ISSN 1674-1056
http://cpb.iphy.ac.cn
http://iopscience.iop.org/cpb
中国物理 B
Chinese Physics
中国物理 Chinese Physics B

The properties of surface nanobubbles formed on different substrates

Zheng-Lei Zou(邹正磊), Nan-Nan Quan(权楠楠), Xing-Ya Wang(王兴亚), Shuo Wang(王硕), Li-Min Zhou(周利民), Jun Hu(胡钧), Li-Juan Zhang(张立娟), Ya-Ming Dong(董亚明)

Citation: Chin. Phys. B . 2018, 27(8): 086803. **doi:** 10.1088/1674-1056/27/8/086803

Journal homepage: http://cpb.iphy.ac.cn; http://iopscience.iop.org/cpb

What follows is a list of articles you may be interested in

Interfacial nanobubbles produced by long-time preserved cold water

Li-Min Zhou(周利民), Shuo Wang(王硕), Jie Qiu(邱杰), Lei Wang(王磊), Xing-Ya Wang(王兴亚), Bin Li(李宾), Li-Juan Zhang(张立娟), Jun Hu(胡钧)

Chin. Phys. B . 2017, 26(10): 106803. **doi:** 10.1088/1674-1056/26/10/106803

Mechanism of contact angle saturation and an energy-based model for electrowetting

Rui Zhao(赵瑞), Zhong-Cheng Liang(梁忠诚)

Chin. Phys. B . 2016, 25(6): 066801. **doi:** 10.1088/1674-1056/25/6/066801

Contact angle hysteresis in electrowetting on dielectric

Zhao Rui, Liu Qi-Chao, Wang Ping, Liang Zhong-Cheng

Chin. Phys. B . 2015, 24(8): 086801. **doi:** 10.1088/1674-1056/24/8/086801

Dynamic surface wettability of three-dimensional graphene foam

Huang Wen-Bin, Wang Guang-Long, Gao Feng-Qi, Qiao Zhong-Tao, Wang Gang, Chen Min-Jiang, Tao Li, Deng Ya, Sun Lian-Feng

Chin. Phys. B . 2014, 23(4): 046802. **doi:** 10.1088/1674-1056/23/4/046802

Superamphiphobic, light-trapping $FeSe_2$ particles with a micro-nano hierarchical structure obtained by an improved solvothermal method

Yu Jing, Wang Hui-Jie, Shao Wei-Jia, Xu Xiao-Liang

Chin. Phys. B . 2014, 23(1): 016803. **doi:** 10.1088/1674-1056/23/1/016803

The properties of surface nanobubbles formed on different substrates*

Zheng-Lei Zou(邹正磊)[1,3], Nan-Nan Quan(权楠楠)[1,3], Xing-Ya Wang(王兴亚)[3,4], Shuo Wang(王硕)[2,4], Li-Min Zhou(周利民)[2,4], Jun Hu(胡钧)[2], Li-Juan Zhang(张立娟)[3,†], and Ya-Ming Dong(董亚明)[1,‡]

[1] *Life and Environment Science College, Shanghai Normal University, Shanghai* 200234, *China*
[2] *Key Laboratory of Interfacial Physics and Technology, Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai* 201800, *China*
[3] *Shanghai Synchrotron Radiation Facility, Shanghai* 201204, *China*
[4] *University of Chinese Academy of Sciences, Beijing* 100049, *China*

(Received 23 March 2018; revised manuscript received 30 May 2018; published online 25 July 2018)

The properties and stability of the reported surface nanobubbles are related to the substrate used and the generation method. Here, we design a series of experiments to study the influence of the hydrophobicity of the substrate and the production method on the formation and properties of nanobubbles. We choose three different substrates, dodecyltrichlorosilane (DTS) modified silicon, octadecyltrichlorosilane (OTS) modified silicon, and highly oriented pyrolytic graphite (HOPG) as nanobubble substrates, and two methods of ethanol–water exchange and 4-°C cold water to produce nanobubbles. It is found that using ethanol-water exchange method could produce more and larger nanobubbles than the 4-°C cold water method. The contact angle of nanobubbles produced by ethanol–water exchange depends on the hydrophobicity of substrates, and decreases with the increase of the hydrophobicity of substrates. More interestingly, nanoscopic contact angle approaches the macroscopic contact angle as the hydrophobicity of substrates increases. It is believed that these results would be very useful to understand the stability of surface nanobubbles.

Keywords: nanobubbles, atomic force microscopy, contact angle, hydrophobic modification

PACS: 68.08.Bc, 81.07.–b, 68.37.Ps, 81.65.–b **DOI:** 10.1088/1674-1056/27/8/086803

1. Introduction

The study on nanoscale gas bubbles has become a hot topic recently due to their significant applications in water recovering, flotation, promoting the growth of plants and animals, and so on.[1–4] Nanobubble on solid-liquid surface, i.e., surface nanobubble, has a lateral size of about several tens of nanometers to several microns but with a height below 100 nm. Although numerous papers have been published since the first atomic force microscopy (AFM) image of nanobubbles was reported in 2000, there are still two issues that need to be solved, namely the super-stability and large macroscopic contact angles (liquid side) of the interfacial nanobubbles. The remarkable stability of the nanobubbles contradicts classical thermodynamics, as the Young–Laplace equation shows that such nanobubbles should not exist at all, due to the smaller radii of curvature and higher pressure inside, causing them to dissolve immediately.[5] Regarding the contact angle of nanobubble on solid surface, it was reported that there were different contact angles at different substrates,[6,7] and the contact angles also depend on different methods to produce the nanobubbles. That is to say, the stability and nanoscopic contact angle of nanobubbles are influenced by substrates, temperature, gas type, and production methods,[8–11] and the physical properties of the interface nanobubbles will also be affected by the properties of the hydrophobic substrates. A lot of substrates have been used to produce nanobubbles, such as highly oriented pyrolytic graphite (HOPG),[12] mica, gold,[13] polystyrene,[14] silicon nitride (Si_3N_4), and silane modified silicon surfaces. The reported nanoscopic contact angles of surface nanobubbles have a large range of variations. Typically, direct immersion,[15] temperature change,[16] electrochemical reactions,[12] ethanol–water exchange,[17] and 4-°C cold water change have been used to produce nanobubbles.[18]

Here, we choose two types substrates and two methods to produce nanobubbles. It is more reasonable to compare their stability and interfacial properties, such as sizes and contact angles on surface. Specifically, one substrate is naturally atomically flat HOPG. Another substrate is silane modified silicon surfaces. Two methods, ethanol–water exchange and long-time preserved cold water, are employed to produce nanobubbles. Ethanol-water exchange is the most effective, and cooling cold water is a convenient and clean method to produce nanobubbles. These designs allow us to study the

*Project supported by the National Natural Science Foundation of China (Grant Nos. 11290165, 11305252, and U1532260), the Knowledge Innovation Program of the Chinese Academy of Sciences, China (Grant No. KJZD-EW-M03), and the Key Research Program of Frontier Sciences, Chinese Academy of Sciences, China (Grant No. QYZDJ-SSW-SLH019).

†Corresponding author. E-mail: zhanglijuan@sinap.ac.cn
‡Corresponding author. E-mail: ymdong@shnu.edu.cn

© 2018 Chinese Physical Society and IOP Publishing Ltd

physical properties of nanobubbles under the same experimental conditions.

2. Experimental section

2.1. Materials

Dodecyltrichlorosilane (DTS) (93%) and octadecyltrichlorosilane (OTS) (95%) were purchased from Sigma Aldrich. Toluene ($\geq$ 99.5%, AR), chloroform ($\geq$ 99.0%, AR), ethanol ($\geq$ 99.8%, GR), H_2SO_4 (98%, GR), and H_2O_2 (30%, GR) were purchased from the Sinopharm Chemical Reagent Co., LTD. The highly oriented pyrolytic graphite (HOPG, ZYH grade) was purchased from NT-MDT, Moscow, Russia. Deionized pure water (room temperature) was prepared with an ELGA Purelab Classic water purification system to obtain a conductivity of 18.2 MΩ·cm. To prevent possible contamination, such as polydimethylsiloxane (PDMS), glass instruments were ultrasonic cleaned with ethanol and deionized pure water for 30 min, and then dried at 120 °C for 2 h before use.

2.2. Substrate modification

Silicon wafers (1.2 cm ×1.2 cm) were cut from a p-type Si wafer. First, silicon wafers were rinsed with a large amount of deionized pure water, then sonicated in ethanol and deionized pure water for 10 min each and dried under a stream of nitrogen gas every time before use. Next, the pre-cleaned silicon wafers were put into the piranha solution (7:3 vol% of H_2SO_4 (98%) and H_2O_2 (30%)) and kept for half an hour at 80 °C. After that, the piranha-cleaned silicon wafers were rinsed with deionized pure water and ethanol and then dried under a stream of nitrogen gas immediately. The DTS and OTS solution was prepared separately by dissolving 0.25 ml of DTS and OTS within 50 ml of toluene each in a clean room (temperature $\sim$ 25 °C, relative humidity $\sim$ 46%). Then we placed the piranha-cleaned wafers into the DTS or OTS solution and kept them in a sealed container for 24 h. When the modified silicon wafers were removed from the solution, they were quickly rinsed and sonicated with chloroform, toluene, ethanol, and deionized pure water in turn for 15 min each. After drying under the nitrogen gas, the modified substrates were kept for half an hour at 70 °C. They can be used at least 24 h later in a clean room. Before being used, they were sonicated in toluene, ethanol, and deionized pure water for 10 min and dried under a stream of nitrogen gas.

2.3. Nanobubble Formation

For a comparison, the HOPG was also used as substrate to produce nanobubbles. The HOPG was fresh cleaved with double faced tapes every time before use. The interfacial nanobubbles were produced by two methods. One was the conventional solvent exchange method in which the ethanol was replaced by deionized water in a AFM fluid cell.[19] Another method was the newly developed cold water method in which the long-time preserved cold water was directly added onto the substrate surface without any exchange process.[18] The cooling cold water was obtained by persevering the deionized water at 4 °C refrigerator for 72 h.

2.4. AFM imaging

PF-QNM imaging was performed on a Bruker Multimode 8 SPM with a NanoScope V controller. The liquid cell, silicone O-ring, and tubing were cleaned with ethanol and then with water before being dried. The A cantilever was silicon nitride with a nominal spring constant of 0.35 $N{\cdot}m^{-1}$ (SNL-10, Bruker). The probe was cleaned with plasma cleaner PDC-32G for 3 min beforehand. The PF-QNM amplitude was set at 200 nm, the PF-QNM frequency was 2 kHz, and the scan rate was 0.977 Hz.

2.5. Contact angle measurement

The macroscopic contact angles of water on the HOPG, DTS modified silicon, and OTS modified silicon substrates were measured using a DSA30 (KRÜSS GmbH, Germany). A digital camera and the supplied calibration software were used to record the profile of the 5-μl water droplet which was dropped onto the prepared surfaces, from which the dynamic contact angles were determined. Every sample was measured at three locations and measured 5 times.

3. Results

3.1. Hydrophobic substrates modified by alkyl silane

In order to compare the properties of nanobubbles on different hydrophobic substrates, we modify the silicon surface with alkyl silane as nanobubble substrates according to Zhang's method.[20] Two kinds of alkyl silane, dodecyltrichlorosilane and octadecyltrichlorosilane, are chosen to modify the silicon surfaces.[21] Another HOPG is also chosen to compare with the two substrates. It is expected that they have different hydrophobicities after the modification. First, we measure the macroscopic contact angles of silicon surfaces modified with DTS and OTS as well as HOPG. The measured macroscopic contact angles of water droplets on DTS, OTS modified silicon, and HOPG surfaces are $106^\circ \pm 4^\circ$, $110^\circ \pm 5^\circ$, and $76^\circ \pm 5^\circ$, respectively. Then we measure the roughness of the modified silicon wafers and HOPG. It is found that they have almost similar roughness, i.e., 0.37 nm, 0.45 nm, and 0.7 nm for DTS modified silicon, OTS modified silicon, and HOPG, respectively. Figure 1 shows the AFM images of modified silicon wafers and HOPG in air. All the surfaces are very clear, except that the modified surfaces have a few small particles, which may be caused by the excessive hydrolysis of alkyl silane during the process of modification.

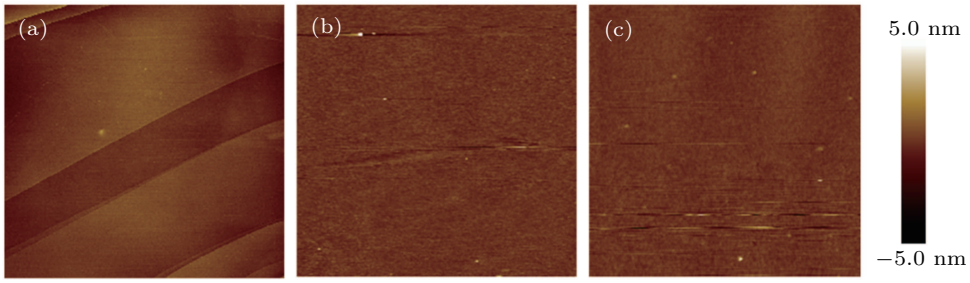


Fig. 1. (color online) TM-AFM images of (a) HOPG, (b) DTS modified silicon, and (c) OTS modified silicon in air. The root-mean-square (RMS) roughnesses of the surface of panels (a), (b), and (c) are 0.7 nm, 0.37 nm, and 0.45 nm, respectively. Scan size is 5 μm ×5 μm, and the data scale is 10 nm.

3.2. PF-QNM AFM imaging of nanobubbles on different substrates

We use two methods, ethanol–water exchange and 4-°C cold water (cooling water), to produce nanobubbles on the above substrates. The detailed experimental steps and mechanisms of the ethanol-water exchange have been described previously.[19,22–24] Typically, ethanol in liquid cell is replaced by a large amount of water and then nanoscale gas bubbles would be produced on the surface. For the 4-°C cold water method reported by Zhou *et al.*,[18] nanobubbles would be generated by quickly injecting 4-°C cold water that is preserved for a long time on substrate due to different temperatures between the cold water and the substrate. The formed nanobubbles are imaged by PF-QNM-mode AFM.[25] In such mode, the interfacial nanobubble could be imaged with a very small force (∼ 400 pN) to avoid possible deformation, as previously reported.[26–28]

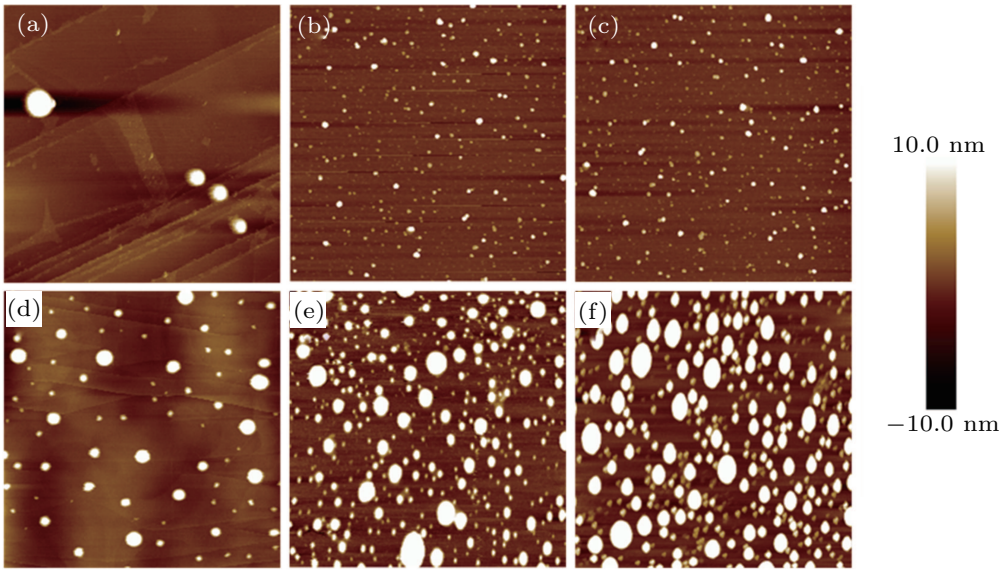


Fig. 2. (color online) The PF-QNM images of nanobubbles on (a) and (d) HOPG, (b) and (e) DTS modified silicon, and (c) and (f) OTS modified silicon substrates. Panels (a), (b), and (c) are images with 4-°C cold water method, and panels (d), (e), and (f) are images with ethanol–water exchange method. Scan size: 5 μm ×5 μm, data scale: 20 nm.

Figure 2 shows AFM images of nanobubbles produced by two different methods on three different substrates. We find that different methods and substrates produce nanobubbles in different conditions. First, nanobubbles produced by 4-°C cold water method could be formed on HOPG, DTS modified silicon, and OTS modified silicon surfaces, as shown in Figs. 2(a)–2(c). Then, by using ethanol–water exchange method, nanobubbles are produced on those surfaces, as shown in Figs. 2(d)–2(f). It can be seen that the sizes and numbers of the formed nanobubbles are quite different. The size and the number of nanobubbles formed on DTS/OTS modified surfaces by using ethanol-water exchange method are larger than those by using 4-°C pure water. However, on the HOPG surface, the nanobubbles formed by using the two methods are similar in size, but the number of nanobubbles with ethanol-water exchange method is larger than that with 4-°C cold water method. Comparing the two nanobubble production methods, it is also found that the number of nanobubbles is always small in the case of 4-°C cold water. This might be due to the fact that less gas is released by the temperature difference between the water and the substrate; while for the ethanol-water exchange method, more gas could be released during the exchange between the water and ethanol. The steps or defect of HOPG will provide the nuclei to form the nanobubbles. Therefore, these results indicate that different substrates and different methods are important for the size and number of

nanobubbles produced.

3.3. Morphology of nanobubbles on different substrates

We further analyze the contact angles of nanobubbles produced by ethanol-water exchange and cooling water methods on the above three substrates. The shape of the nanobubble is fitted by a spherical cap, as shown in Fig. 3. The contact angle of nanobubbles could be obtained by the following equation:

$$\theta = 180^\circ - 2\tan^{-1}\left[\frac{H}{W}\right], \tag{1}$$

where θ is the contact angle, H is the height of nanobubble, and W is the half lateral size of the nanobubble. The height and the lateral width of nanobubbles can be measured by using the offline software of AFM.

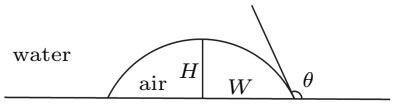


Fig. 3. The schematic diagram of the nanobubble on the surface. The contact angle can be calculated from Eq. (1).

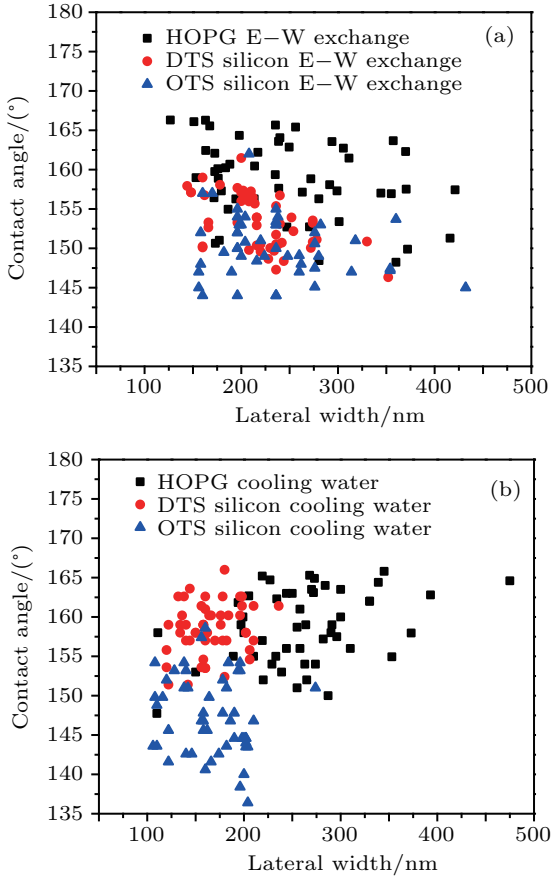


Fig. 4. (color online) The relationship between contact angles of nanobubbles and their lateral widths on different surfaces produced by (a) ethanol–water (E–W) exchange, and (b) 4-°C water method.

Figure 4(a) shows the relationship between contact angles of nanobubbles and their lateral widths on HOPG, DTS modified silicon, and OTS modified silicon surfaces by ethanol-water exchange method. It is found that the ranges of nanoscopic contact angles of nanobubble produced on HOPG, DTS silicon, and OTS silicon surfaces are 155°–170°, 145°–160°, and 140°–160°, respectively. By analyzing more details, it can be found that the average contact angle of nanobubble formed on HOPG is slightly higher than that of the other two modified surfaces but with a larger variance, and the contact angle of nanobubbles formed on DTS or OTS modified silicon slightly decreases with the increase of the size. For the case of 4-°C cold water, as shown in Fig. 4(b), the ranges of nanoscopic contact angles of nanobubble produced on HOPG, DTS silicon, and OTS silicon are 150°–170°, 155°–175°, and 135°–160°, respectively. The results are more complicated. First, the size of the bubbles formed on HOPG is evidently larger than those on the other two substrates, and the average contact angle is almost constant as the size changes. Meanwhile, the size of the bubbles formed on DTS and OTS modified silicon is very small, and the lateral size is below 200 nm. The contact angle of nanobubbles on DTS modified silicon is larger than that on OTS modified silicon, which implies that the contact angle might depend on the modified surfaces while the lateral size of nanobubbles is below 200 nm.

Figure 5 shows the comparison of macroscopic contact angle and nanoscopic contact angle of nanobubbles using two methods on three substrates. It can be seen that the macroscopic contact angle of droplet and the nanoscale contact angle of nanobubble on the same substrate are quite different for each substrate used here. More interestingly, with the increase of the macroscopic contact angle of the substrates, the difference between macroscopic contact angle and nanoscopic contact angle is getting smaller and smaller.

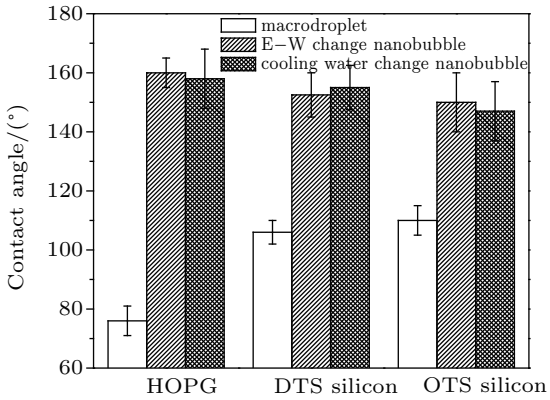


Fig. 5. Contact angles of nanobubbles produced on HOPG, DTS modified silicon, and OTS modified silicon by different methods compared with macroscale contact angles of macrodroplets.

4. Discussion

Before discussing the results above, it should be noted that we have prepared several very flat substrates based on known chemical methods, which allows us to produce nanobubbles under the same conditions. Therefore, we can compare the properties of nanobubbles more reasonably.

1) The sizes and numbers of the nanobubbles depend on the substrate and the method of production. Comparing hydrophobic surfaces, less hydrophobic HOPG and more hydorphobic DTS/OTS modified silicon, the number of nanobubbles produced on DTS/OTS modified silicon are larger than on less hydrophobic HOPG. Generally, the ethanol-water exchange method can produce more nanobubbles on the same substrate than 4-°C cold water method, due to the fact that the exchange method can release more dissolved gas during the exchange process comparing to the gentle temperature difference.

2) The contact angles of nanobubbles are different for different substrates and methods. We know that contact angle is an important parameter to describe the hydrophobicity of the surface. It can be seen from the above results that in both cases of ethanol-water exchange method and 4-°C cold water method, the average nanoscopic contact angles of nanobubbles produced by two methods decrease slightly with the increase of the hydrophobicity of the substrates, even though some data points have a large error bar. Some studies have reported that the shape of a surface nanobubble is simply determined by the degree of gas supuersaturation and is independent of the hydrophobicity of the surface.[29,30] It can be explained that the contact angle of nanobubble would become smaller at a more hydrophobic surface. This might be caused by the interaction between the bubbles and the substrates.

5. Conclusions

In this study, we use three substrates and two production methods to investigate the influence of substrate and method used on the formation of surface nanobubbles. The results show that more and larger nanobubbles could be produced using ethanol-water exchange method than using the 4-°C cold water method. More nanobubbles will be formed on hydrophobic modified DTS/OTS silicon than on less hydrophobic HOPG. For small nanobubbles, such as lateral size below 200 nm, the contact angles strongly depend on the hydrophobicity of the substrates compared to the large bubble. More interestingly, with the increase of the macroscopic contact angle of the substrates, the difference between the macroscopic contact angle and the nanoscopic contact angle is getting smaller and smaller. These results will help to understand and further study the stability of surface nanobubbles.

Acknowledgment

The authors would like to thank the staff of the beamline 08U1 A at the Shanghai Synchrotron Radiation Facilities (SSRF) for their suggestions and help.

References

[1] Wu Z, Chen H, Dong Y, Mao H, Sun J, Chen S, Craig V S and Hu J 2008 *J. Colloid Interface Sci.* **328** 10
[2] Sobhy A and Tao D 2013 *Int. J. Miner. Process.* **124** 109
[3] Ebina K, Shi K, Hirao M, Hashimoto J, Kawato Y, Kaneshiro S, Morimoto T, Koizumi K and Yoshikawa H 2013 *PLoS One* **8** e65339
[4] Zhu J, An H, Alheshibri M, Liu L, Terpstra P M, Liu G and Craig V S 2016 *Langmuir* **32** 11203
[5] Plesset M S and Sadhal S S 1982 *Appl. Sci. Res.* **38** 133
[6] Wang X, Zhao B, Ma W, Wang Y, Gao X, Tai R, Zhou X and Zhang L 2015 *ChemPhysChem.* **16** 1003
[7] Wang L, Wang X, Wang L, Hu J, Wang C L, Zhao B, Zhang X, Tai R, He M, Chen L and Zhang L 2017 *Nanoscale* **9** 1078
[8] Borkent B M, De B S, Mugele F and Lohse D 2010 *Langmuir* **26** 260
[9] Limbeek M A J V and Seddon J R T 2011 *Langmuir* **27** 8694
[10] Berkelaar R P, Seddon J R, Zandvliet H J and Lohse D 2012 *ChemPhysChem.* **13** 2213
[11] Zhao R and Liang Z C 2016 *Chin. Phys. B* **25** 066801
[12] Zhang L, Zhang Y, Zhang X, Li Z, Shen G, Ye M, Fan C, Fang H and Hu J 2006 *Langmuir* **22** 8109
[13] Kameda N and Nakabayashi S 2008 *Chem. Phys. Lett.* **461** 122
[14] Abhinandan Agrawal, Juhyun Park, Du Yeol Ryu, Hammend T, Russell P and Mckinley H 2005 *Nano Lett.* **5** 1751
[15] Otelaja O, Gatica S and Misra P *APS March Meeting*
[16] Xu C, Peng S, Qiao G G, Gutowski V, Lohse D and Zhang X 2014 *Soft Matter* **10** 7857
[17] Lou S, Gao J, Xiao X, Li X, Li G, Zhang Y, Li M, Sun J, Li X and Hu J 2002 *Mater. Charact.* **48** 211
[18] Zhou L M , Wang S, Qiu J, Wang L, Wang X Y, Li B, Zhang L J and Hu J 2017 *Chin. Phys. B* **26** 106803
[19] Zhang X H, Maeda N and Craig V S 2006 *Langmuir* **22** 5025
[20] Wang X L, Di Q F, Zhang R L, Gu C Y, Ding W P and Gong W 2012 *Acta Phys. Sin.* **61** 166801 (in Chinese)
[21] Ishida N, Inoue T, Miyahara M and Higashitani K 2000 *Langmuir* **16** 6377
[22] Lohse D and Zhang X 2015 *Rev. Mod. Phys.* **87** 981
[23] Zhang X H, Zhang X D, Lou S T, Zhang Z X, Sun J L and Hu J 2004 *Langmuir* **20** 3813
[24] Lou S T, Ouyang Z Q, Zhang Y, Li X J, Hu J, Li M Q and Yang F J 2000 *J. Vac. Sci. Technol. B* **18** 2573
[25] Ji C, Zhang L Y, Dou S X and Wang P Y 2011 *Acta Phys. Sin.* **60** 1358 (in Chinese)
[26] Zhao B, Song Y, Wang S, Dai B, Zhang L, Dong Y, Lü J and Hu J 2013 *Soft Matter* **9** 8837
[27] Walczyk W, Schon P M and Schonherr H 2013 *J. Phys.: Condens. Matter.* **25** 184005
[28] Walczyk W and Schonherr H 2013 *Langmuir* **29** 620
[29] Lohse D and Zhang X 2015 *Phys. Rev. E* **91** 031003
[30] Liu Y and Zhang X 2014 *J. Chem. Phys.* **141** 8468