Supporting Materials

In situ tunable bubble wettability with fast response induced by

solution surface tension

Yunlong Jiao,^{†, a)} Chuanzong Li,^{‡, a)} Xiaodong Lv, [‡] Yiyuan Zhang,[†] Sizhu Wu,^{*, ‡} Chao Chen, [†] Yanlei Hu,[†] Jiawen Li,[†] Dong Wu,^{*, †} and Jiaru Chu, [†]

[†] CAS Key Laboratory of Mechanical Behavior and Design of Materials, Department of Precision Machinery and Precision Instrumentation, University of Science and Technology of China, Hefei 230026, PR China.

[‡] School of Instrument Science and Opto-electronics Engineering, Hefei University of Technology, Hefei, 230009, PR China.

^{a)} Y.L. Jiao and C.Z. Li contributed equally to this work.

* Corresponding author: <u>dongwu@ustc.edu.cn</u> and <u>sizhuwu@hfut.edu.cn</u>



Figure S1. Schematic of laser manufacturing process. It can be seen that square-pillar arrays are distributed regularly on the surface after vertically crossed laser scanning.



Figure S2. WCA and BCA on the laser induced substrate and heated sample. (a-b) The laser-induced sample shows superhydrophilic with a WCA of $\sim 1^{\circ}$ and superaerophobic with a BCA of $\sim 157^{\circ}$. (c-d) After heating 30 min, the sample shows superhydrophobic with a WCA of $\sim 156^{\circ}$ and superaerophilic with a BCA of $\sim 6^{\circ}$.



Figure S3. Exhibition of capturing smaller bubbles in carbonic acid solution by utilizing the heated samples. (a) No air-film formed on the unheated titanium surface because of its superaerophobicity. (b) There is a bubble forming at the fabricated area because of superaerophilicity after heating.



Original surface

Figure S4. Relationship between liquid contact angle in air and gas contact angle in liquid on the same original surface.

According to the Young's equation, the liquid contact angle on the original surface can be expressed as follows

$$Cos\theta_L = (\gamma_{SG} - \gamma_{LS})/\gamma_{LG}$$
 (1)

For the same substrate and certain organics (alcohol), γ_{SG} keeps constant and γ_{LG} decreases with the increase of alcohol volume fraction in solution. Figure 2d shows that θ_L gradually becomes small so the surface shows a high adhesion to the liquid with high alcohol volume fraction. In short, as all of LCA measurements are conducted on the same substrate and we just employ different concentrations of alcohol solution as test liquid. Therefore, the surface shows different wettability with

certain organics due to the variation of γ_{LG} . According to the Young's wetting theory, the liquid with smaller surface tension tends to wet the surface and shows a smaller contact angle. While the liquid with high surface tension tends to keep sphere on the substrate with a high contact angle. It should be noted that surface roughness is not discussed in the Young's equation, the tunable range of LCA on the laser induced sample is much wider than that of on the original surface, which is closely related to the amplifying effect of wettability by multiscale micro/nanostructure.^[3,4]

When the same substrate is placed under liquid (FigureS4), the gas contact angle on the original surface can be expressed as follows:

$$Cos\theta_{G} = (\gamma_{LS} - \gamma_{SG}) / \gamma_{LG} (2)$$

It can be calculated from equation (1) and (2) that θ_L and θ_G meet the following relationship:^[5]

$$\theta_G = 180^\circ - \theta_L$$
 (3)

According to the equation (3), the hydrophobic substrate will be aerophilic in an aqueous medium in an ideal case, while the hydrophilic substrate will be aerophobic. Therefore, the variation trend between LCA and BCA is opposite in **Figure 2e**.



Figure S5. The mechanism of in situ tunable bubble wettability on the original substrate in alcohol solution. (a-d) The BCA keeps constant all the time despite of the increase of alcohol volume fraction in solution. (e) The original substrate shows aerophobic and the bubble is full of air molecules. (f) The competition process between air molecule and alcohol molecule at the triple contact line. It can be seen that the alcohol molecule could not move into the bubble because of lack of micro/nanostructure which provides entrance, so the bubble on the smooth substrate could not be compressed using in situ tunable method. (g) The pinning effect of triple contact line at solid/air/liquid interface.



Figure S6. Theoretical analysis for selectively absorbing gas bubbles in solution. (a) The heated Ti foil shows superaerophilicity in pure water so a thin air-film covers the surface at initial moment. When a bubble contacts the air-film, it would be merged and pass though the microholes under the effect of buoyancy. With the increase of bubble volume, the bubble gradually grows bigger and finally escapes from the upper side of the foil. (b) The heated Ti foil shows superaerophobicity in alcohol solution with high volume fraction so the liquid would fill in the microholes and forms a layer of water-film. When a bubble contacts the water film, it would be blocked because of incompatibility. So the bubbles are blocked by the Ti foil on the low side.

Movie S1-S5



Movie S1. Process of capturing smaller bubbles in carbonic acid solution on the unheated/heated titanium samples.



Movie S2. In situ tunable process of BCA on the laser induced sample from a thin gas-film (superaerophilic) to a big bubble (superaerophobic) and escaping from the solid substrate.



Movie S3. In situ tunable process of BCA on the original sample.



Movie S4. Dynamically controlling underwater light path on-off.



Movie S5. CO_2 collection process in water medium by using designed device.