

Microwave Induced Interfacial Nanobubbles

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28 **ABSTRACT**

29 A new method for generating nanobubbles via microwave irradiation was
30 verified and quantified. AFM measurement showed that nanobubbles with
31 diameters ranging in 200 - 600 nm were generated at water-HOPG surface
32 by applying microwave to aqueous solutions with 9.0 - 30.0 mg/L of
33 dissolved oxygen. Graphite displays strong microwave absorption and
34 transmits high thermal energy to surface. Due to high dielectric constant
35 (20 °C, 80 F/m) and dielectric loss factor, water molecule has strong
36 absorption ability for microwave. The thermal and non-thermal effects of
37 microwave both had contributions to decrease gas solubility and that
38 facilitated nanobubble nucleation. The yield of nanobubbles increased
39 about ten times when irradiation time increased from 60 s to 120 s at 200
40 W microwave. The nanobubbles density increased from 0.8 to 15
41 numbers/ μm^2 by improving working power from 200 to 600 W. An
42 apparent improvement of nanobubbles yield was obtained between 300 and
43 400 W, and the resulting temperature was 34 - 52 °C. When the initial
44 dissolved oxygen increased from 11.3 to 30.0 mg/L, the density of
45 nanobubbles increased from 1.2 to 13 numbers/ μm^2 . The generation of
46 nanobubbles could be well controlled by adjusting gas concentration,
47 microwave power or irradiation time. The method maybe valuable in
48 preparing surface nanobubbles quickly and conveniently for various
49 applications, such as catalysis, hypoxia/anoxia remediation or as templates

50 to prepare nanoscale materials.

51 **1. INTRODUCTION**

52 Surface nanobubbles are gaseous domains that are typically tens to
53 hundreds of nanometers in radius and 10 - 100 nm high. Nanobubbles were
54 first reported by Parker et al.¹ for explaining the effect of hydrophobic
55 long-range force. In 2000, two research groups reported the first images of
56 nanobubbles on various hydrophobic surfaces in water by AFM which
57 demonstrated the existence of nanobubbles directly^{2, 3} and this is a
58 significant milestone of nanobubbles study. Since then, nanobubbles have
59 attracted increasing attention in various fields including nanofluidics,⁴
60 nanomedicine,^{5, 6} nanochemistry^{7, 8} and environmental remediation.^{9, 10, 11,}
61 ¹² Investigations focus on unraveling the mystery behind nanobubble
62 nucleation,^{13, 14, 15, 16, 17}, nanobubble stability mechanism including
63 contamination layer and contact line pinning,^{18, 19} quantifying bubble
64 dynamics as a function of different parameters,^{20, 21, 22, 23, 24} as well as
65 developing potential applications in lubrication,²⁵ cleaning,^{26, 27, 28} flotation
66 of minerals²⁹ and synthesizing highly porous metallic surfaces.³⁰ To fully
67 exploit these possibilities, there is the need to prepare various types of gas
68 nanobubbles by simple methods, which can be used to generate
69 nanobubbles in a controlled way.

70 Research advances on various physical aspects of surface nanobubbles
71 in the past decade include methods of nanobubble generation based on

72 solvent exchange,^{20, 31, 32, 33} temperature gradient,^{21, 34} plasmonic effect³⁵
73 and water electrolysis.^{36, 37, 38, 39, 40} Alcohol–water exchange is proved to be
74 an effective method that can generate large amount of air nanobubbles with
75 high repeatability.^{16, 41, 42} Its efficiency may be attributed to the transient
76 and local gas supersaturation close to the surface, when the alcohol, having
77 a high gas solubility, is replaced by water, having a lower gas solubility.
78 This local supersaturation presumably triggers the nucleation of small
79 gaseous domains, the nanobubbles. However, exchange of organic solvents
80 with water has some limitations. It needs large amount of organic solvents
81 and fast exchanging process and a stable surface resistant to organic
82 solvents, meanwhile organic solvents are more likely to introduce
83 contaminations to the system and make the analysis complicated. Methods
84 without solvent exchange to nucleate nanobubbles are required for
85 nanobubble researches. Generation of plasmonic nanobubbles has drawn
86 attention in the past few years.^{43, 44} Irradiation gold nanoparticles (AuNPs)
87 with nanosecond laser pulses, at a wavelength that matches their plasmon
88 resonance, is an approach commonly used to generate vapor nanobubbles
89 in both water and biological mediums. This method only applies to certain
90 plasmonic nanoparticles and presents a promising diagnostic and
91 therapeutic avenue for various pathologies.^{45, 46} In recent years,
92 electrochemical method has been employed to produce nanobubbles on the
93 surface of electrode. Zhang et al.³⁶ and Chen et al.⁴⁷ confirmed that

94 electrolysis of water induced the formation of hydrogen nanobubbles on
95 highly orientated pyrolytic graphite (HOPG) surfaces or Pt electrode.
96 Oxygen nanobubbles were determined simultaneously as a by-product of
97 obtaining hydrogen gas by water electrolysis.⁴⁸ However, the yield of
98 oxygen nanobubble was much lower than that of hydrogen nanobubble.³⁷
99 More recently, Chen et al.⁴⁹ reported the generation of N₂ nanobubbles at
100 Pt nanoelectrode by irreversible electrooxidation of hydrazine. However,
101 nanobubble generation by electrolysis is restricted by the type of
102 electrolyte. For now, only water with or without acid and hydrazine have
103 been used as electrolyte. System temperature proved to be an important
104 factor for the formation of nanobubbles, however, there is the need to
105 advance this method with high efficient and low energy cost.

106 Microwave has pronounced thermal effect. The working principle of
107 microwave is based on water molecule's fast shear flow and molecules
108 friction.⁵⁰ Water molecules can rotate in time with electric field frequencies
109 of 2.45 GHz in liquids. Due to this process, "internal friction" takes place
110 in the polar medium, which leads to a direct heating of the mixture.
111 Graphite presents strong microwave absorption ability because of its low
112 resistance, being able to transmit high thermal energy to surface and
113 resulting in dramatic temperature increase on surface.^{51, 52, 53} The hot
114 substrate may provide possibilities for interfacial nanobubbles formation
115 in the aqueous solution. Microwave also presents non-thermal effect.⁵⁴ So

116 far, there are no previous studies on the use of microwave for nanobubble
117 generation.

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

125 **2. EXPERIMENTAL**

126 **2.1. Chemicals and materials**

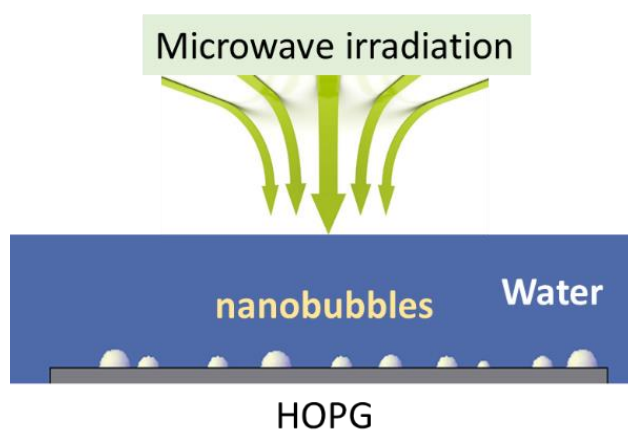
127 Highly ordered pyrolytic graphite (HOPG) (1.2 cm × 1.2 cm, Bruker)
128 was used as the substrate. HOPG was freshly cleaved before each
129 experiment by peeling off the outermost layers with scotch tape.

130 Water with conductivity of 18.2 MΩ cm and pH 7.0 was obtained from
131 a milli-Q system (Millipore Corp., Boston, MA). All glass containers for
132 the liquid and tweezer were cleaned by acetone and ethanol, respectively,
133 and then rinsed with water. The high pure oxygen (99.995%) was used as
134 gas source to prepare nanobubbles. Experiments were carried out under
135 ambient lab conditions.

136 **2.2. Formation of nanobubbles by microwave**

137 Microwave was used to prepare interfacial nanobubbles. The water was

138 first degassed by keeping it for 1 h under a reduced pressure of 30 mbar.
139 Then pure oxygen was aerated to the degassed ultrapure water with a flow
140 rate of 160 mL per minute. A dissolved oxygen meter (JPSJ605, Shanghai
141 REX Instrument Factory) was used to detect the concentration of dissolved
142 oxygen (DO). In order to get the in situ nanobubbles images, the freshly
143 cleaved HOPG was fixed on an iron stub by tape and put into the obtained
144 50 mL solution and then started the microwave treatment (OTG Motor Co.
145 Ltd). The schematic diagram of nanobubbles generation was shown in
146 figure 1. After this process, the HOPG covered with the microwave treated
147 water was carefully and quickly transferred to the liquid cells and measured
148 by AFM.



149

150 Figure 1. The schematic diagram of nanobubbles generation by

151 microwave

152 2.3. Characterization of nanobubbles

153 The AFM used in the experiment was a Multimode Nanoscope IIIa from
154 Digital Instruments (Bruker AXS GmbH), equipped with a liquid cell and
155 an O-ring which sealed the cell and the substrate to prevent liquid leakage

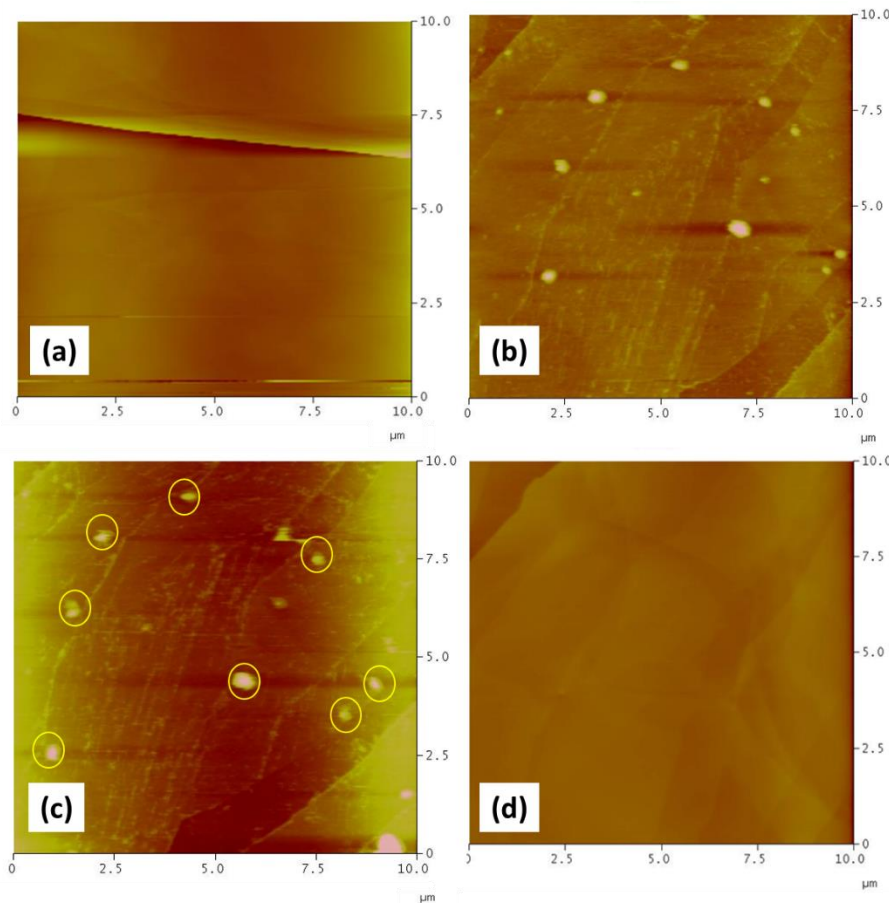
156 during the measurement. During the scanning, a vertical engage J scanner
157 ($120 \times 120 \mu\text{m}^2$) and silicon nitride cantilevers with their spring constant
158 around 0.32 N/m were used. The probes were cleaned by immersing them
159 in acetone and ethanol, respectively, and then rinsed with water. For
160 imaging in fluid, the resonance frequency in tapping mode was from 7 kHz
161 to 12 kHz and the amplitude set point was 80–90% of the free amplitude.

162 **3. RESULTS**

163 **3.1. Generation of interfacial nanobubbles**

164 The AFM image of HOPG substrate (Figure 2a) showed that no
165 nanobubbles were observed when the freshly cleaved HOPG substrate was
166 simply immersed into water with 9.0 mg/L of dissolved oxygen at ambient
167 environment. Nanobubbles were formed after 30 s treatment by 400 W
168 microwave irradiation (Figure 2b). The apparent diameter (lateral size) of
169 nanobubbles was 200 - 600 nm. As shown in Figure 2c, oxygen
170 nanobubbles still existed on the HOPG surface after 12 h. Once
171 nanobubbles formed on the hydrophobic surface, they remained stable
172 even in high temperature conditions and did not evolve into macroscopic
173 bubbles.⁵⁵ The mechanism behind such stability may be related to the
174 strong pinning at the three-phase boundary, which needs to be confirmed
175 by more quantitative experiments. In the degassed control system, the
176 treatment of microwave did not result in particle objects on the HOPG
177 surface (Figure S1). A clear surface was revealed when the nanobubbles

178 area was scanned under contact mode (Figure 2d). The tip always contacted
179 with the substrate, and its force was strong enough to penetrate through
180 soft nanobubbles. This result confirmed that microwave irradiation
181 induced the formation of nanobubbles on the HOPG surface in water.

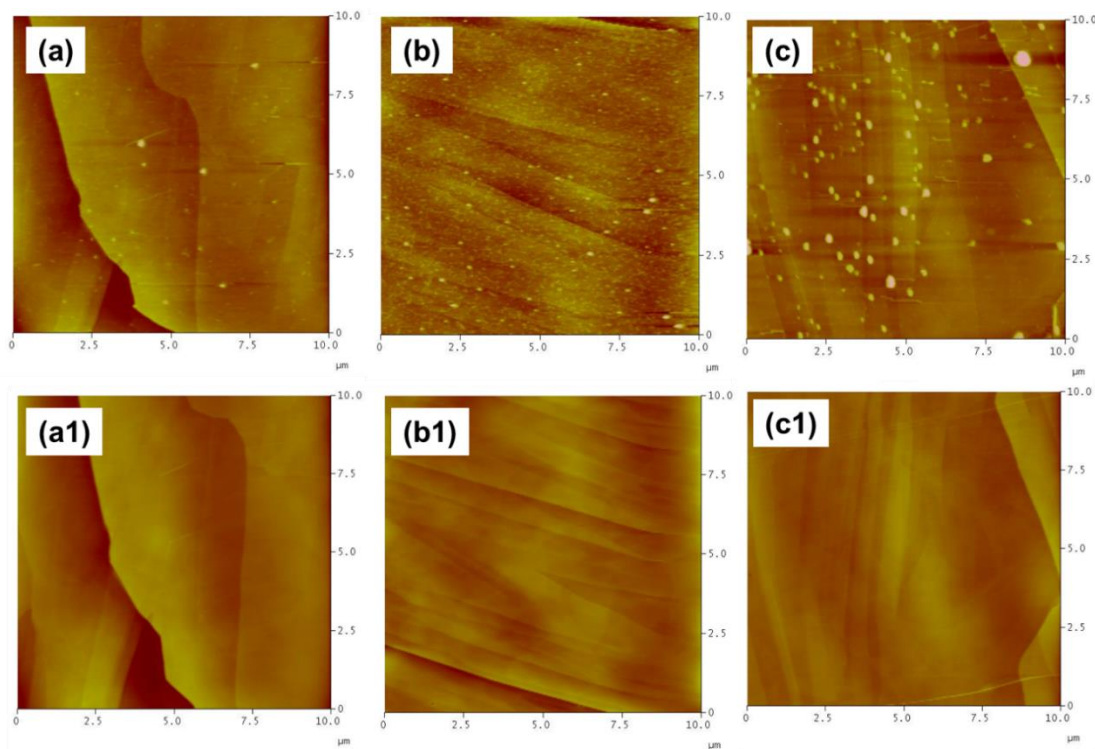


182
183 Figure 2. AFM images of HOPG substrate and nanobubbles: (a) the HOPG
184 surface in water without microwave treatment, (b) images of nanobubbles
185 generated by microwave irradiation, (c) nanobubbles images after 12 h
186 scanning and (d) AFM contact mode of the same treatment sample. The
187 scan sizes is $10\ \mu\text{m} \times 10\ \mu\text{m}$ and height scale is 30 nm.

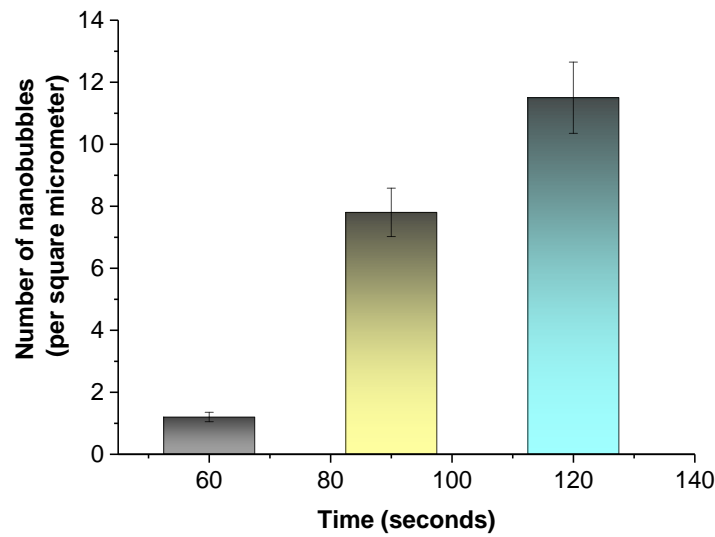
188 3.2. Effect of irradiation time and microwave working power

189 Typical images of nanobubbles generated by microwave as function of

190 irradiation time were presented in Figure 3a-c. The irradiation power was
191 set at 200 W and the initial oxygen concentration was 15.0 mg/L. The
192 density of nanobubbles on HOPG increased significantly with the increase
193 of irradiation time. AFM images in contact mode proved that the generated
194 bubbles-like domains were indeed nanobubbles. The yield of oxygen
195 nanobubbles increased about ten times when irradiation time increased
196 from 60 s to 120 s (Figure 4).



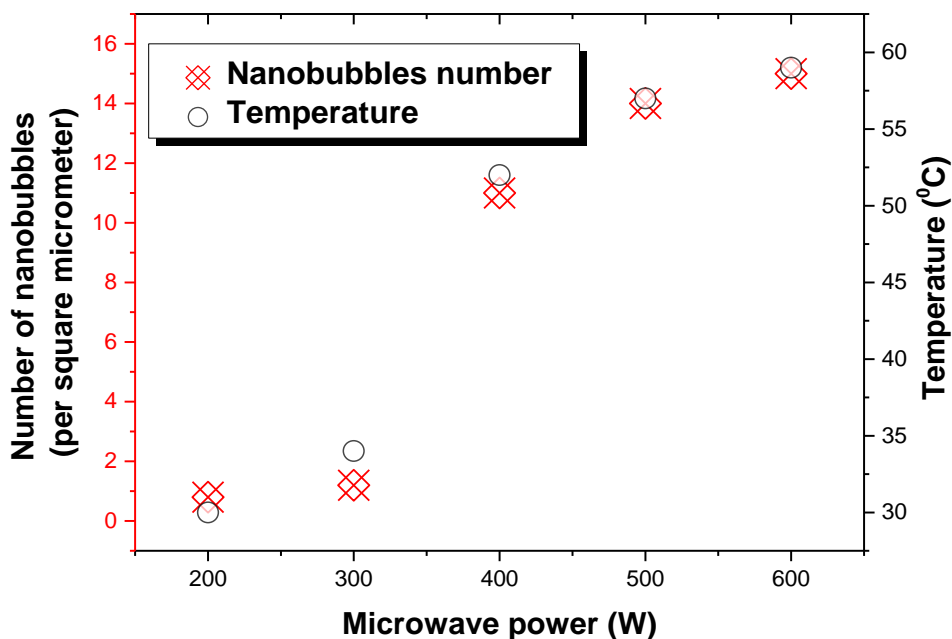
197
198 Figure 3. (a-c) AFM tapping mode height images of nanobubbles on water-
199 HOPG surface with different microwave irradiation time: (a) 60 s, (b) 90 s
200 and (c) 120 s; (a1-c1) AFM images of these same samples by contact mode.
201 The scan sizes is $10 \mu\text{m} \times 10 \mu\text{m}$, height scale is 30 nm.



202

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

205 The effect of microwave power was also studied. All water samples
206 with initial oxygen of 15.0 mg/L were treated for 30 s by microwave at
207 different working power. The yield of nanobubbles and the associated
208 temperature profile were shown in Figure 5. The nanobubble formation
209 was well correlated to the resulting temperature. An apparent improvement
210 of nanobubbles yield was found between 300 and 400 W, where the
211 resulting temperature was 34 - 52 °C. The nanobubbles density increased
212 from 0.8 to 15 numbers/ μm^2 by improving working power from 200 to 600
213 W, suggesting that increasing work power improved the yield of
214 nanobubbles.

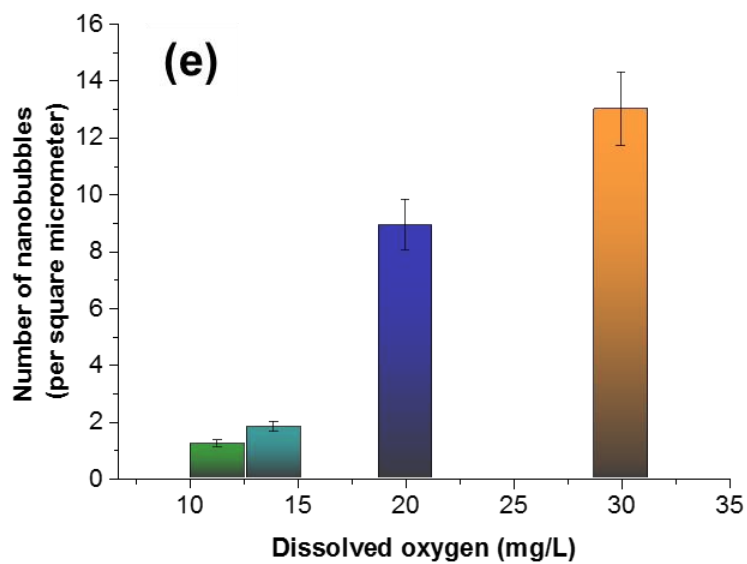
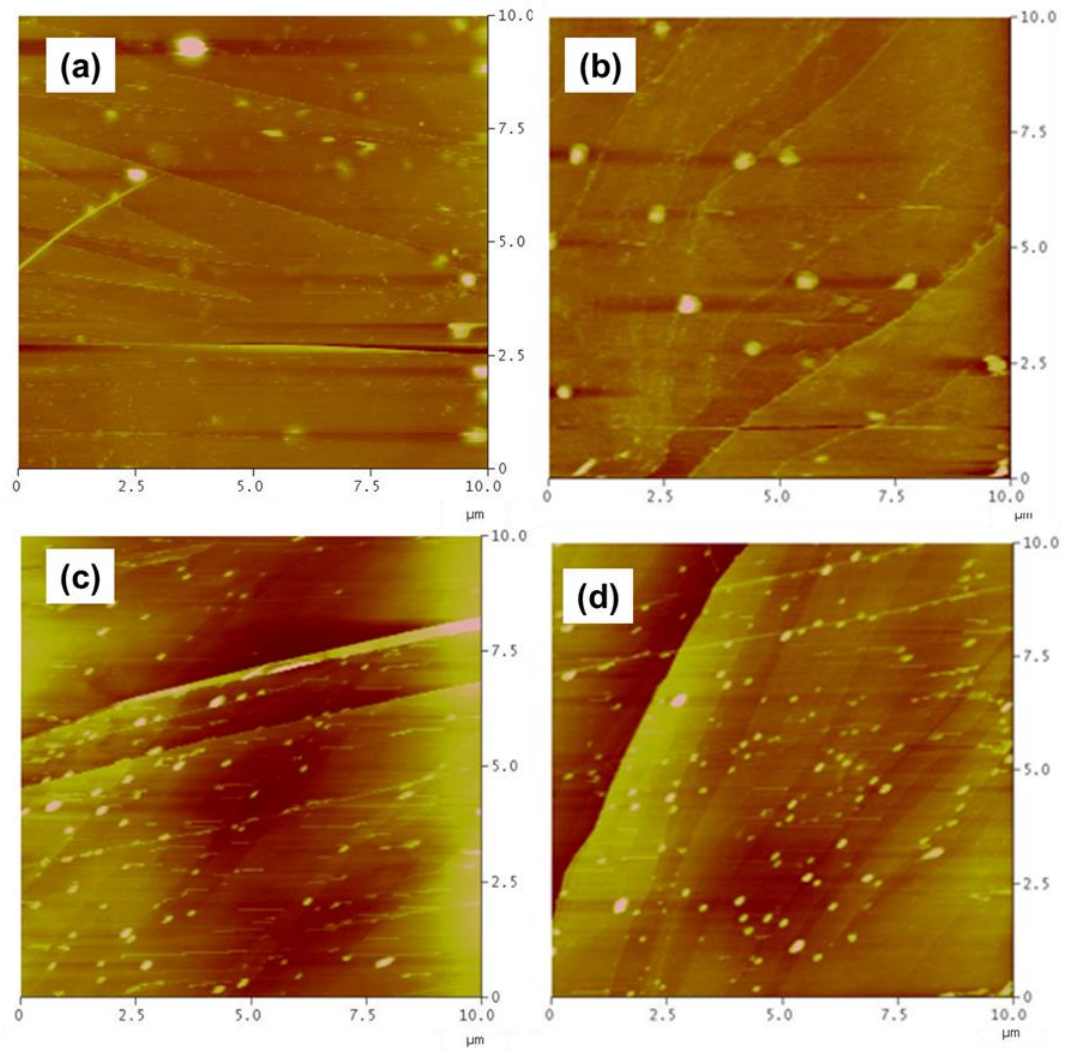


215

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

217 3.3. Oxygen concentration effect

218 Gas concentration was proved to be an important factor affecting the
 219 formation of nanobubbles.⁵⁶ In order to study the oxygen concentration
 220 effect, we prepared water with different initial oxygen concentrations from
 221 11.3 to 30.0 mg/L. The initial temperature was 19 °C. Samples were treated
 222 60 s by 300 W microwave irradiation and then followed with AFM
 223 measurement. The resulting temperature was 45 °C after switching off the
 224 microwave. Typical images of nanobubbles as function of oxygen
 225 concentration were shown in Figure 6. The yield of nanobubbles increased
 226 with increasing oxygen concentration (Figure 6e).

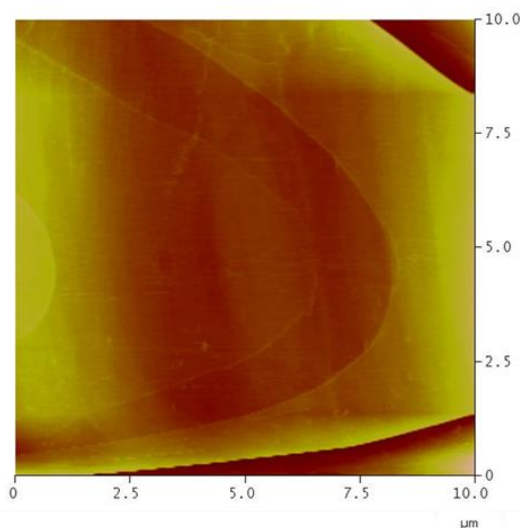


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228 Figure 6. AFM height images of oxygen nanobubbles generated by
 229 microwave in water with different oxygen concentrations: (a) 11.3 mg/L,

230 (b) 13.9 mg/L, (c) 20.0 mg/L, (d) 30.0 mg/L and (e) the number of
231 nanobubbles versus oxygen concentration. The scan sizes is $10\ \mu\text{m} \times 10$
232 μm and height scale is 30 nm.

233 When HOPG was immersed in an oversaturated oxygen water with
234 30.0 mg/L of DO with no microwave treatment, no interfacial nanobubbles
235 were observed (Figure 7).



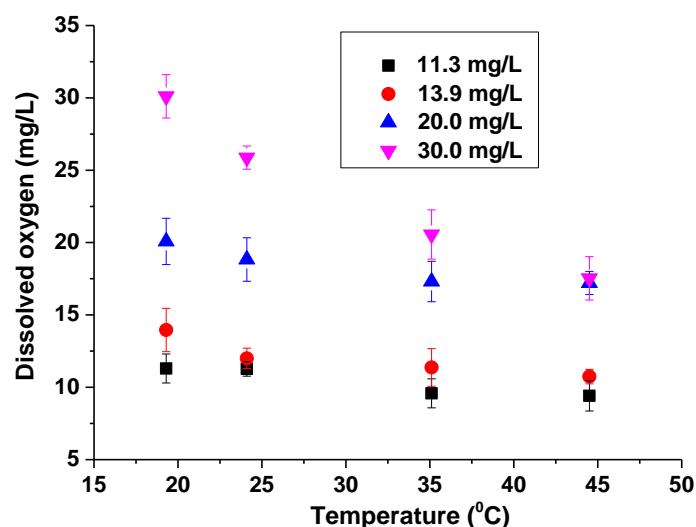
236
237 Figure 7. AFM image of HOPG surface in water with 30.0 mg/L of DO
238 without microwave treatment

239 4. DISCUSSION

240 4.1. Generation of interfacial nanobubbles by microwave

241 It is well known that water molecule is polar with high dielectric
242 constant ($20\ \text{°C}$, 80 F/m) and dielectric loss factor, thus has strong ability
243 to absorb microwave. Graphite displays strong microwave absorption
244 ability and may yield “hot spots”.^{50, 51} Microwave treatment and
245 temperature change in water are related (Table S1). The combination of hot
246 HOPG substrate and temperature change in water by microwave irradiation

247 may be responsible for the formation of interfacial nanobubbles.
 248 Experimental results demonstrated the yield of nanobubbles was well
 249 associated with the irradiation time and working power. The yield of
 250 nanobubbles increased about ten times when irradiation time increased
 251 from 60 s to 120 s by 200 W microwave treatment (Figure 4). The
 252 nanobubbles density increased from 0.8 to 15 numbers/ μm^2 by improving
 253 work power from 200 to 600 W (Figure 5). Microwave irradiation
 254 significantly enhanced nanobubble generation. By adjusting microwave
 255 working power or irradiation time, it is possible to achieve desired
 256 nanobubbles (amount and size) quickly and conveniently.



257
 258 Figure 8. Oxygen concentration versus system temperature

259 Gas concentration played an important role on the nanobubble
 260 formation.^{56, 57} Figure 8 shows the relationship between the oxygen
 261 concentration in water solution and the temperature variation caused by
 262 microwave irradiation. The higher initial concentration of oxygen, the

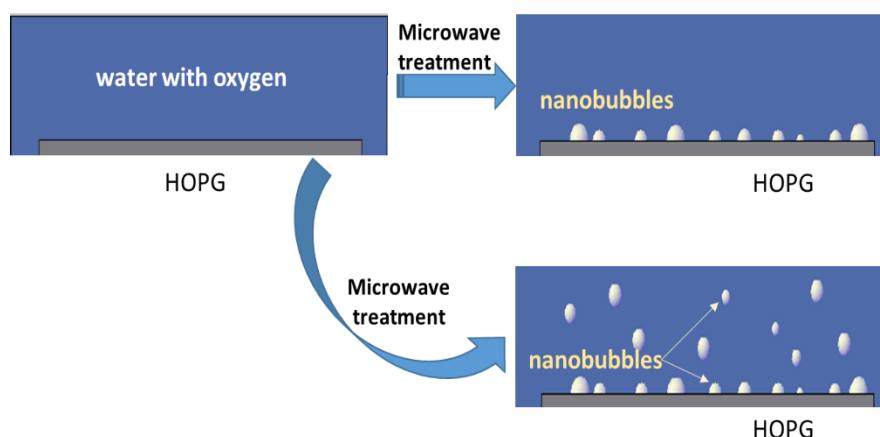
263 more oxygen released from aqueous phase and thus induced the
264 nanobubble nucleation. The yield of nanobubble was apparently increased
265 from 1.2 to 13 numbers/ μm^2 when initial oxygen was increased from 11.3
266 to 30 mg/L (Figure 6). While the yield of oxygen nanobubbles can be
267 largely manipulated by oxygen concentration, it remains an interesting
268 topic to study their stability under various water conditions such as the
269 oxygen delivery effect in aerobic environment.

270 **4.2. Possible mechanism of nanobubble formation**

271 In this study, nanobubbles were not observed by AFM when the freshly
272 cleaved HOPG substrate was immersed into water with rather high oxygen
273 concentration (9.0 - 30 mg/L) at ambient environment without microwave
274 treatment (Figure 2a and Figure 7). This agreed with literature that few
275 nanobubbles can be detected simply by immersing a hydrophobic substrate
276 into water.^{20, 57, 58} Zhang et al.⁵⁹ reported that interfacial nanobubbles were
277 not observed when a smooth OTS-Si wafer was put in a CO_2 saturated
278 water solution, and the interfacial bubbles are only formed through a fast
279 solvent exchange treatment. It is widely accepted that the fast variation of
280 gas solubility in water solution is key in inducing the nucleation of
281 nanobubbles.

282 In this work, oxygen solubility in water was rapidly decreased with the
283 temperature increase caused by microwave treatment (Figure 8). The
284 positive/negative direction of electric field in the microwave could change

285 2.45 billion times per second.⁵⁰ The fast changing electric fields of the
286 microwave radiation lead to a rotation of the water molecule. The fast water
287 shear flow and molecules friction can open the hydrogen bond between
288 oxygen and water molecule and result in the decrease of oxygen solubility
289 in the aqueous solution. This is a physical process caused by microwave
290 non-thermal effect.⁵⁴ Meantime, severe temperature variation by
291 microwave thermal effect also helped to decrease the oxygen solubility.
292 The nanobubble formation mechanism is described in the schematic
293 diagram of Figure 9. One possible pathway is that interfacial nanobubbles
294 could be formed by direct oxygen molecule nucleation and accumulated on
295 HOPG surface as nanoscale gas state. When irradiated by the microwaves,
296 HOPG could absorb microwave energy and result in a rapid heating of the
297 surface. The violent release of heat by the HOPG resulted in a rapid
298 decrease of gas solubility in the surrounding domain, which contribute to
299 the nanobubble nucleation on HOPG-water surface. Another possible
300 pathway is that free oxygen nanobubbles could be formed in the bulk
301 solution and then attached to HOPG surface to form surface nanobubbles.¹⁶
302 Due to the strong microwave absorption ability, both water and HOPG
303 substrate temperature could be well controlled by microwave, which is
304 different from the non-selective temperature change method.³⁵ In addition,
305 the selective heating by microwave may be more energy efficient than the
306 conventional heating conduction through the whole media.



307

308 Figure 9. The possible mechanism of nanobubbles formation

309 4.3. Potential impacts

310 This work confirmed that microwave irradiation was an effective way
 311 in preparing surface nanobubbles. In order to present direct evidence of
 312 nanobubbles, oxygen nanobubbles was generated and determined on
 313 HOPG surface in this study. Recent study demonstrated that oxygen
 314 nanobubbles could be quantified at particle-water interfaces by scanning
 315 transmission soft X-ray microscopy.⁶⁰ The controlled formation of
 316 nanobubbles via microwave maybe valuable in preparing surface
 317 nanobubbles at various solid surfaces for practical applications, such as
 318 catalysis, hypoxia/anoxia remediation or as templates to prepare
 319 nanoscale materials. It is interesting to study whether other gas type of
 320 nanobubbles can be produced by microwave treatment. It remains a
 321 challenge in the future to study the many mysteries related to nanobubbles
 322 such as the gas density inside nanobubbles and the stability on particle
 323 surfaces.

324 5. CONCLUSIONS

325 This work found that surface nanobubbles can be generated by
326 microwave treatment. The yield of nanobubbles can be manipulated by
327 adjusting the irradiation and gas concentration. Both thermal and non-
328 thermal effects of microwave may be responsible for the formation of
329 nanobubble nucleation due to the decrease of oxygen solubility in aqueous
330 system. The study provides a quick and convenient way to produce
331 nanobubbles that may be useful for various applications.

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337 **REFERENCES**

- 338 1. Parker, J. L.; Claesson, P. M.; Attard, P. Bubbles, cavities, and the long-ranged attraction between
339 hydrophobic surfaces. *J. Phys. Chem.* **1994**, *98* (34), 8468-8480.
- 340 2. Ishida, N.; Inoue, T.; Miyahara, M.; Higashitani, K. Nano bubbles on a hydrophobic surface in water
341 observed by tapping-mode atomic force microscopy. *Langmuir* **2000**, *16* (16), 6377-6380.
- 342 3. Lou, S. T.; Ouyang, Z. Q.; Zhang, Y.; Li, X. J.; Hu, J.; Li, M. Q.; Yang, F. J. Nanobubbles on solid surface
343 imaged by atomic force microscopy. *J. Vac. Sci. Technol. B* **2000**, *18* (5), 2573-2575.
- 344 4. Wang, Y.; Bhushan, B. Boundary slip and nanobubble study in micro/nanofluidics using atomic
345 force microscopy. *Soft matter* **2010**, *6* (1), 29-66.
- 346 5. Cavalli, R.; Bisazza, A.; Giustetto, P.; Civra, A.; Lembo, D.; Trotta, G.; Guiot, C.; Trotta, M. Preparation
347 and characterization of dextran nanobubbles for oxygen delivery. *Int. J. Pharmaceut.* **2009**, *381* (2), 160-
348 165.
- 349 6. Chang, S.; Si, T.; Zhang, S.; Merrick, M. A.; Cohn, D. E.; Xu, R. X. Ultrasound mediated destruction
350 of multifunctional microbubbles for image guided delivery of oxygen and drugs. *Ultrason. Sonochem.*
351 **2016**, *28*, 31-38.
- 352 7. Belova, V.; Gorin, D. A.; Shchukin, D. G.; Moehwald, H. Controlled effect of ultrasonic cavitation on
353 hydrophobic/hydrophilic surfaces. *Acs Appl. Mater. Inter.*
354 **2011**, *3* (2), 417-425.
- 355 8. Ibrahimkutti, S.; Kim, J.; Cammarata, M.; Ewald, F.; Choi, J.; Ihee, H.; Plech, A. Ultrafast structural

356 dynamics of the photocleavage of protein hybrid nanoparticles. *Acs Nano* **2011**, *5* (5), 3788-3794.

357 9. Brooks, M. Impossibubbles. *New Sci.* **2012**, *215* (2872), 38-41.

358 10. Pan, G.; Yang, B.; Wang, D.; Chen, H.; Tian, B.; Zhang, M.; Yuan, X.; Chen, J. In-lake algal bloom
359 removal and submerged vegetation restoration using modified local soils. *Ecol. Eng.* **2011**, *37* (2), 302-
360 308.

361 11. Pan, G.; Dai, L.; Li, L.; He, L.; Li, H.; Bi, L.; Gulati, R. D. Reducing the recruitment of sedimented algae
362 and nutrient release into the overlying water using modified soil/sand flocculation-capping in eutrophic
363 lakes. *Environ. Sci. Technol.* **2012**, *46* (9), 5077-5084.

364 12. Li, H.; Pan, G. Simultaneous removal of harmful algal blooms and microcystins using
365 microorganism- and chitosan-modified local soil. *Environ. Sci. Technol.* **2015**, *49* (10), 6249-6256.

366 13. Craig, V. S. J. Very small bubbles at surfaces-the nanobubble puzzle. *Soft matter* **2011**, *7* (1), 40-48.

367 14. Seddon, J. R. T.; Kooij, E. S.; Poelsema, B.; Zandvliet, H. J. W.; Lohse, D. Surface bubble nucleation
368 stability. *Phys. Rev. Lett.* **2011**, *106* (5), 056101.

369 15. Dammer, S. M.; Lohse, D. Gas enrichment at liquid-wall interfaces. *Phys. Rev. Lett.* **2006**, *96* (20),
370 206101.

371 16. Pan, G.; Yang, B. Effect of surface hydrophobicity on the formation and stability of oxygen
372 nanobubbles. *ChemPhyschem* **2012**, *13* (8), 2205-2212.

373 17. An, H.; Liu, G.; Atkin, R.; Craig, V. S. J. Surface nanobubbles in nonaqueous media: looking for
374 nanobubbles in DMSO, formamide, propylene carbonate, ethylammonium nitrate, and
375 propylammonium nitrate. *Acs Nano* **2015**, *9* (7), 7596-7607.

376 18. Peng, H.; Hampton, M. A.; Nguyen, A. V. Nanobubbles do not sit alone at the solid-liquid interface.
377 *Langmuir* **2013**, *29* (20), 6123-6130.

378 19. Peng, H.; Birkett, G. R.; Nguyen, A. V. Origin of interfacial nanoscopic gaseous domains and
379 formation of dense gas layer at hydrophobic solid-water interface. *Langmuir* **2013**, *29* (49), 15266-15274.

380 20. Zhang, X. H.; Maeda, N.; Craig, V. S. J. Physical properties of nanobubbles on hydrophobic surfaces
381 in water and aqueous solutions. *Langmuir* **2006**, *22* (11), 5025-5035.

382 21. Yang, S.; Dammer, S. M.; Bremond, N.; Zandvliet, H. J. W.; Kooij, E. S.; Lohse, D. Characterization of
383 nanobubbles on hydrophobic surfaces in water. *Langmuir* **2007**, *23* (13), 7072-7077.

384 22. Weijs, J. H.; Lohse, D. Why surface nanobubbles live for hours. *Phys. Rev. Lett.* **2013**, *110* (5),
385 054501.

386 23. Lohse, D.; Zhang, X. Pinning and gas oversaturation imply stable single surface nanobubbles. *Phys.*
387 *Rev. E* **2015**, *91* (3), 031003.

388 24. Borkent, B. M.; Dammer, S. M.; Schoenherr, H.; Vancso, G. J.; Lohse, D. Superstability of surface
389 nanobubbles. *Phys. Rev. Lett.* **2007**, *98* (20), 204502.

390 25. Lauga, E.; Brenner, M. P. Dynamic mechanisms for apparent slip on hydrophobic surfaces. *Phys.*
391 *Rev. E* **2004**, *70* (2), 026311.

392 26. Liu, G.; Craig, V. S. J. Improved cleaning of hydrophilic protein-coated surfaces using the
393 combination of nanobubbles and SDS. *Acs Appl. Mater. Inter.* **2009**, *1* (2), 481-487.

394 27. Liu, G.; Wu, Z.; Craig, V. S. J. Cleaning of protein-coated surfaces using nanobubbles: an
395 investigation using a quartz crystal microbalance. *J. Phys. Chem. C* **2008**, *112* (43), 16748-16753.

396 28. Yang, S.; Duisterwinkel, A. Removal of nanoparticles from plain and patterned surfaces using
397 nanobubbles. *Langmuir* **2011**, *27* (18), 11430-11435.

398 29. Calgaroto, S.; Wilberg, K. Q.; Rubio, J. On the nanobubbles interfacial properties and future
399 applications in flotation. *Miner. Eng.* **2014**, *60*, 33-40.

400 30. Plowman, B. J.; Jones, L. A.; Bhargava, S. K. Building with bubbles: the formation of high surface
401 area honeycomb-like films via hydrogen bubble templated electrodeposition. *Chem. Commun.* **2015**, *51*
402 (21), 4331-4346.

403 31. Yang, J. W.; Duan, J. M.; Fornasiero, D.; Ralston, J. Very small bubble formation at the solid-water
404 interface. *J. Phys. Chem. B* **2003**, *107* (25), 6139-6147.

405 32. Guo, W.; Shan, H.; Guan, M.; Gao, L.; Liu, M.; Dong, Y. Investigation on nanobubbles on graphite
406 substrate produced by the water-NaCl solution replacement. *Surface Science* **2012**, *606* (17-18), 1462-
407 1466.

408 33. Liu, M.; Zhao, W.; Wang, S.; Guo, W.; Tang, Y.; Dong, Y. Study on nanobubble generation: saline
409 solution/water exchange method. *ChemPhysChem* **2013**, *14* (11), 2589-2593.

410 34. van Limbeek, M. A. J.; Seddon, J. R. T. Surface nanobubbles as a function of gas type. *Langmuir*
411 **2011**, *27* (14), 8694-8699.

412 35. Lombard, J.; Biben, T.; Merabia, S. Nanobubbles around plasmonic nanoparticles: Thermodynamic
413 analysis. *Phys. Rev. E* **2015**, *91* (4), 043007.

414 36. Zhang, L.; Zhang, Y.; Zhang, X.; Li, Z.; Shen, G.; Ye, M.; Fan, C.; Fang, H.; Hu, J. Electrochemically
415 controlled formation and growth of hydrogen nanobubbles. *Langmuir* **2006**, *22* (19), 8109-8113.

416 37. Yang, S.; Tsai, P.; Kooij, E. S.; Prosperetti, A.; Zandvliet, H. J. W.; Lohse, D. Electrolytically generated
417 nanobubbles on highly orientated pyrolytic graphite surfaces. *Langmuir* **2009**, *25* (3), 1466-1474.

418 38. Kikuchi, K.; Nagata, S.; Tanaka, Y.; Salhara, Y.; Ogumi, Z. Characteristics of hydrogen nanobubbles in
419 solutions obtained with water electrolysis. *J. Electroanal. Chem.* **2007**, *600* (2), 303-310.

420 39. Kikuchi, K.; Tanaka, Y.; Saihara, Y.; Maeda, M.; Kawamura, M.; Ogumi, Z. Concentration of hydrogen
421 nanobubbles in electrolyzed water. *J. Colloid Interf. Sci.* **2006**, *298* (2), 914-919.

422 40. Kikuchi, K.; Tanaka, Y.; Saihara, Y.; Ogumi, Z. Study of hydrogen nanobubbles in solution in the
423 vicinity of a platinum wire electrode using double-potential step chronoamperometry. *Electrochim. Acta*
424 **2006**, *52* (3), 904-913.

425 41. Zhang, X. H.; Li, G.; Maeda, N.; Hu, J. Removal of induced nanobubbles from water/graphite
426 interfaces by partial degassing. *Langmuir* **2006**, *22* (22), 9238-9243.

427 42. Hampton, M. A.; Donose, B. C.; Nguyen, A. V. Effect of alcohol-water exchange and surface
428 scanning on nanobubbles and the attraction between hydrophobic surfaces. *J. Colloid Interf. Sci.* **2008**,
429 *325* (1), 267-274.

430 43. Lachaine, R.; Boulais, E.; Meunier, M. From thermo- to plasma-mediated ultrafast laser-induced
431 plasmonic nanobubbles. *Acs Photonics* **2014**, *1* (4), 331-336.

432 44. Baffou, G.; Polleux, J.; Rigneault, H.; Monneret, S. Super-heating and micro-bubble generation
433 around plasmonic nanoparticles under cw illumination. *J. Phys. Chem. C* **2014**, *118* (9), 4890-4898.

434 45. Boulais, E.; Lachaine, R.; Hatef, A.; Meunier, M. Plasmonics for pulsed-laser cell nanosurgery:
435 Fundamentals and applications. *J. Photoch. Photobio. C* **2013**, *17*, 26-49.

436 46. Kitz, M.; Preisser, S.; Wetterwald, A.; Jaeger, M.; Thalmann, G. N.; Frenz, M. Vapor bubble
437 generation around gold nanoparticles and its application to damaging of cells. *Biomed. Opt. Express*
438 **2011**, *2* (2), 291-304.

439 47. Chen, Q.; Luo, L.; White, H. S. Electrochemical generation of a hydrogen bubble at a recessed
440 platinum nanopore electrode. *Langmuir* **2015**, *31* (15), 4573-4581.

441 48. Kikuchi, K.; Ioka, A.; Oku, T.; Tanaka, Y.; Saihara, Y.; Ogumi, Z. Concentration determination of
442 oxygen nanobubbles in electrolyzed water. *J. Colloid Interf. Sci.* **2009**, *329* (2), 306-309.

443 49. Chen, Q.; Wiedenroth, H. S.; German, S. R.; White, H. S. Electrochemical nucleation of stable N₂

444 nanobubbles at Pt nanoelectrodes. *J. Am. Chem. Soc.* **2015**, *137* (37), 12064-12069.

445 50. Nuchter, M.; Ondruschka, B.; Bonrath, W.; Gum, A. Microwave assisted synthesis - a critical
446 technology overview. *Green Chem.* **2004**, *6* (3), 128-141.

447 51. Nie, H.; Zhang, T.; Cui, M.; Lu, H.; Lovley, D. R.; Russell, T. P. Improved cathode for high efficient
448 microbial-catalyzed reduction in microbial electrosynthesis cells. *Phys. Chem. Chem. Phys.* **2013**, *15* (34),
449 14290-14294.

450 52. Zheng, J.; Liu, H.; Wu, B.; Guo, Y.; Wu, T.; Yu, G.; Liu, Y.; Zhu, D. Production of high-quality carbon
451 nanoscrolls with microwave spark assistance in liquid nitrogen. *Adv. Mater.* **2011**, *23* (21), 2460-2463.

452 53. Luo, Z.; Lu, Y.; Somers, L. A.; Johnson, A. T. C. High yield preparation of macroscopic graphene oxide
453 membranes. *J. Am. Chem. Soc.* **2009**, *131* (3), 898-899.

454 54. Wroe, R.; Rowley, A. T. Evidence for a non-thermal microwave effect in the sintering of partially
455 stabilized zirconia. *J. Mater. Sci.* **1996**, *31* (8), 2019-2026.

456 55. Xu, C.; Peng, S.; Qiao, G. G.; Gutowski, V.; Lohse, D.; Zhang, X. Nanobubble formation on a warmer
457 substrate. *Soft matter* **2014**, *10* (39), 7857-7864.

458 56. German, S. R.; Wu, X.; An, H.; Craig, V. S. J.; Mega, T. L.; Zhang, X. Interfacial nanobubbles are leaky:
459 permeability of the gas/water interface. *Acs Nano* **2014**, *8* (6), 6193-6201.

460 57. McKee, C. T.; Ducker, W. A. Refractive index of thin, aqueous films between hydrophobic surfaces
461 studied using evanescent wave atomic force microscopy. *Langmuir* **2005**, *21* (26), 12153-12159.

462 58. Takata, Y.; Cho, J. H. J.; Law, B. M.; Aratono, M. Ellipsometric search for vapor layers at liquid-
463 hydrophobic solid surfaces. *Langmuir* **2006**, *22* (4), 1715-1721.

464 59. Zhang, X. H.; Quinn, A.; Ducker, W. A. Nanobubbles at the interface between water and a
465 hydrophobic solid. *Langmuir* **2008**, *24* (9), 4756-4764.

466 60. Pan, G.; He, G.; Zhang, M.; Zhou, Q.; Tyliczszak, T.; Tai, R.; Guo, J.; Bi, L.; Wang, L.; Zhang, H.
467 Nanobubbles at hydrophilic particle water interfaces. *Langmuir* **2016**, DOI:
468 10.1021/acs.langmuir.6b01483.

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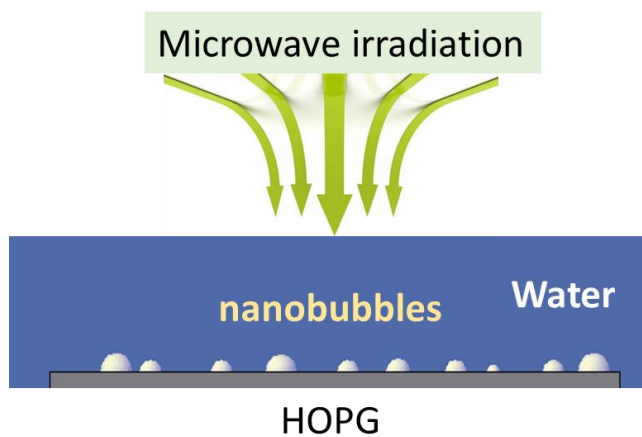
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