Microwave-Induced Interfacial Nanobubbles

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S Supporting Information

ABSTRACT: A new method for generating nanobubbles via microwave irradiation was verified and quantified. AFM measurement showed that nanobubbles with diameters ranging from 200 to 600 nm were generated at a water-HOPG surface by applying microwave radiation to aqueous solutions with 9.0–30.0 mg/L dissolved oxygen. Graphite displays strong microwave absorption and transmits high thermal energy to the surface. Because of the high dielectric constant (20 °C, 80 F/m) and dielectric loss factor, water molecules have a strong ability to absorb microwave radiation. The thermal and nonthermal effects of microwave radiation made contributions to decreasing the gas solubility, thus facilitating nanobubble nucleation. The yield of nanobubbles increased about 10-fold when the irradiation time increased from 60 to 120 s at 200 W of microwave radiation. The nanobubble density increased from 0.8 to 15 μm^{-2} by improving the working power from 200 to 600 W. An apparent improvement in nanobubbles yield was obtained between 300 and 400 W, and the resulting temperature was 34–52 °C. When the initial dissolved oxygen increased from 11.3 to 30.0 mg/L, the density of nanobubbles increased from 1.2 to 13 μm^{-2} . The generation of nanobubbles could be well controlled by adjusting the gas concentration, microwave power, or irradiation time. The method may be valuable in preparing surface nanobubbles quickly and conveniently for various applications, such as catalysis, hypoxia/anoxia remediation, and templates for preparing nanoscale materials.

1. INTRODUCTION

Surface nanobubbles are gaseous domains that are typically tens to hundreds of nanometers in radius and 10–100 nm high. Nanobubbles were first reported by Parker et al.¹ to explain the effect of the hydrophobic long-range force. In 2000, two research groups reported the first images of nanobubbles on various hydrophobic surfaces in water by AFM, which demonstrated the existence of nanobubbles directly,^{2,3} and this is a significant milestone in nanobubble study. Since then, nanobubbles have attracted increasing attention in various fields, including nanofluidics,⁴ nanomedicine,^{5,6} nanotechnology,^{7,8} and environmental remediation.^{9–12} Investigations have focused on unraveling the mystery behind nanobubble nucleation^{13–17} and the nanobubble stability mechanism including the contamination layer and contact line pinning,^{18,19} quantifying bubble dynamics as a function of different parameters,^{20–24} and developing potential applications in lubrication,²⁵ cleaning,^{26–28} mineral flotation,²⁹ and the synthesis of highly porous metallic surfaces.³⁰ To fully exploit these possibilities, there is the need to prepare various types of gas nanobubbles by simple methods, which can be used to generate nanobubbles in a controlled way.

Research advances in various physical aspects of surface nanobubbles in the past decade include methods of nanobubble generation based on solvent exchange,^{20,31–33} temperature gradients,^{21,34} the plasmonic effect,³⁵ and water electroly-

sis.^{36–40} Alcohol–water exchange is proven to be an effective method that can generate a large number of air nanobubbles with high repeatability.^{16,41,42} Its efficiency may be attributed to the transient and local gas supersaturation close to the surface when the alcohol, having a high gas solubility, is replaced with water having a lower gas solubility. This local supersaturation presumably triggers the nucleation of small gaseous domains, the nanobubbles. However, the exchange of organic solvents with water has some limitations. It needs large amounts of organic solvents, a fast exchange process, and a stable surface resistant to organic solvents; meanwhile, organic solvents are more likely to introduce contamination into the system and make the analysis complicated. Methods without solvent exchange to nucleate nanobubbles are required for nanobubble research. The generation of plasmonic nanobubbles has drawn attention in the past few years.^{43,44} The irradiation of gold nanoparticles (AuNPs) with nanosecond laser pulses, at a wavelength that matches their plasmon resonance, is an approach commonly used to generate vapor nanobubbles in both water and biological media. This method applies only to

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certain plasmonic nanoparticles and presents a promising diagnostic and therapeutic avenue for various pathologies.^{45,46} In recent years, the electrochemical method has been employed to produce nanobubbles on the surface of an electrode. Zhang et al.³⁶ and Chen et al.⁴⁷ confirmed that the electrolysis of water induced the formation of hydrogen nanobubbles on highly oriented pyrolytic graphite (HOPG) surfaces or Pt electrodes. Oxygen nanobubbles were determined simultaneously as a byproduct of obtaining hydrogen gas by water electrolysis.⁴⁸ However, the yield of oxygen nanobubble was much lower than that of hydrogen nanobubbles.³⁷ More recently, Chen et al.⁴⁹ reported the generation of N₂ nanobubbles at Pt nanoelectrode by the irreversible electrooxidation of hydrazine. However, nanobubble generation by electrolysis is restricted by the type of electrolyte. For now, only water with or without acid and hydrazine have been used as electrolytes. The system temperature proved to be an important factor in the formation of nanobubbles; however, there is the need to advance this method with high efficiency and low energy cost.

Microwave irradiation has pronounced thermal effects. The microwave working principle is based on a water molecule's fast shear flow and molecular friction.⁵⁰ Water molecules can rotate in time with an electric field frequency of 2.45 GHz in liquids. Because of this process, internal friction takes place in the polar medium, which leads to direct heating of the mixture. Graphite has a strong microwave absorption ability because of its low resistance, being able to transmit high thermal energy to the surface, resulting in a dramatic temperature increase on the surface.^{51–53} The hot substrate may provide possibilities for interfacial nanobubble formation in an aqueous solution. Microwave irradiation also has a nonthermal effect.⁵⁴ So far, there are no previous studies on the use of microwave irradiation for nanobubble generation.

Here, we propose to use microwave irradiation to generate interfacial nanobubbles. Oxygen was used as the gas source, and nanobubbles were measured by AFM on an HOPG surface. Influential factors in the formation process such as dissolved oxygen concentration, microwave power, and irradiation time were studied. The objective of the study is to develop a convenient and efficient method for the controlled formation of nanobubbles.

2. EXPERIMENTAL SECTION

2.1. Chemicals and Materials. Highly oriented pyrolytic graphite (HOPG) (1.2 cm × 1.2 cm, Bruker) was used as the substrate. HOPG was freshly cleaved before each experiment by peeling off the outermost layers with Scotch tape.

Water with a conductivity of 18.2 MΩ cm at pH 7.0 was obtained from a Milli-Q system (Millipore Corp., Boston, MA). All glass containers for the liquid and tweezers were cleaned with acetone and ethanol, respectively, and then rinsed with water. High-purity oxygen (99.995%) was used as the gas source for preparing nanobubbles. Experiments were carried out under ambient laboratory conditions.

2.2. Formation of Nanobubbles by Microwave Irradiation. Microwave irradiation was used to prepare interfacial nanobubbles. The water was first degassed by keeping it for 1 h under a reduced pressure of 30 mbar. Then pure oxygen was used to aerate degassed ultrapure water at a flow rate of 160 mL/min. A dissolved oxygen meter (JPSJ60S, Shanghai REX Instrument Factory) was used to detect the concentration of dissolved oxygen (DO). To obtain in situ nanobubble images, freshly cleaved HOPG was fixed on an iron stub with tape and placed into the obtained 50 mL of solution before the microwave treatment (OTG Motor Co. Ltd.) was started. A schematic diagram of nanobubble generation is shown in Figure 1. After this

process, HOPG covered with microwave-treated water was carefully and quickly transferred to the liquid cells and measured with AFM.

Figure 1. Schematic diagram of nanobubble generation via microwave.

2.3. Characterization of Nanobubbles. The AFM used in the experiment was a Multimode Nanoscope IIIa from Digital Instruments (Bruker AXS GmbH) equipped with a liquid cell and an O-ring that sealed the cell and the substrate to prevent liquid leakage during the measurement. During scanning, a vertical engage J scanner (120 × 120 μm²) and silicon nitride cantilevers with a spring constant of around 0.32 N/m were used. The probes were cleaned by immersing them in acetone and ethanol, respectively, and then rinsing with water. For imaging in fluid, the resonance frequency in tapping mode was from 7 to 12 kHz and the amplitude set point was 80–90% of the free amplitude.

3. RESULTS

3.1. Generation of Interfacial Nanobubbles. The AFM image of the HOPG substrate (Figure 2a) showed that no nanobubbles were observed when the freshly cleaved HOPG substrate was simply immersed in water with 9.0 mg/L dissolved oxygen under an ambient environment. Nanobubbles were formed after 30 s of treatment by 400 W microwave irradiation (Figure 2b). The apparent diameter (lateral size) of nanobubbles was 200–600 nm. As shown in Figure 2c, oxygen nanobubbles still existed on the HOPG surface after 12 h. Once nanobubbles formed on the hydrophobic surface, they remained stable even at high temperature and did not evolve into macroscopic bubbles.⁵⁵ The mechanism behind such stability may be related to the strong pinning at the three-phase boundary, which needs to be confirmed by more quantitative experiments. In the degassed control system, the microwave treatment did not result in particle objects on the HOPG surface (Figure S1). A clear surface was revealed when the nanobubble area was scanned in contact mode (Figure 2d). The tip always contacted the substrate, and its force was strong enough to penetrate the soft nanobubbles. This result confirmed that microwave irradiation induced the formation of nanobubbles on the HOPG surface in water.

3.2. Effect of Irradiation Time and Microwave Working Power. Typical images of nanobubbles generated by microwave irradiation as a function of irradiation time were presented in Figure 3a–c. The irradiation power was set at 200 W, and the initial oxygen concentration was 15.0 mg/L. The density of nanobubbles on HOPG increased significantly with the increase in irradiation time. AFM images in contact mode proved that the generated bubblelike domains were indeed nanobubbles. The yield of oxygen nanobubbles increased about

Figure 2. AFM images of the HOPG substrate and nanobubbles: (a) the HOPG surface in water without microwave treatment, (b) images of nanobubbles generated by microwave irradiation, (c) nanobubble images after 12 h of scanning, and (d) AFM contact mode of the same treatment sample. The scan size is $10\ \mu\text{m} \times 10\ \mu\text{m}$, and the height scale is 30 nm.

10-fold when the irradiation time increased from 60 to 120 s (Figure 4).

The effect of microwave power was also studied. All water samples with an initial oxygen concentration of 15.0 mg/L were treated for 30 s by microwave irradiation at different working powers. The yield of nanobubbles and the associated temperature profile are shown in Figure 5. Nanobubble formation is well correlated to the resulting temperature. An apparent improvement in nanobubble yield was found between 300 and 400 W, where the resulting temperature was 34–52 °C. The nanobubble density increased from 0.8 to $15\ \mu\text{m}^{-2}$ by improving the working power from 200 to 600 W, suggesting that increasing work power improved the yield of nanobubbles.

3.3. Oxygen Concentration Effect. The gas concentration has been proven to be an important factor affecting the formation of nanobubbles.⁵⁶ To study the oxygen concentration effect, we prepared water with different initial oxygen concentrations from 11.3 to 30.0 mg/L. The initial temperature was 19 °C. Samples were treated for 60 s with 300 W microwave irradiation, followed by AFM measurement. The

resulting temperature was 45 °C after switching off the microwave irradiation. Typical images of nanobubbles as a function of oxygen concentration are shown in Figure 6. The yield of nanobubbles increased with increasing oxygen concentration (Figure 6e).

When HOPG was immersed in water oversaturated with oxygen with 30.0 mg/L DO and no microwave treatment, no interfacial nanobubbles were observed (Figure 7).

4. DISCUSSION

4.1. Generation of Interfacial Nanobubbles by Microwave. It is well-known that water molecules are polar and have a high dielectric constant (20 °C, 80 F/m) and dielectric loss factor and thus a strong ability to absorb microwave radiation. Graphite displays a strong microwave absorption ability and may yield “hot spots”.^{50,51} Microwave treatment and temperature change in water are related (Table S1). The combination of a hot HOPG substrate and temperature change in water by microwave irradiation may be responsible for the formation of interfacial nanobubbles. Experimental results demonstrated that

Figure 3. (a–c) AFM tapping mode height images of nanobubbles on the water–HOPG surface with different microwave irradiation times: (a) 60 s, (b) 90 s, and (c) 120 s. (a1–c1) AFM images of these same samples in contact mode. The scan size is $10\ \mu\text{m} \times 10\ \mu\text{m}$, and the height scale is 30 nm.

Figure 4. Effect of microwave irradiation time on the formation of nanobubbles.

the yield of nanobubbles was well associated with the irradiation time and working power. The yield of nanobubbles increased about 10-fold when the irradiation time increased from 60 to 120 s by 200 W microwave treatment (Figure 4). The nanobubble density increased from 0.8 to $15\ \mu\text{m}^{-2}$ by improving the work power from 200 to 600 W (Figure 5). Microwave irradiation significantly enhanced nanobubble generation. By adjusting the microwave working power or irradiation time, it is possible to achieve the desired nanobubbles (number and size) quickly and conveniently.

Figure 5. Effect of microwave power on the formation of nanobubbles.

Gas concentration played an important role in nanobubble formation.^{56,57} Figure 8 shows the relationship between the oxygen concentration in water solution and the temperature variation caused by microwave irradiation. The higher the initial concentration of oxygen, the more oxygen released from the aqueous phase and thus a greater amount of induced nanobubble nucleation. The nanobubble yield was apparently increased from 1.2 to $13\ \mu\text{m}^{-2}$ when the initial concentration of oxygen was increased from 11.3 to 30 mg/L (Figure 6). Although the yield of oxygen nanobubbles can be largely manipulated by the oxygen concentration, it remains an

Figure 6. AFM height images of oxygen nanobubbles generated by microwave irradiation in water with different oxygen concentrations: (a) 11.3, (b) 13.9, (c) 20.0, and (d) 30.0 mg/L. (e) Number of nanobubbles versus oxygen concentration. The scan size is $10\ \mu\text{m} \times 10\ \mu\text{m}$, and the height scale is 30 nm.

interesting topic to study their stability under various water conditions such as the oxygen delivery effect in an aerobic environment.

4.2. Possible Mechanism of Nanobubble Formation.

In this study, nanobubbles were not observed by AFM when the freshly cleaved HOPG substrate was immersed in water with a rather high oxygen concentration (9.0–30 mg/L) in an ambient environment without microwave treatment (Figures 2a and 7). This agreed with the literature in that few nanobubbles can be detected simply by immersing a hydrophobic substrate in water.^{20,57,58} Zhang et al.⁵⁹ reported that interfacial nanobubbles were not observed when a smooth OTS-Si wafer was placed in a CO_2 -saturated water solution, and the interfacial bubbles are formed only through a fast solvent exchange treatment. It is widely accepted that the fast variation

of gas solubility in water solution is key to inducing the nucleation of nanobubbles.

In this work, oxygen solubility in water was rapidly decreased with the temperature increase caused by the microwave treatment (Figure 8). The positive/negative direction of the electric field in microwave irradiation can change 2.45 billion times per second.⁵⁰ The fast-changing electric fields of microwave irradiation lead to a rotation of the water molecule. The fast water shear flow and molecular friction can open the hydrogen bond between oxygen and the water molecule, resulting in the decrease in oxygen solubility in the aqueous solution. This is a physical process caused by the microwave nonthermal effect.⁵⁴ In the meantime, severe temperature variations by the microwave thermal effect also helped to decrease the oxygen solubility. The nanobubble formation mechanism is described in the schematic diagram in Figure 9.

Figure 7. AFM image of the HOPG surface in water with 30.0 mg/L DO without microwave treatment.

Figure 8. Oxygen concentration versus system temperature.

Figure 9. Possible mechanism of nanobubble formation.

One possible pathway is that interfacial nanobubbles could be formed by direct oxygen molecule nucleation and could accumulate on the HOPG surface as a nanoscale gas state. When irradiated with microwaves, HOPG could absorb microwave energy, resulting in a rapid heating of the surface. The violent release of heat by HOPG resulted in a rapid decrease in gas solubility in the surrounding domain, which contributes to nanobubble nucleation on the HOPG–water

surface. Another possible pathway is that free oxygen nanobubbles could be formed in the bulk solution and then attached to the HOPG surface to form surface nanobubbles.¹⁶ Because of the strong microwave absorption ability, both the water and HOPG substrate temperatures could be well controlled by microwave irradiation, which is different from the nonselective temperature change method.³⁵ In addition, the selective heating by microwave irradiation may be more energy efficient than conventional heating conduction through the whole medium.

4.3. Potential Impacts. This work confirmed that microwave irradiation is an effective way to prepare surface nanobubbles. To present direct evidence of nanobubbles, oxygen nanobubbles were generated and determined on a HOPG surface in this study. A recent study demonstrated that oxygen nanobubbles could be quantified at particle–water interfaces by scanning transmission soft X-ray microscopy.⁶⁰ The controlled formation of nanobubbles via microwave may be valuable in preparing surface nanobubbles at various solid surfaces for practical applications, such as catalysis, hypoxia/anoxia remediation, and templates for preparing nanoscale materials. It is interesting to study whether other types of nanobubbles can be produced by microwave treatment. It remains a challenge in the future to study the many mysteries related to nanobubbles such as the gas density inside nanobubbles and the stability on particle surfaces.

5. CONCLUSIONS

This work found that interfacial nanobubbles can be generated by microwave treatment. The yield of nanobubbles can be manipulated by adjusting the irradiation and gas concentration. Both thermal and nonthermal effects of microwave irradiation may be responsible for nanobubble nucleation as a result of the decrease in oxygen solubility in aqueous systems. The study provides a quick and convenient way to produce nanobubbles that may be useful for various applications.

■ ASSOCIATED CONTENT

§ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.6b01620.

AFM image of HOPG after microwave treatment in the control system and temperature change with microwave power and interaction time (PDF)

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Notes

The authors declare no competing financial interest.

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