [78,79]. Recently, LPSA has been applied to detect NBs in flotation of different solids such as hematite, coal, quartz, and phosphate [80-83]. This method has many advantages, including fast measurement (from two seconds to ten minutes), easy operation, and control of the dispersion process. In addition, It is repeatable for large numbers of entities. The assumption of spherical shape of the entities, which is not valid neither for particles nor for bubbles is known as the main limitation of this method [2].

Electron Microscopy

Electron microscopy (EM) technologies like Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM) are known as powerful tools to detect and characterize nanobubbles provides. Although these methods are very high resolution, the disadvantages are that they are costly, time consuming, and need much training. Furthermore, the sample preparation and analysis may potentially affect the sample. Today, many sample preparation and imaging methods have been suggested within EM, of which primarily cryogenic methods and liquid transmission electron microscopy have been employed for nanobubbles. Additionally, contrast agent bubbles with thick coatings have been imaged successfully in dry condition [40,74]. It has been reported that electron Microscopy (EM) can be employed only for shell-stabilized NBs because they need the dried sample covered with depositions to obtain enough contrast. In order to imaging liquid samples with methods such as liquid-TEM or Electron Energy Loss Spectroscopy (EELS), a thin and closed liquid cell-like Si_3N_4 window is needed, and therefore, the movement of NBs is severely restrained, and they are regarded as surface NBs [40].

Optical microscopy by transmission and Scanning Electron Microscopy (SEM) are the other method for measurement of the bubble size. Also, Cyro-EM or freeze-fracture electron microscopy with high resolution is a promising method for the observation of NBs suspensions owing to the capability of providing direct evidences among bubbles, solids, and droplets. This method can

preserve the original structure of the sample by rapid freezing and have been demonstrated as the promising tools in the study of BNBs [2,40]. If a water sample freezes very rapidly, gaseous bubbles can be trapped and subsequently imaged using SEM or TEM. There are different sample preparation techniques for imaging of nanobubbles such as direct imaging in TEM of enclosed bubbles, fracturing of the frozen water so that the bubbles can be visible as voids in a flat surface, followed by coating with gold and finally SEM imaging. Submicron voids are not a general feature of rapidly frozen water, and therefore this method is valid. However, there are some potential artefact sources. Damage from the electron beam can be a potential source of artefactual bubbles which causes bubbling in the ice surface. Although such bubbling effects have only been seen in frozen water with a substantial amount of dissolved organic materials. Based on a study, the size distribution of nanobubbles determined with cryo-EM appeared to correlate with the size distribution optically determined using DLS. The result of researches show that NBs in suspensions may agglomerate or coalesce to larger bubbles after the freezing process. One study reports that the size of nanobubbles detected by cryo-EM is 5-10 times bigger than those bubbles optically measured using NTA [84], which is due to bubble coalescence during sample preparation. Although this method is easily modifiable, applicable for viscous liquids, relatively cheap, it has some limitations including being slow, manual, and also extremely time-consuming to obtain statistically significant data. Furthermore, this method is able to measure the size of a single bubble accurately but cannot measure a large number of bubbles at the same time. Additionally, it needs more time to adjust the light intensity and focus on the individual bubbles in the case of smaller bubbles. Also, the effects of cryofixation, fracture and replication upon the sample structure should, however, be carefully evaluated [2,40,74].

EM methods are usually applied to dry samples or frozen liquid samples, because imaging takes place under vacuum. Recently, imaging of liquid samples using TEM has become increasingly popular. As the sample must be very thin for TEM analysis, the height of microchip cells are between 0.1 and 1 mm and the enclosing windows need to be of very thin and strong material. The volume of the cell is only about one nanoliter. The proximity of the cell surface slows down the Brownian movement of dispersed particles significantly and could leads to adsorption of colloids. Liquid TEM provides a very interesting possibility to distinguish between bubbles, particles, and droplets. However, a prominent feature of Liquid TEM method is that the electron beam supplies much energy to a very small volume of liquid, which can easily causes generation of hydrogen bubbles by radiolysis. It also has been observed that Electron beam damage to sample cells of graphene can form bubbles. This must be attentively considered when using the technique to detect pre-existing bubbles [74].

Light that is transmitted through a liquid will carry phase information, which is not available from scattered light alone. Light that passes a solid particle will slow down and achieve a phase shift in comparison with light not passing the particle. The phase shift will be of opposite sign for a gaseous bubble, and it is possible to distinguish gaseous bubbles from solid particles and droplets by measuring the phase shift [74]. In fact, Holographic microscopy is able to record the whole wave front containing both amplitude and phase information with two coherent beams unlike a conventional optical microscope records only the intensity of light reflected or transmitted by an object. The 3D structure, as well as the phase image of the sample with computer algorithms recover using the interference pattern. The holographic microscopy has the ability to distinguish different nanoparticles in suspensions from their refractive index due to the dependence of the phase contrast on the particle size and the refractive index. Recently it has been reported that NTA in an off axis digital holographic microscope could effectively differentiate nanoparticles from gas NBs with their distant phase shift (particles are positive while bubbles are negative) [85]. The holographic particle characterization technique is capable to process thousands of bubbles and particles with both their sizes and refractive index determined. Therefore, this method can be a promising and powerful tool to study BNBs in the future [86]. Midtvedt, Eklund et al. studied tracking and analysis of surfactant-stabilized nanobubbles as small as 0.3 mm and distinguished them from solid particles in the same dispersion [87]. A lower detection limit has been reached with more improvements. For strong light scatterers, such as bubbles, the smallest detectable size is 0.15 mm at present. With this technique it is possible to detect and separately characterize different particle populations in the same dispersion. Moreover, in addition to hydrodynamic size, an optical size can also be measured [74,88].

Resonance Mass Measurement

Resonance mass measurement (RMM) is known as a relatively novel technique that can detects particle buoyant mass by measuring the change in frequency with its unique microelectromechanical systems resonator. This innovative tool is able to distinguish nanobubbles from nanoparticles on the basis of the difference in density. When a solution containing nanoparticles flow through the resonator, the resonant frequency changes because of the variation in density. If we know the liquid density and a predefined flow velocity, RMM offers the possibility to probe both the gas density and the concentration of BNBs suspensions. The resonance frequency increases if the particles density are lower than the carrier fluid and decreases if the particles are denser than that of the liquid. Therefore, the sign of the variation in frequency is a tool to identify positively buoyant particles from negatively buoyant particles. In fact, The changes in resonant frequency shows the buoyancy mass of the nanoparticles [40,63,74]. Several research groups have reported the density measurements of colloidal particles by RMM [89-91]. RMM technique can be adapted for determination of the existence and density of nanobubbles because the nanobubbles density is very different from nanoparticles and nanodroplets [74]. This method has high precision and

can be employed to distinguish bubbles from solid particles with density greater than that of surrounding liquid. In the case of bubbles the buoyancy mass is positive and resonance frequency increases. While, solid particles have negative buoyancy mass and resonance frequency reduces [63].

Spectroscopy techniques

Spectroscopy techniques such as Fourier Transform infrared spectroscopy of CO_2, near-edge X-ray absorption spectroscopy of O_2, Raman spectroscopy of N_2, and small-angle neutron scattering of water vapor, X-ray fluorescence spectroscopy of Kr and SF_6, can provide chemical information, which are necessary to probe the gas state and composition of BNBs in liquids. The spectroscopies based on synchrotron radiation like X-ray absorption/emission spectroscopy and resonant inelastic soft X-ray scattering, which probe the electronic or chemical structure of the sample, are capable to provide element-sensitive information with both high spatial resolution and photon energy resolution. Recently, these promising methods have been developed and can be conducted in-situ/operando experiments in a liquid [40].

Zeta potential measurement

As we mentioned before, nowadays, NBs are at the tip of the spear of the research because of their unique properties. A lot of scientific works have been done to prove the existence of NBs and explain their super-long stability, far beyond the theoretical predictions. Some researchers are still skeptical about the existence of ultra-fine bubbles. This is one of the main questions: what causes nanobubbles have much longer lifetime than predicted by the Epstein- Plesset theory, about milliseconds vs. days? In fact, this huge difference has been a big puzzle for decades and the stability mechanism has not been solved. Nanobubbles presents many properties that large bubbles do not have [63]. Both SNBs and BNBs provide long residence times with perfect stability. Based on the results of many studies the solubility of the gases in water is higher in the cases of bulk nanobubbles formations which increases gas content in the solution. Also, large specific surface area, very high zeta potential (ζ-potential) values, and production of hydroxyl radicals from the bubbles are reported in these systems [63]. Nanobubbles can also act as nucleation sites for crystal growth, and the water–nanobubbles interfaces can be loaded with surfactants, whiles the nanobubbles are known as systems with small buoyancy force. This phenomenon cab also be attributed to the long-time stability of BNBs.

Measuring the mobility of colloids in an electric field enables us to obtain the potential at the slip plane, which is known as the zeta potential. The zeta potential is a quite good measure of the actual surface potential. A high positive or negative zeta potential has great practical importance for colloidal stability and interaction of nanobubbles with other colloids and surfaces, because it can prevent colloidal particles, droplets or bubbles from agglomeration or coalescing. It is possible to modify the zeta potential by adsorption of surface-active material on bubbles. Zeta potential is an important property of colloids that only can provide information about the surface of the colloids, not their interior [74]. The size and zeta potential are two key surface properties of bubbles and researchers have measured them under different experimental conditions [92]. Zeta potential or the surface charge density of nanobubbles depends on many factors including temperature, pH, viscosity and density of liquid, type and concentration of electrolyte, chemical materials as surfactants. Bubbles can have high zeta potential by providing sufficient energy or pressure under controlled gas flow rates. Higher gas flow rate with higher concentration of bubbles and high zeta potential cause high possibility for bubbles to merge to produce larger unstable macrobubbles. The smaller bubbles having very negligible rising velocity are stable and contain high-magnitude zeta potential values to decrease the possibility of bubble coalescence. High surface charge density leads to high zeta potential values. Nanobubble surface charge is dependent on the OH- ions or less hydrated and more polarized anions at the bubble gas–water interface. It is possible to create a favorable environment to form OH- ions/less hydrated and more polarized anions at the gas–water interface by adding surfactants or increasing pH, and hence, stable nanobubbles [8]. Bulk nanobubbles tend to interact strongly with a variety of soft matter systems such as various colloidal suspensions, liposomes and viral capsid proteins. Also, they can interact with different nanoparticles and change the surface charge [93].

Many of the literature report that the measured zeta potentials for BNB often have a negative value ranging from -50 mV to -20 mV. The fundamental principle of zeta potential measurement technique is briefly introduced in the following: if an external electric field, E applies across the sample solution, the movement of particles causes a small frequency shift, Δf which is related to the particle velocity v_p as relationship (4) where θ and λ are the scattering angle and the wavelength of the scattering beam, respectively.

$$\Delta f = 2v_p \frac{\sin\left(\frac{\theta}{2}\right)}{\lambda} \quad (4)$$

There are some other methods that determine the phase change Δf .t with time t instead of frequency shift to improve the performance. The equation (4) can convert the electrophoretic mobility of dispersed particles $\mu_e=v_p/E$ to zeta potential Z where ε and η are the dielectric constant and the absolute zero-shear viscosity of the medium, respectively. $f(\kappa.\alpha)$ is the Henry's equation where $1/\kappa$ and α are the Debye length and the radius of a spherical particle, respectively.

$$\mu_e = Z.\frac{2\varepsilon}{3\eta} f(\kappa.\alpha) \quad (5)$$

The measured zeta potential highly depends on the pH and salt concentrations of the solutions. The electrical potentials cannot determine whether they are from the gas/liquid interface or solid/liquid interface. Thus, the application of zeta potentials as an indicator for the surface charge properties of BNBs and their stable mechanism must be carefully evaluated [40].

CONCLUSION

- The methods for production of nanobubbles mainly include cavitation, ceramic membrane filtration, pressure reduction of saturated solution, gas-water circulation, electrochemical techniques, solvent exchange, and application of electric/magnetic fields.
- Although all the above methods are suitable for laboratory studies of nanobubbles, few of these techniques can be used for the production of NBs on an industrial scale [24]. One of the most important points in choosing the best method for the production of nanobubbles is the sufficient speed of the production process and the cost of electricity and energy consumption.
- Among the mentioned methods, hydrodynamic cavitation is the most popular and promising method for the creation of nanobubbles due to its high throughput and simple design, which can probably be extended to industrial applications of NBs in the future.
- The nanoparticle tracking analysis, light scattering methods, electron microscopy, atomic force microscopy, resonance mass measurement, and spectroscopy techniques are employed to characterize the hydraulic diameter, size distribution and concentration, shape, stability, surface charge properties, and kinetics of nanobubbles.
- The most commonly characterization and detection techniques of BNBs mainly include DLS or NTA methods, which are limited by the concentration range (above 109/ml for DLS) and the resolution range (larger than 50 nm for NTA). These methods could not provide the chemical information of the analyzed particles. It is very important to find and develop new detection methods with both sensitive chemical resolutions and high spatial resolution.

Competing Interests and Funding

There is no competing interests and funding.

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