Facile fabrication of hierarchical structured superhydrophobic surface and its ultra dynamic water repellency

Yizhou Shen^{1,2,*}, Senyun Liu¹, Chunling Zhu^{1,*}, Jie Tao² and Guanyu Wang²

¹ *College of Aerospace Engineering, Nanjing University of Aeronautics and Astronautics, Nanjing 210016, P. R. China*

² *College of Material Science and Technology, Nanjing University of Aeronautics and Astronautics, Nanjing 210016, P. R. China*

*Corresponding author: Dr. Yizhou Shen E-mail: shenyizhou@nuaa.edu.cn

Abstract: Here we presented an ultra water-repellent surface with the ternary composite structures, expecting to provide an inspiration to the application research. Our strategy is to design macro ridge structures on the superhydrophobic surface, which is prepared by modifying the composite micro-nanoscale hierarchical structures with FAS-17. The effect of micro-nanoscale hierarchical structures on the non-wettability were firstly analyzed and examined for achieving a perfect unity of microstructures and property. On this basis, we designed the macro ridge structures and obtained the final sample surface, which could not only display a strong superhydrophobicity with the apparent contact angle reaching 161° and the contact angle hysteresis reducing to 1.5° , but also exhibit the capacity to compel the impact water droplet to bounce off within an extreme short time (5.5 ms).

Keywords: ultra water-repellency; composite structures; superhydrophobicity; impact droplet

1. Introduction

Extreme non-wetting (superhydrophobic; the contact angle $> 150^\circ$, the contact angle hysteresis $< 10^\circ$) behavior on the solid surface has been a well discussed topic in the past decades, and is also considered to be one of the most valuable research issues due to its wide applications in our daily life, such as self-cleaning [1-3], staying dry [4], drag reduction [5,6], anti-icing [7,8], anti-corrosion [9], *etc.* With the unremitting efforts of scientists for many years, some significant progresses have been gained in understanding the principles of the non-wetting behavior based on the nature-inspired investigation ranging from the plant leaves to the skin of organisms (like fish, butterfly, and water strider, *etc.*) [10-12]. The non-wetting behavior of the superhydrophobic surface mainly depends on the cooperation of surface textures and chemical compositions (surface free energy). On a flat substrate, the water contact angle can reach only 120° by lowering the surface free energy (the lowest surface free energy value yet recorded, 6.7 mJ m^{-2} , was attained for a surface with regularly aligned closest-hexagonal-packed CF_3 groups) [13]. However, through designing the composite micro-nanoscale hierarchical structures on the basis of low surface free energy, the water contact angle may be raised to 150° or beyond [14].

Currently, various strategies have been proposed for imparting surface textures to the metal or glass substrates, such as micromachining [15,16], laser or plasma etching [17,18], sol-gel processing [19], colloidal self-assembly [20], template technique [21,22], electrostatic spinning [23], and physical or chemical vapor deposition [24], and the generated superhydrophobic surfaces also show a high non-wettability (water

contact angle being up to 160° and contact angle hysteresis below 5°) and exhibit a potential application value in various industrial fields [25]. However, their practical application competence cannot be thoroughly evaluated only based on the static characterizations of the contact angle and the contact angle hysteresis. In practical application situations, these superhydrophobic surfaces will be continuously impacted by the water droplets, *i.e.*, under a dynamic condition, and compel the impact water droplets to spread out to maximum deformation, then retracts to a certain extent and finally bounce off the surfaces [26]. The entire contact time between the impact water droplet and the surface is considered to be crucial, because it directly determines the extents of thermal and energy conversions in the practical application situations [27]. Thus, the real evaluations on the superhydrophobic surfaces should not only characterize the contact angle and the contact angle hysteresis, but also take into account the contact time of the impact water droplet with the superhydrophobic surface.

Previously reported literatures indicate that the contact time mainly depends on the properties of the liquid droplets, the surface non-wettability, kinematic parameters, and a minimum contact time value (about 12 ms) has been also proposed based on a water droplet impacting on an extreme hydrophobic surface (the contact angle reaching 150° and contact angle hysteresis lower than 5°) [28-30]. However, this contact time is still higher than the other significant timescales, not meeting the actual applied requirement, such as freezing.

In our opinion, the really non-wetting surface should not only display a high

superhydrophobicity with a high contact angle and a low contact angle hysteresis, but also cause an extreme short contact time between the impact water droplet and the surface. Herein, we reported an ultra water-repellent surface with the ternary composite structures (macro ridge, microscale patterns, and nanowire structures), furthermore probed the capacity to compel the impact water droplet to bounce off within an extreme short time.

2. Experimental section

2.1 Materials

Ti6Al4V titanium alloy was provided by Baoji Titanium Industry Co., Ltd., P. R. China, and processed into some small square pieces ($10\text{ mm} \times 10\text{ mm} \times 1\text{ mm}$) via a wire-electrode cutting machine. Fluoroalkylsilane (FAS-17) was purchased from Tokyo Chemical Industry Co., Ltd. to modify the hierarchical micro/nanoscale structures. All the other chemicals in this experiment were analytical grade and purchased from the Sinopharm chemical reagent Co., Ltd., P. R. China.

2.2 Operation procedure

The proposed ultra water-repellent surface was prepared via adding the macro ridge structures to the micro-nanoscale hierarchical structured superhydrophobic surface, as illustrated schematically in Fig. 1. For the preparation of the superhydrophobic surface, a smooth Ti6Al4V substrate (purchased from Baoji Titanium Industry Co., Ltd., China, and cut into a square sample with the size of $10\text{ mm} \times 10\text{ mm} \times 1\text{ mm}$) was firstly sand-blasted to construct the microscale pit structures with an adjacent distance of $\sim 30\text{ }\mu\text{m}$ using the 150 grit alumina particles at

0.5 MPa for 10 s. Then, a hydrothermal growth technique was used to plant a layer of TiO₂ nanowires on the surface of microscale pit structures. The sand-blasted sample was placed in an autoclave containing 30 ml 1 M NaOH aqueous solution at a certain temperature for a certain time. Subsequently, the sample was sufficiently rinsed with distilled water and immersed in a dilute 0.1 M HCl aqueous solution for 0.5 h. And an annealing treatment at 500 °C (heating rate is 2 °C min⁻¹) for 3 h was necessary to obtain the TiO₂ nanowires [31,32]. Lastly, the sample containing the composite structures of microscale pits and nanowires was modified in 1 wt% FAS-17 ethanol solution for 24 h and dried for 2 h at 120 °C, obtaining the primary superhydrophobic sample.

To reduce the contact time between the impact water droplet and the superhydrophobic surface, we designed some special macro ridge structures (cross section is an equilateral triangle with 0.6 mm side length), and initially manufactured on the smooth substrate using a hyperfine CNC milling machine. Subsequently, based on the optimal process parameters (*i.e.*, hydrothermal growth time and temperature) for the as-prepared superhydrophobic surface, we finally achieved the ultra water-repellent surface with the ternary composite structures of the special macro ridge, microscale patterns, and nanowire structures.

2.3 Characterizations and non-wettability test

The morphologies of the sample surface were observed using a field emission scanning electron microscopy (FE-SEM; Hitachi S4800, Japan). The 3D morphology of the microscale pit structures was obtained via a 3D microscope (Laica

DVM5000HD, Germany). Transmission electron microscopy (TEM) was performed on a JEOL JEM-2010 transmission electron microscope. The X-ray diffraction (XRD) analysis was carried out by an X-ray diffractometry (GAXRD; UltimaIV, Rigaku Co., CuK α radiation, Japan) operating at 50 kV and 40 mA. The chemical component of the surfaces was studied by X-ray photoelectron spectroscopy (XPS) using an X-ray photoelectron spectrometer (Kratos AXIS UltraDLD, Japan).

Regarding the characterization of the superhydrophobicity, we chose a 4 μ L water droplet as the reference droplet for ensuring the water droplet not to produce gravity deformation. According to C. Dorrer's reported result [33], the reference measured droplet should meet the demand, that the diameter of the water droplet was less than capillary length of 2.7 mm (for water). The apparent contact angle (APCA) and contact angle hysteresis (CAH) of a 4 μ L water droplet on the sample surfaces were measured by a contact angle analyzer (Kruss DSA100, Germany). And the average value of three measurements was determined. In order to ensure that the 4 μ L water droplet successfully dripped on the surfaces, we chose the ultrafine syringe needle with the inner diameter of only 0.03 mm, which was also hydrophobized with FAS-17.

A high-speed camera (Photron Mini 100 and Olympus i-speed 716), each filming at a 10,000 frames per second, was used to record the contact process of an impact droplet on the sample surface, and the contact time was directly obtained from the CCD camera. In this measurement, the droplets were released from a fixed height of 50 mm over the samples, and the initial impact velocity is approximately 1 m s⁻¹,

following the formula $v = \sqrt{2gh}$).

3. Results and discussion

3.1 Growth mechanism of nanowires for superhydrophobic surfaces

Our strategy is to design macro ridge structures based on the as-prepared superhydrophobic surfaces in this study. As mentioned above, the microstructure is a very key factor in maintaining the non-wetting performance of the solid surface. Generally, the ideal microstructure for the superhydrophobicity is widely considered to be a class of hierarchical textures containing the microscale (dozens of micrometers) and nanoscale (hundreds of nanometers) structures [34]. Therefore, the morphology and structure are also firstly studied in this work, as shown in Fig. 2. After hydrothermally growing, a layer of nanowires are successfully planted on the surface of the sand-blasted microscale pits (see Fig. 2c). Combining the observation of the microscale pits (Fig. 2b), we find that the composite micro-nanoscale structures exhibit a greater dimension span from $\sim 30\ \mu\text{m}$ to hundreds of nanometers, and uniformly distribute on the substrate surface. Such composite structures are well expected to improve the hydrophobicity.

Considering the subsequent self-assembly of hydrophobic groups on the sample surfaces, it is necessary to analyze the component and the formation of the outside nanowires. We therefore track and analyze each step in the hydrothermal growth process. Fig. 2d-f depicts the morphologies of the nanowire structures after the hydrothermal synthesis, acid pickling and annealing. It can be found that the morphology of the nanowire structures has been determined in the hydrothermal

synthesis process, and the diameter of nanowires is approximately 100 nm. The subsequent processes, *i.e.*, acid pickling and annealing, have little or even no effect on the nanowire morphology and dimension. Additionally, rows of the regular crystal planes and the dot diffraction are observed in the HRTEM images and FFT images (see Fig. 2g-i), indicating the synthetic nanowire being single-crystal. The regular crystal planes with a interplanar distance of 0.7 nm in Fig. 2g are corresponding to the (200) crystal planes of $\text{Na}_2\text{Ti}_2\text{O}_4(\text{OH})_2$. This interplanar distance seems to be less than the theoretical value (0.936 nm) of d_{200} in $\text{Na}_2\text{Ti}_2\text{O}_4(\text{OH})_2$ titanate, because the sample dehydration is caused by the impact high-speed electrons in TEM measuring process [35]. Furthermore, after acid pickling, the regular crystal planes ($d_{020} = 0.2$ nm) is corresponding to the (020) crystal planes of $\text{H}_2\text{Ti}_2\text{O}_5 \cdot \text{H}_2\text{O}$, as shown in Fig. 2h. Also, the interplanar distance of 0.34 nm is almost coinciding with the value of interplanar distance (101 crystal planes) of anatase TiO_2 , demonstrating the final product being the single-crystal anatase TiO_2 . The XRD can also further prove the change of component of the nanowire structures, as shown in Fig. 3. We can draw a conclusion that although the morphology of the nanowires can be firstly formed in the hydrothermal growing process, the component is transferred to the single-crystal anatase TiO_2 in the final annealing process. In the entire process, the related chemical reactions are as following:

The produced TiO_2 nanowires covering on the surface of microscale pit structures will be fluoridated to achieve the hydrophobicity. Therefore, a self-assembling technique is applied to graft a layer of hydrophobic groups to the surface of TiO_2 nanowires, as shown in Fig. 4. Under the action ethanol hydrolysis, the polar end-groups in the FAS-17 will be transferred to Si-OH groups. Subsequently, the dehydration condensation reaction is taken place between the Si-OH groups and the TiO_2 nanowires to form the Si-O-Ti bonds, resulting in the long-chain hydrophobic groups grafting to the surface of the composite micro-nanoscale structures. Meanwhile, the other Si-OH groups can also engage the condensation reaction each other to produce a layer of hydrophobic groups' membrane.

Comparing the XPS chemical component before and after the hydrophobic groups self-assembling (Fig. 5), it is worth noting that the intensity peaks of F1s and FKLL can be seen after the FAS-17 modification. Also, the peaks corresponding to the $-\text{CF}_2$ and $-\text{CF}_3$ are both seen in the high resolution XPS spectrum of C1s (Fig. 5b), indicating the hydrophobic molecular membrane being successfully grafted to the surface of TiO_2 nanowire structures, and changing the chemical components of the surface of micro-nanoscale structures.

3.2 Effect of nanowires on superhydrophobicity

As we know, nanowires play a significant important role in the superhydrophobicity comparing the microscale structures [36]. In order to provide a better as-prepared superhydrophobic sample for designing macro ridge structures, we examine the influences of hydrothermal growth time and temperature on the

morphology and non-wettability. Fig. 6 shows the morphologies of the TiO₂ nanowire structures with the different hydrothermal growth time. It can be easily found that increasing the growth time benefits to promote the growth of nanowires, showing the length change (from 1 to 5 μm) and the various morphologies. When the growth time is 3 h, the produced TiO₂ nanowires do not twine at the distal ends, exhibiting acicular structures. With the time increasing, the phenomenon of distal ends twining becomes more and more obvious, along with the increase of length of nanowires. After modifying with FAS-17, the superhydrophobicity also seems to appear some changes with APCA increasing from 153° to 161°, and the CAH lowering from 5.5° to ~ 1.5°, as shown in Fig. 8a.

Generally, the water droplet on the composite micro-nanostructured superhydrophobic surface follows the Cassie-Baxter wetting model, *i.e.*, the heterogeneous contact interface of solid/liquid and liquid/gas [37]. In this case, the apparent contact interface of the water droplet is actually composed of solid/liquid and liquid/gas. Since the contact angle of a droplet on air is considered as 180°, the APCA (θ^*) can be expressed as:

$$\cos \theta^* = f \cos \theta + f - 1 \quad (1)$$

where f and θ are the area fraction and Young contact angle of the solid, respectively. Thus, we can draw the conclusion that reducing the solid contact area fraction (*i.e.*, capturing more air pockets) is important for improving the superhydrophobic properties. Thus, under the action of the micro-nanoscale structures, a large amount of air pockets are induced and locked underneath the water droplet, leading to the

apparent contact angle reaching a high value ($> 150^\circ$) and a low contact angle hysteresis ($< 10^\circ$) [38]. Thus, when the hydrothermal growth time reaches 8 h, the gradually elongating TiO_2 nanowires trap more air pockets, causing an increased superhydrophobicity, especially greatly reducing the contact angle hysteresis (to $\sim 1.5^\circ$). This also should be attributed to the distal ends twining of the nanowires, because the air pockets underneath the droplet become easy to flow with the assistance of twining ridge. However, the length of nanowires is so long with the hydrothermal growth time being up to 10 h or 12h that the hierarchical structures are un conspicuous, resulting in the apparent contact angle slightly lowering. But the contact angle hysteresis does not exhibit an obvious difference because of the distal ends of nanowires still twining.

As another important parameter, the hydrothermal growth temperature is also analyzed how to influence the nanowires and the superhydrophobicity. Fig. 7 shows the morphologies of TiO_2 nanowires with different hydrothermal growth temperatures. We can find that there is a significant difference among the morphologies of these sample surfaces. Below the 200°C , nanowires cannot be well grown on the sand-blasted substrate with the replacement of nanosheets. And the dimensions of these nanosheets are too small to cause a good size coordination effect for the superhydrophobicity. The apparent contact angle only locates between 145° and 155° , and the contact angle hysteresis is also very high (from 12° to 6°), as shown in Fig. 8b. When the temperature reaches 200°C , nanowire structures successfully appear on the surfaces, and cause a high apparent contact angle of 158° and a contact angle

hysteresis of 4° . Subsequently, with the temperature further increasing to 240°C , the diameter of nanowires gradually reduces with the increasingly bushy distribution, and the superhydrophobicity also shows a corresponding change (the highest apparent contact angle (161°) and the lowest contact angle hysteresis (1.5°) are yet at 220°C). This is mainly because when the temperature is 240°C , the as-synthesized TiO_2 nanowires are very fine and bushy so that the air pockets trapped under the water droplet slightly decrease, resulting in a little reduction of superhydrophobicity.

Here, it can be concluded that the optimal hydrothermal growth parameters are 220°C and 8 h for the as-prepared superhydrophobic sample surface with the apparent contact angle reaching 161° and the contact angle hysteresis reducing to 1.5° .

3.3 Addition of macrostructures to superhydrophobic surfaces

As mentioned above, the basic idea of this work is to design macrostructures on the as-prepared superhydrophobic surface to reduce the contact time of the impact water droplet on the surface, proposing a class of ultra water-repellent surface containing the ternary composite structures. According our previous studies, a minimum contact time of approximately 12 ms has been theoretically proposed and experimentally verified based on the water droplet impacting on an extreme hydrophobic surface without any macrostructures. However, the contact time will be further reduced by adding the macrostructure to the superhydrophobic surface and properly altering the water droplet hydrodynamics. Based on the as-prepared superhydrophobic surface with the optimal hydrothermal growth parameters, we

therefore designed the ‘minus-shaped’, ‘three-forked’, and ‘cross-shaped’ macro ridge structures (cross section is an equilateral triangle with 0.6 mm side length). According to the reported results [39], the retraction speed of the impact water droplet on the macroscopic ridge peak follows:

$$V_p \approx \sqrt{(2\gamma)/[\rho(h-a)]} \quad (2)$$

where a is the height of the ridge structures, h is the thickness of the flattened water droplet after impacting. Meanwhile, combining the other expressions, the contact time reduction (Δt) is given by

$$\Delta t \approx \frac{\sqrt{6}}{6} (1 - \sqrt{1 - \frac{a}{h}}) \quad (3)$$

based on the 'minus-shaped' macroscopic ridge on the superhydrophobic surface. If there is no macroscopic ridge ($a = 0$), the contact time reduction (Δt) is zero. Furthermore, the contact time reduction is considered to be almost constant, no matter whether the height of the ridge structures is equal to or greater than the thickness of the flattened water droplet. Thus, we designed a large enough height ($a \approx 520 \mu\text{m}$ with an equilateral triangle of 0.6 mm side length) of the ridge structures to significantly influence the retraction hydrodynamics of a bouncing water droplet.

Subsequently, we filmed the contact processes of the water droplets impacting on these surfaces using a high-speed camera, as shown in Fig. 9. It takes about 12 ms for the impact water droplet (initial diameter $D_0 = 2 \text{ mm}$, impact velocity $V_0 = 1 \text{ m s}^{-1}$) on the above as-prepared superhydrophobic surface without macro structure to complete the spreading and retracting processes, (see Fig. 9a). However, when the water droplet impacts on the macro ridge structured superhydrophobic surfaces, the contact time is

further reduced from 12 ms to 5.6 ms, as shown Fig. 9b-d. Comparing the superhydrophobic surface without macrostructures, the macrostructured superhydrophobic surfaces can alter the water droplet hydrodynamics, causing the impact water droplet being divided into several smaller water droplets. When the water droplet impacts on the ‘minus-shaped’ macrostructures, the contact time is shorted to 7.8 ms. Under the triggering of the macrostructure, an asymmetry retracting process is employed to reduce the distance and time required for retracting, resulting in the contact time decreasing to 7.8 ms. Also, the retracting process is partly integrated into the process of spreading out to the maximum deformation.

As we see, the overall contact process of the water impacting on these surfaces mainly consists of the spreading and retracting processes. Considering the initial kinematic behavior of the impact water droplets, the time required for spreading out to the maximum deformation is a constant. According to the law of conservation of mass, the time (t) required for a water droplet spreading out to maximal deformation can be also calculated by assuming the water droplet spreads into a cylinder of diameter D and thickness h (see Fig. 10). This spreading process is followed by the law of mass conservation, and the relationship can be expressed by:

$$\frac{1}{4}\pi d^2 V_0 = \pi D h V_R \quad (4)$$

Where d is the diameter of the truncated sphere, V_0 is the impact velocity, and V_R is the velocity at the edge of the splat during spreading. And the equation (4) can change to

$$\frac{V_R}{V_0} = \frac{d^2}{4Dh} \quad (5)$$

At the time of the impact water droplet spreading out to maximum diameter (D_{max}), the height of the flattened water droplet can be given by

$$h = \frac{2D_0^3}{3D_{max}^2} \quad (6)$$

It can be considered to be a constant value owing to a little variation of the height (h).

Equation (5) and (6) can give

$$\frac{dD}{dt} = 2V_R = \frac{3}{16}V_0 \frac{D_{max}^2}{D_0} \frac{1}{D} \quad (7)$$

Integrating equation (7) can deduce

$$t = \frac{8D_0D^2}{3V_0D_{max}^2} \quad (8)$$

Thus, when the diameter D of the spreading cylinder reaches the maximum diameter (D_{max}), the time (t) can be obtained by

$$t = \frac{8D_0}{3V_0} \quad (9)$$

Thus, the time (t) of water droplet spreading out to maximal deformation is also calculated as about 5.5 ms.

Also, it can be seen that the overall contact time of the water droplet impacting on the superhydrophobic surfaces containing the ‘three-forked’ or ‘cross-shaped’ macro ridge structure is very closed to the calculated spreading time. This is attributed to the retracting process being completely integrate into the spreading process under the action of the complex macro ridge structures. And we reasonably believe this spreading time is a limited contact time of an water droplet impacting on a solid surface.

4. Conclusions

In conclusion, we firstly fabricated a class of superhydrophobic surface via modifying the composite micro-nanoscale hierarchical structures constructed by a cooperation of sand-blasting and hydrothermally growing with FAS-17. Then, some complex macro ridge structures were designed and added to the as-prepared superhydrophobic surfaces, achieving the ultra water-repellent surfaces with ternary composite structures. These macrostructured superhydrophobic surfaces not only displayed a strong superhydrophobicity with the apparent contact angle reaching 161° and the contact angle hysteresis reducing to 1.5° , but also exhibited the capacity to compel the impact water droplet to bounce off within an extreme short time (5.5 ms). The new surface will provide some inspirations to design the superhydrophobic surfaces with more outstanding dynamic water-repellent properties.

Acknowledgments

The authors gratefully acknowledge the National Basic Research Program of China (“973” Project) (Grant No. 2015CB755800), the Postdoctoral Innovative Talents Support Program (BX201600073), the National Science Foundation of China (No. 51671105, 51475231, and 11372335), and A Project Funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions.

References

- [1] S. Nishimoto, B. Bhushan, Bioinspired self-cleaning surfaces with superhydrophobicity, superoleophobicity, and superhydrophilicity, RSC Adv. 3 (2013) 671-690.

- [2] Y. Lai, Y. Tang, J. Gong, D. Gong, L. Chi, C. Lin, Z. Chen, Transparent superhydrophobic/superhydrophilic TiO_2 -based coatings for self-cleaning and anti-fogging, *J. Mater. Chem.* 22 (2012) 7420-7426.
- [3] D. Kumar, X. Wu, Q. Fu, J. W. C. Ho, P. D. Kanhere, L. Li, Z. Chen, Hydrophobic sol-gel coatings based on polydimethylsiloxane for self-cleaning applications, *Mater. Design* 86 (2015) 855-862.
- [4] H. Ogihara, J. Xie, J. Okagaki, T. Saji, Simple method for preparing superhydrophobic paper: spray-deposited hydrophobic silica nanoparticle coatings exhibit high water-repellency and transparency, *Langmuir* 28 (2012) 4605-4608.
- [5] C. Lee, C. J. Kim, Underwater restoration and retention of gases on superhydrophobic surfaces for drag reduction, *Phys. Rev. Lett.* 106 (2011) 014502.
- [6] S. Srinivasan, W. Choi, K. C. Park, S. S. Chhatre, R. E. Cohen, G. H. McKinley, Drag reduction for viscous laminar flow on spray-coated non-wetting surfaces, *Soft Matter* 9 (2013) 5691-5702.
- [7] P. Guo, Y. Zheng, M. Wen, C. Song, Y. Lin, L. Jiang, Icephobic/anti-icing properties of micro/nanostructured surfaces, *Adv. Mater.* 24 (2012) 2642-2648.
- [8] S. Zheng, C. Li, Q. Fu, W. Hu, T. Xiang, Q. Wang, M. Du, X. Liu, Z. Chen, Development of stable superhydrophobic coatings on aluminum surface for corrosion-resistant, self-cleaning, and anti-icing applications, *Mater. Design* 93 (2016) 261-270.

- [9] N. Wang, D. Xiong, Superhydrophobic membranes on metal substrate and their corrosion protection in different corrosive media, *Appl. Surf. Sci.* 305 (2014) 603-608.
- [10] M. Liu, L. Jiang, Switchable adhesion on liquid/solid interfaces, *Adv. Funct. Mater.* 20 (2010) 3753-3764.
- [11] X. Deng, L. Mammen, Y. Zhao, P. Lellig, K. Müllen, C. Li, H. J. Butt, D. Vollmer, Transparent, thermally stable and mechanically robust superhydrophobic surfaces made from porous silica capsules, *Adv. Mater.* 23 (2011) 2962-2965.
- [12] Y. Lin, Y. Shen, A. Liu, Y. Zhu, S. Liu, H. Jiang, Bio-inspired fabricating the hierarchical 3D porous structure superhydrophobic surfaces for corrosion prevention, *Mater. Design* 103 (2016) 300-307.
- [13] T. Nishino, M. Meguro, K. Nakamae, M. Matsushita, Y. Ueda, The lowest surface free energy based on- CF_3 alignment, *Langmuir* 15 (1999) 4321-4323.
- [14] N. Wang, D. Xiong, Y. Deng, Y. Shi, K. Wang, Mechanically robust superhydrophobic steel surface with anti-icing, UV-durability, and corrosion resistance properties, *ACS Appl. Mater. Interfaces* 7 (2015) 6260-6272.
- [15] W. M. Zhu, A. Q. Liu, X. M. Zhang, D. P. Tsai, T. Bourouina, J. H. Teng, X. H. Zhang, H. C. Guo, H. Tanoto, T. Mei, G. Q. Lo, D. L. Kwong, Switchable magnetic metamaterials using micromachining processes, *Adv. Mater.* 23 (2011) 1792-1796.
- [16] F. He, Y. Cheng, L. Qiao, C. Wang, Z. Xu, K. Sugioka, K. Midorikawa, J. Wu, Two-photon fluorescence excitation with a microlens fabricated on the fused silica chip by femtosecond laser micromachining, *Appl. Phys. Lett.* 96 (2010) 041108.

- [17] G. S. Oehrlein, R. J. Phaneuf, D. B. Graves, Plasma-polymer interactions: A review of progress in understanding polymer resist mask durability during plasma etching for nanoscale fabrication, *J. Vac. Sci. Technol. B* 29 (2011) 010801.
- [18] B. Balu, V. Breedveld, D. W. Hess, Fabrication of “roll-off” and “sticky” superhydrophobic cellulose surfaces via plasma processing, *Langmuir* 24 (2008) 4785-4790.
- [19] Q. Zhao, L. Y. L. Wu, H. Huang, Y. Liu, Ambient-curable superhydrophobic fabric coating prepared by water-based non-fluorinated formulation, *Mater. Design* 92 (2016) 541-545.
- [20] B. D. Hatton, J. Aizenberg, Writing on superhydrophobic nanopost arrays: Topographic design for bottom-up assembly, *Nano Lett.* 12 (2012) 4551-4557.
- [21] Y. Gao, I. Gereige, A. E. Labban, D. Cha, T. T. Isimjan, P. M. Beaujuge, Highly transparent and UV-resistant superhydrophobic SiO₂-coated ZnO nanorod arrays, *ACS Appl. Mater. Interfaces* 6 (2014) 2219-2223.
- [22] Y. Li, W. Jia, Y. Song, X. Xia, Superhydrophobicity of 3D porous copper films prepared using the hydrogen bubble dynamic template, *Chem. Mater.* 19 (2007) 5758-5764.
- [23] B. K. Brettmann, S. Tsang, K. M. Forward, G. C. Rutledge, A. S. Myerson, Free surface electrospinning of fibers containing microparticles, *Langmuir* 28 (2012) 9714-9721.

- [24] N. Miljkovic, D. J. Preston, R. Enright, E. N. Wang, Electric-field-enhanced condensation on superhydrophobic nanostructured surfaces, *ACS Nano* 7 (2013) 11043-11054.
- [25] N. Wang, D. Xiong, M. Li, Y. Deng, Y. Shi, K. Wang, Superhydrophobic surface on steel substrate and its anti-icing property in condensing conditions, *Appl. Surf. Sci.* 355 (2015) 226-232.
- [26] T. Deng, K. K. Varanasi, M. Hsu, N. Bhate, C. Keimel, J. Stein, M. Blohm, Nonwetting of impinging droplets on textured surfaces, *Appl. Phys. Lett.* 94 (2009) 133109.
- [27] L. Chen, Z. Li, Bouncing droplets on nonsuperhydrophobic surfaces, *Phys. Rev. E* 82 (2010) 016308.
- [28] M. Reyssat, A. Pépin, F. Marty, Y. Chen, D. Quéré, Bouncing transitions on microtextured materials, *Europhys. Lett.* 74 (2006) 306-312.
- [29] D. Richard, C. Clanet, D. Quéré, Surface phenomena: Contact time of a bouncing drop, *Nature* 417 (2002) 811.
- [30] N. Wang, D. Xiong, Y. Lu, S. Pan, K. Wang, Y. Deng, Y. Shi, Design and fabrication of the lyophobic slippery surface and its application in anti-icing, *J. Phys. Chem. C* 120 (2016) 11054-11059.
- [31] J. Y. Liao, B. X. Lei, H. Y. Chen, D. B. Kuang, C. Y. Su, Oriented hierarchical single crystalline anatase TiO_2 nanowire arrays on Ti-foil substrate for efficient flexible dye-sensitized solar cells, *Energy Environ. Sci.* 5 (2012) 5750-5757.

- [32] L. F. Que, Z. Lan, W. X. Wu, J. H. Wu, J. M. Lin, M. L. Huang, High-efficiency dye-sensitized solar cells based on ultra-long single crystalline titanium dioxide nanowires, *J. Power Sources* 266 (2014) 440-447.
- [33] C. Dorrer, J. Rühe, Some thoughts on superhydrophobic wetting, *Soft Matter* 5 (2009) 51-61.
- [34] X. Liu, W. Wu, X. Wang, Z. Luo, Y. Liang, F. Zhou, A replication strategy for complex micro/nanostructures with superhydrophobicity and superoleophobicity and high contrast adhesion, *Soft Matter* 5 (2009) 3097-3105.
- [35] B. Liu, J. E. Boercker, E. S. Aydil, Oriented single crystalline titanium dioxide nanowires, *Nanotechnology* 19 (2008) 505604.
- [36] D. J. Lee, H. M. Kim, Y. S. Song, J. R. Youn, Water droplet bouncing and superhydrophobicity induced by multiscale hierarchical nanostructures, *ACS Nano* 6 (2012) 7656-7664.
- [37] G. Whyman, E. Bormashenko, How to make the Cassie wetting state stable?, *Langmuir* 27 (2011) 8171-8176.
- [38] M. Sun, C. Luo, L. Xu, H. Ji, Q. Ouyang, D. Yu, Y. Chen, Artificial lotus leaf by nanocasting, *Langmuir* 21 (2005) 8978-8981.
- [39] J. C. Bird, R. Dhiman, H. M. Kwon, K. K. Varanasi, Reducing the contact time of a bouncing drop, *Nature* 503 (2013) 385-388.

Figure caption list

Fig. 1. The schematic diagram of the fabrication of the ultra water-repellent surface.

Fig. 2. The SEM images of (a) smooth substrate, (b) microscale pit structure, and (c) micro-nanoscale hierarchical structures. Also, the TEM images of the (d) as-synthesized titanate nanowire, (e) hydrogen titanium oxide nanowire, and (f) TiO₂ nanowire. (g), (h), and (i) are the corresponding HRTEM photos of these nanowires, insets are the FFT (fast fourier transformation) images.

Fig. 3. The XRD patterns of the nanowires, (a) sand-blasted substrate; (b) after hydrothermally growing; (c) after acid pickling; (d) after annealing.

Fig. 4. Schematic representation of the self-assembling process of the hydrophobic groups.

Fig. 5. The XPS spectrum (1) before and (2) after the hydrophobic groups self-assembling, (a) survey spectrum; (b) high resolution spectrum.

Fig. 6. The SEM images of the TiO₂ nanowires with the hydrothermal growth time of (a) 3 h, (b) 5 h, (c) 8 h, (d) 10 h, and (e) 12 h.

Fig. 7. The SEM images of the TiO₂ nanowires with the hydrothermal growth temperature of (a) 140 °C, (b) 160 °C, (c) 180 °C, (d) 200 °C, (e) 220 °C, and (f) 240 °C.

Fig. 8. The superhydrophobicity with the changing hydrothermal growth time (a) and temperature (b).

Fig. 9. The macro ridge structures on the as-prepared superhydrophobic surface, and the corresponding the contact processes of the impact water droplets. For more details,

please see Supplementary video 1-4.

Fig. 10. Schematic diagram of the law of the mass conservation during the spreading process.

Fig. 1. The schematic diagram of the fabrication of the ultra water-repellent surface.

Fig. 2. The SEM images of (a) smooth substrate, (b) microscale pit structure, and (c) micro-nanoscale hierarchical structures. And, the TEM images of the (d) as-synthesized titanate nanowire, (e) hydrogen titanium oxide nanowire, and (f) TiO_2 nanowire. (g), (h), and (i) are the corresponding HRTEM photos of these nanowires, insets are the FFT (fast fourier transformation) images.

Fig. 3. The XRD patterns of the nanowires, (a) sand-blasted substrate; (b) after hydrothermally growing; (c) after acid pickling; (d) after annealing.

Fig. 4. Schematic representation of the self-assembling process of the hydrophobic groups.

Fig. 5. The XPS spectrum (1) before and (2) after the hydrophobic groups self-assembling, (a) survey spectrum; (b) high resolution spectrum.

Fig. 6. The SEM images of the TiO₂ nanowires with the hydrothermal growth time of (a) 3 h, (b) 5 h, (c) 8 h, (d) 10 h, and (e) 12 h.

Fig. 7. The SEM images of the TiO₂ nanowires with the hydrothermal growth temperature of (a) 140 °C, (b) 160 °C, (c) 180 °C, (d) 200 °C, (e) 220 °C, and (f) 240 °C.

Fig. 8. The superhydrophobicity with the changing hydrothermal growth time (a) and temperature (b).

Fig. 9. The macro ridge structures on the as-prepared superhydrophobic surface, and the corresponding the contact processes of the impact water droplets. For more details, please see Supplementary video 1-4.

Fig. 10. Schematic diagram of the law of the mass conservation during the spreading process.