Characterization and Application of Nanomaterials (2021) Volume 4 Issue 2
doi:10.24294/can.v4i2.1334

REVIEW ARTICLE

Review of super-hydrophobic materials research

Chengbao Liu[1,2*], Minjia Li[1], Xiaojie Liu[1,2], Zhigang Chen[1,2]

[1] School of Chemistry, Biology and Materials Engineering, Suzhou University of Science and Technology, Suzhou 215009, Jiangsu Province, China. E-mail: lcb@mail.usts.edu.cn

[2] Jiangsu Key Laboratory for Environmental Functional Materials, Suzhou 215009, Jiangsu Province, China

ABSTRACT

We reviewed the research on super-hydrophobic materials. Firstly, we introduced the basic principles of super-hydrophobic materials, including the Young equation, Wenzel model, and Cassie model. Then, we summarized the main preparation methods and research results of super-hydrophobic materials, such as the template method, soft etching method, electrospinning method, and sol-gel method. Among them, the electrospinning method that has developed in recent years is a new technology for preparing micro/nanofibers. Finally, the applications of super-hydrophobic materials in the field of coatings, fabric and filter material, anti-fogging, and antibacterial were introduced, and the problems existing in the preparation of super-hydrophobic materials were pointed out, such as unavailable industrialized production, high cost, and poor durability of the materials. Therefore, it is necessary to make a further study on the application of the materials in the selection, preparation, and post-treatment.

Keywords: Super-hydrophobic Materials; Basic Principles; Preparation Method; Application

ARTICLE INFO

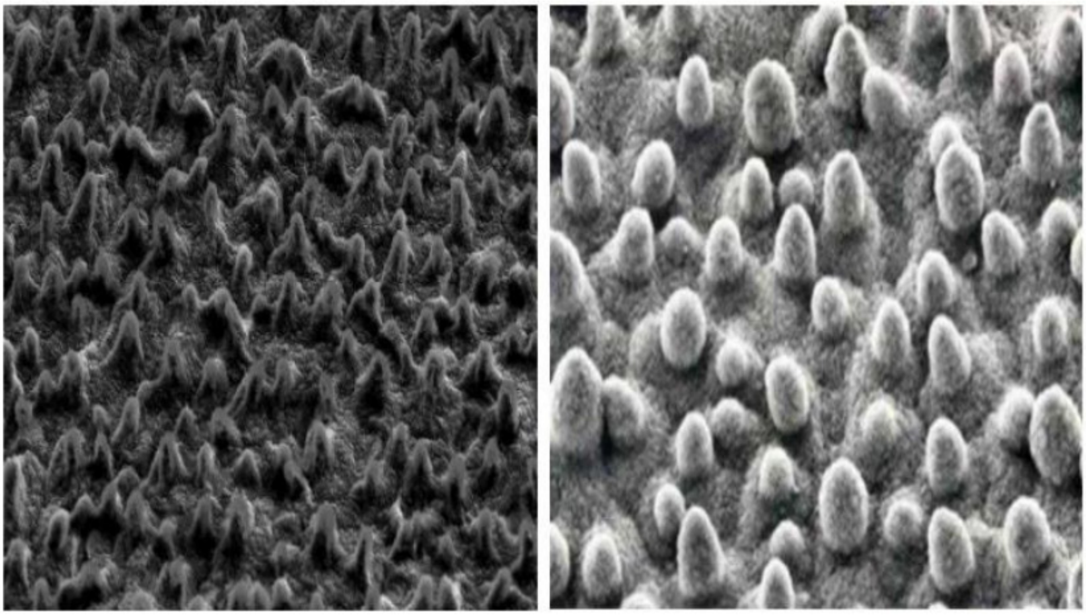
Received: 22 June 2021
Accepted: 14 August 2021
Available online: 21 August 2021

COPYRIGHT

1. Introduction

Super-hydrophobic material refers to a material with a contact angle of the material surface and water greater than 150° and a rolling angle less than 10^{o}[1,2]. In nature, many plant foliage and waterfowl feathers have super-hydrophobic water characteristics, such as dragonfly wing[3], water strider leg[4], lotus leaf[5], etc. (**Figure 1**), among which the most typical is the "lotus leaf effect". The surfaces of these moving, plants contain special geometry with contact angles with water above 150°. In the lotus leaf[6–8], the lotus leaf surface (**Figure 2**) is composed of many papillae with an average diameter of 5 to 9 m, and the contact and rolling angles of water on that surface are (161.0 ± 2.7)° and 2°, respectively[6–8]. Each papilla is composed of a nanostructured branching with an average diameter of (124.3 ± 3.2) nm. These nanostructures on micromastoid especially, play an important role in super-hydrophobicity.

Figure 1. Dragonfly wings **(a)**, water strider legs **(b)**, lotus leaf **(c)**.



(a) SEM plot of the surface of the lotus leaf

(b) SEM plot of high magnification

Figure 2. Microstructure of the surface of the lotus leaf.

Through the research, people do not only find many super-hydrophobic phenomena in nature and their surface structures but also make artificial synthetic super-hydrophobic surfaces by various methods. At present, there are two ways to prepare super-hydrophobic surfaces[9]: (1) modification of low surface energy material on a surface with micro-nano rough structure; and (2) construction of a micro-nano rough structure on the surface of the material with low surface energy.

In recent years, the preparation of super-hydrophobic surface materials with biological tissues and structures as bionic objects has become one of the hotspots in the field of material research. Jiang Lei research group is the first research group involved in this field in China. Their main preparation methods are the template method, soft etching method, electrospinning method, and at present, its research focus is ultra-super-hydrophobic materials, namely ultra-hydrophobic ultra-hydrophobic oil. It will introduce the super-hydrophobic materials from the basic principles of super-hydrophobic water, its preparation method and its application.

2. The rationale of super-hydrophobic water

The wettability of the solid surface is mainly determined by the chemical composition of the solid surface and surface microstructure. The wettability of the solid liquid, that is, hydrophilic and hydrophobicity is generally expressed by the contact angle θ of the liquid and solid phase. The shape formed when the droplet stays on a smooth solid surface by the droplet on its surface is determined by the interface tension of the three-phase contact surface of the solid, liquid and gas, whose contact angle can be described by the Young equation[10]:

$$\cos\theta = (\gamma_{SA} - \gamma_{SL}) / \gamma_{LA} \qquad (1)$$

γ_{SA}, γ_{SL} and γ_{LA} represent the interface tension of solid-gas, solid-liquid and liquid-gas individually. At this time, the three surface tension interactions are at equilibrium.

But the Young equation is an idealized model suitable only for ideally smooth solid surfaces. If it is a solid surface with a certain roughness, there are some D-value between the apparent and intrinsic contact angles. The actual contact area of solid and liquid is more than the apparent contact area. The droplets fully enter the empty groove of the rough surface structure. Therefore, it must consider the impact of roughness on the hydrophobic performance. At present, Wenzel model[11] and Cassie model[12] are

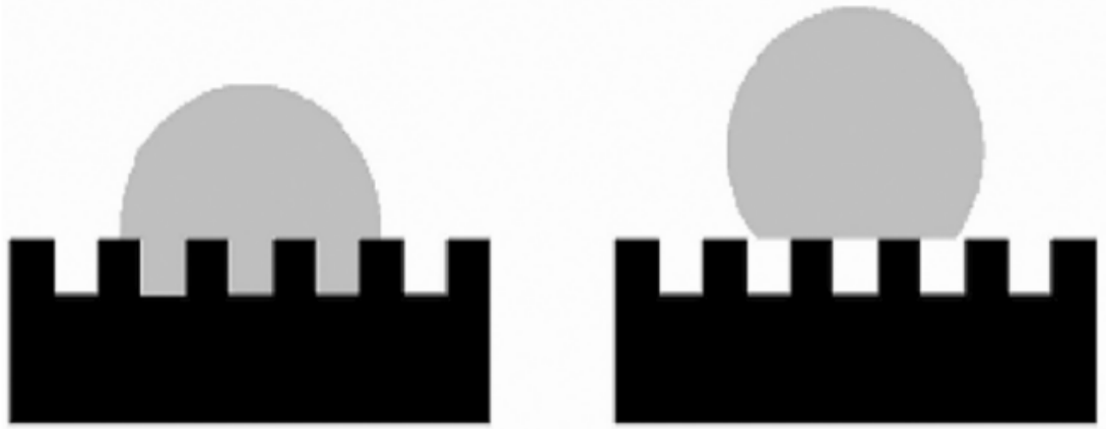


Figure 3. Schematic diagram of the Wenzel and Cassie models[13].

relatively mature in the related basic theoretical research. The schematic diagram shows in **Figure 3**.

2.1 Wenzel model

The Wenzel model considers that the droplets contact with the solid surface, and infiltrate into the surface groove. It increases the surface contact area, and the apparent geometrically observed contact area is less than the actual solid-liquid contact area when the apparent contact angle is greater than the intrinsic contact angle:

$$\cos\theta_w = \mathrm{r}(\gamma_{\mathrm{SA}} - \gamma_{\mathrm{SL}})/\gamma_{\mathrm{LA}} = r\cos\theta \qquad (2)$$

In the formula, r is the surface roughness factor, the ratio of the actual surface area to the projected area, and θ_w is the apparent contact angle of the rough surface.

From Equation (2), increasing the value of the surface rough factor r can make the original hydrophobic surface more hydrophobic. However, the Wenzel model also has its limitations, which do not apply in the case of solid surfaces composed of different types of chemicals.

2.2 Cassie model

The Cassie model suggests that water droplets are suspended on solid surface convex grooves and that liquid droplets fall on a composite phase composed of solid-liquid and solid-gas interfaces. Therefore, its equation is:

$$\cos\theta' = f_1\cos\theta_1 + f_2\cos\theta_2 \qquad (3)$$

θ' is the apparent contact angle in the Cassie model, f_1 and f_2 are the ratio of liquid contact to the solid surface and air, respectively, and 1 and 2 are the contact angles of liquid to solid surface and air, respectively. Where $f_1 + f_2 = 1$, 2 = 180°, the formula (3) can be written as:

$$\cos\theta' = f_1\cos\theta_1 - f_2 = f_1\cos\theta_1 + f_1 - 1 \qquad (4)$$

From the above model, preparing a surface with a special structure can improve the contact angle of the surface. The Cassie model suggests that droplets are suspended on solid surface convex grooves and do not seep into the surface topography. In the Cassie model, droplets are usually scrollable on the surface.

The Wenzel and Cassie models provide a strong theoretical basis for the preparation of super-hydrophobic surfaces, and although they are currently under some controversy[14,15].

Moreover, the contact angles in the above three cases characterize the performance of water droplets on the horizontal surface and are more oblique in reality. The state of the droplet on the slope can be characterized by the rolling angle, the critical surface tilt angle of the drop when the droplet begins to roll on the solid surface. The smaller tilt angle if the droplet begins to roll indicates that the super-hydrophobic water on this surface is better[16].

In conclusion, the contact and rolling angles jointly characterize the mutual permeability of the solid-liquid and the hydrophilic-hydrophobicity exhibited. The larger contact angle and the smaller rolling angle indicate the stronger hydrophobicity of the material surface[17–19].

3. Preparation method of super-hydrophobic materials

3.1 Template method

The template method takes a substrate with a cavity structure as a template, and covers the casting film liquid on the template by dumping, casting and spin coating. The proposed method has the advantages of simplicity, effectiveness and large area replication, and has good application prospects in practice.

Zheng Jianyong *et al.* used calcium carbonate particles to form a polymer super-hydrophobic surface by thermal pressure and acid etching[20]. After the test, its droplet static contact angle reached 152.7° while its rolling angle was < 3°.

Liu *et al.* coated a PDMS film with candle soot as a template, and calcination removed the template to form super-hydrophobic fiberglass cotton with a rough fiber mesh surface on the glass substrate[21]. After detection, the material has a contact angle with the water of up to 163° and can be used to optimize oil-water separation and air filtration, showing excellent thermal stability.

Ke *et al.* took taro leaves as the parent plate, constructed the surface structure with subtle cavity by template method, and then modified by an impregnated coating method, which significantly improved the hydrophobic performance[22].

3.2 Etching method

Etching technology refers to the process of etching the target surface into a micro rough appearance by physical or chemical methods. Laser etching, plasma, chemical and, photo etching are several commonly used micro etching methods. The etching method can make more accurate operation and design of the surface structure to regulate surface hydrophobicity. While the cost is high, and it is not suitable for large-scale production.

Qi *et al.*[23] used the chemical etching method assisted by metal ions (e. g., Ag^+, Cu^{2+}, Cr^{3+}) to process Zinc substrate to get rough structure surface, and the water contact angle measured by fluoro silane modification is up to (161 ± 2)°. In addition, they explored the effects of different metal ions on the surface morphology and hydrophobic properties, and then they found that the addition of metal ions could enhance the strength and stability of the super-hydrophobic surface.

Sung-Woon *et al.*[24] took SF_6 as a plasma source, obtained with the plasma etching method, and then C_4F_8 as a plasma source, and then a carbon-fluorine membrane was deposited on the silicon surface with a micron-grade rod structure. After testing, the contact angle with water is 165°.

3.3 Phase separation method

The phase separation method is the membrane form in which the system produces two or multiple phases during the control conditions. This method is easy to regulate and simple to operate. It can prepare uniform and large areas of superhydrophobic films, which has great value in practical aspects.

Liu *et al.*[25] put butyl methacrylate (BMA) and glycol dimethyl acrylic (EDMA) in a mixture of 1, 4-cis-butanediol (BDO) with N-methyl-pyrrolidone (NMP) to in situ polymerization. A super-hydrophobic porous polymer surface with a micro-nano rough structure with a water contact angle of 159.5° and a rolling angle below 3.1°.

Liu Jianfeng *et al.*[26] used butyl methyl acrylate (BMA) and ethylene glycol dimethyl acrylate (EDMA) as monomers and azo diisonitrile (AIBN) as an initiator for thermal polymerization on the glass substrate, thus forming a micro/nanocomposite roughness structure on the surface with a static water contact angle of up to 159.5°.

3.4 Chemical vaporous deposition

Chemical vapor deposition is a simple, efficient, inexpensive, and effective method, which prepares rough structures without the limitation of substrate shape.

Deng Tao *et al.* prepared aligned dense nanowire structures on silicon wafers by chemical vapor deposition[27]. They placed washed silicon wafers in inductively coupled plasma bins, deposited silicon nanowires while etching, and then modified them with fluoro silane to create a silicon nanowire surface structure with a line width of about 100 nm.

3.5 Electrospinning method

Electrospinning is a new technology to prepare micro/nanoscale fibers. It places a polymer solution or melt in a high-pressure electrostatic field, and is stretched under the electric field Coulomb force to form a jet fine flow that falls on the substrate to form a micro/nanofiber membrane.

Jiang Lei *et al.*[28] used electrospinning technology to build a rough surface and then used cheap low surface-energy silicon oil during calcination to prepare TiO_2 super-hydrophobic surfaces with a contact angle greater than 150° and a rolling angle less than 5°.

Huang *et al.*[29] constructed a coating with SiO_2 nanoparticles and silicic acid solution. They adjusted the roughness of the coating by changing the ratio of SiO_2 nanoparticles and silica acid. The coating was modified by perfluorooctyl trichlorosilane with a water contact angle of 160°, less than 10°. It also has high light transmittance, excellent thermal stability and mechanical stability. However, when the organic modifier of the coating surface contacts water for a long time, the turnover of its hydrophilic group results in poor hydrophobic stability, increasing the uncertainty in its practical application.

Li Fang *et al.*[30] used polyvinylidene difluoride (PVDF) and N, N-dimethylformamide (DMF) as the test materials, and prepared the ultra hydrophobic material with hollow microsphere structure by electrospinning. and the ultra hydrophobic material has super lipophilic properties. The contact angle between the material and the water was 153.5°.

3.6 Layer upon layer assembly method

Layer assembly technology refers to the technology of membrane layer by layer deposition under the action of electrostatic action, hydrogen bonding, and coordination bonding. Zhang Qunbing, Wang Jun *et al.* of Ningbo University used layer by layer assembly method to prepare the superhydrophobic surface of sea urchin TiO_2 with silicon sheet as the substrate[31]. The contact angle of the surface was 151.2° and a rolling angle of 4.5°.

Shang *et al.*[32] used polypropylene dimethyl ammonium chloride (PDDA) and poly4-styrene sodium sulfonate (PSS) as the polyelectrolyte, and then dipped the glass in the polyelectrolyte solution. Then dipped it in polystyrene modified SiO_2 particle suspension. Finally, a high transparent superhydrophobic porous SiO_2 glass coating made from perfluoroctane by chemical gas deposition, measuring water contact angle greater than 150° and a rolling angle of less than 10°.

3.7 Sol-gel method

The sol-gel method is a preparation method for condensing the solvent obtained after hydrolysis of high chemical activity compounds and drying the resulting gel to form a micro/nanopore structure to make it superhydrophobicity, but there are disadvantages such as long preparation process route, poor surface structure control, and solvent contamination.

Sanjay *et al.*[33]. prepared a methyl triethoxysilane (MTES) and porous silicon membrane into superhydrophobic surfaces with contact angles up to 160° on a glass substrate by solvent-gel method It is shown that the superhydrophobic films prepared by this method are transparent, adherent, good thermal stability and moisture resistant.

Wei *et al.*[34] used potassium titanate and TEOS as precursors and used a solvent-gel method to prepare a perfect titanium-silicon mesh composite aerosol structure, and the water contact angle of aerogel samples obtained after trimethylchlorosilane modification reached (145 ± 5)°.

After Zheng Yansheng *et al.*[35] hybridized TFE with a SiO_2 solvent modified by epoxy propoxy propyl trimethoxysilane, the glass was coated with a hyper-hydrophobic coating with a contact angle of up to 156°.

3.8 Electrochemical deposition method

Su *et al.*[36] deposit a layer of nickel on the copper substrate, and then fluoro silane modification yields a superhydrophobic surface with a contact angle of 162°. The material is capable of maintaining superhydrophobic by moving 1 m on silicon carbide (SiC) sandpaper for 800 at a load pressure of 4.8 kPa, indicating that the surface has excellent micro hardness and mechanical wear resistance.

Ding, *et al.* used electrochemical method, and deposited a layer of micro/nanostructure copper oxide (Cu_2O) membrane on the conductive glass (ITO) surface. It has a water contact angle up to about 170°, achieving a superhydrophobic effect. Meanwhile, it could obtain the Cu_2O films of different micromorphology by regulating electrodeposition time.

Xu *et al.*[38] electrochemical deposition of Tridecafluoroctyl triethoxysilane (POTS) on a films of poly pyrene and SiO_2 prepared a superhydrophobic complex coating of petal micronano layered structures highly transparent, thermal and mechanical stability with a static water contact angle up to (163 ± 1)° and a rolling angle below 2°

Hyper hydrophobic ZnO films were prepared on an aluminum alloy substrate after Huang *et al.*[39] functionally tionalized nanoZnO to 0. 01 $mol \cdot L^{-1}$ stearate ethanol solution, a mixture of isopropanol and butanol. It found that the roughness of the surface and the water contact angle of the surface gradually increased with the deposition temperature, and the film obtained at 50 ℃ had excellent superhydrophobic properties, with a water contact angle reaching (1553)°.

3.9 Solution immersion method

Li *et al.*[40] first impregnated the aluminum alloy plate in lanthanum nitrate aqueous solution for heat treatment to form a nano structure similar to Ginkgo biloba leaves on the surface, and then modified the super hydrophilic aluminum alloy surface with Dodecafluoroheptyl propyl trimethoxysilane. The water contact angle reached 160°, and the superhydrophobic surface had a relatively good surface Strong thermal stability, corrosion resistance, wear resistance and other advantages.

Yao Jiannian *et al.*[41] prepared superhydrophobic materials by solution soaking. After first soaking the smooth copper sheet in a specific $[Ag(NH_3)_2]OH$ solution for 6 h, a structure similar to the rose petals could appear on the surface of the copper sheet, and its contact angle reached 156°.

3.10 Other methods

Yang and *et al.*[43]were prepared by microemulsion, then heated on a glass plate to form porous rough structural films during the volatile process, and then modified with Xinji trimethoxysilane to make honeycomb-like superhydrophobic films with a contact angle of 156.3°, which is simple, fast and economical[42]. Furthermore, inspired by the microstructure of plant leaf surfaces, researchers like Liu *et al.* prepared superhydrophobic surfaces with a high contact angle of around 170° and a rolling angle of about 6° on an aluminum alloy by a one-step anodized method.

4. Application of hytra hydrophobic materials

Hyper hydrophobic materials have self-cleaning, pollution resistance and other characteristics, therefore, superhydrophobic materials can be developed and applied, so that they have broad prospects in the fields of aerospace and military industry, agriculture, pipeline nondestructive transportation, housing construction, as well as the equipment working in various open-air environments.

4.1 Application of superhydrophobic materials in fabric and filter materials

Various micronanostructural fibers with superhydrophobic water are produced by electrophospinning or treatment of the material surface to obtain anti-polluting superhydrophobic fabrics. Such materials can be used to make waterproof film, hydrophobic filter film, etc., or make the fabric have new functions such as hydrowaterproof, pollution prevention and dust prevention due to hydrophobic properties. For example, Xue *et al.* creates a friction-resistant superhydrophobic fiber fabric coating with sodium hydroxide etched polyethylene terephthalate (PET) fiber fabric[44].

4.2 Application of superhydrophobic materials in building coatings

Due to their unique hydrophobic properties, superhydrophobic materials have wide application prospects in water resistance, snow prevention and pollution resistance. At present, the ultra-hydrophobic surface materials in building pollution prevention materials are mainly coating and protective fluid, for example, Ji Haiyan, Chen Gang *et al.*[45] using etching glass also prepared ultra-hydrophobic glass surface. Yang *et al.*[46] developed a modified dodecthiol ZnO/PDMS complex with a water contact angle of 159.5° and 8.3° and excellent ice resistance at –10 and –5 °C, showing great potential for application.

4.3 Application of superhydrophobic materials in fog prevention and self-cleaning

Liquidation of water vapor in the air forms water mist covering the surface of transparent materials such as glass can cause reduced visibility of these materials[47]. Some bionic ultra-hydrophobic surface effectively reduce the condensation of water vapor, to achieve a certain anti-fog, self-cleaning effect. After alternating self-assembly of raspberry polystyrene and SiO_2 particles on slides, a highly transparent porous SiO_2 coating was obtained by high-temperature calcination. Finally, an ultra-hydrophobic transparent coating was obtained by chemical vapor deposition with a water contact angle of (1592)°. The coating improves the evaporation rate of water mist with excellent anti-fog performance.

4.4 Application of superhydrophobic surface materials in metal anticorrosion protection

Hyperhydrophobic materials have corrosion-resistant properties because a membrane of air occurs between solid and liquid, making it difficult for corrosive ions to contact the surface of the material[49,50].

Many people have researched in this regard, such as Guo Haifeng *et al.*[51] praying the inner surface of the natural gas pipeline to prepare superhydrophobic films to further improve the corrosion resistance of the pipeline. The subject group, Lu Si *et al.*, adhered the disordered carbon nanotubes to the surface of the substrate aluminum plate to form a composite structure surface and then modified with PTFE to form a hyper-hydrophobic PTFE.

4.5 Application of superhydrophobic surface materials in other aspects

Mobina *et al.*[52] co-modified the trimonomomer copolymer with methanol and nano SiO_2 and the water contact angle of the composite superhydrophobic coating was greater than 150° and could be applied to the surface of biomedical materials.

Wang *et al.*[53] immersed aluminum alloy, silicon plates, polypropylene and other substrate in a buffer of dopamine-hydrochloride for a period, transferred to different concentrations of silver ammonia solution, added formaldehyde solution, and finally modified the substrate into a mixture of ethanol and dodecyl thiol to make a superhydrophobic silver substrate with a water contact angle up to 170°.

5. Conclusion

The application range of superhydrophobic materials is quite wide, which has had certain development in various aspects, and its application prospect is very broad. However, due to the current technology and development costs are limited, the actual industrialization and commercialization are not much[54,55]. First, from a theoretical perspective, the geometry of superhydrophobic, size, functional group influence of superhydrophobic surface structure needs to be deepened. Secondly, in the preparation process, the low surface energy substances used are more expensive, mostly fluoride or silane compounds. Finally, in terms of technology, it is mainly the durability and aging resistance of surface coating. Many superhydrophobic structures are prone to lose superhydrophobicicity due to infirmness. Therefore, in the selection of materials, preparation process and post-processing, further research and solution. Research on how to automatically recover or regenerate superhydrophobic surfaces after reduced or disrupted performance will be an important research direction in this field.

Conflict of interest

The authors declare that they have no conflict of interest.

Acknowledgements

Fund Project: National Natural Science Foundation Grant Project (51478285); Natural Science Foundation of Jiangsu University Grant Project

(14KJA430004); Suzhou Science and Technology Development Plan Project (SYG201742); Jiangsu University Water Treatment Technology and Material Collaborative Innovation Center Project.

References

1. Manatunga DC, Silva RMD, Silva KMND. Double layer approach to create durable superhydrophobicity on cotton fabric using nano silica and auxiliary non fluorinated materials. Applied Surface Science 2016; 360: 777–788.
2. Brassard JD, Sarkar DK, Perron J. Studies of drag on the nanocomposite superhydrophobic surfaces. Applied Surface Science 2015; 324: 525–531.
3. Darvizeh M, Darvizehv A, Rajabi H, *et al.* Freevibration analysis of dragon fly wings using finite element method. The International Journal of Multiphysics 2009; 3(1): 101–110.
4. Khila A, Abouheif E, Rowe L. Evolution of a novel appendage ground plan in water striders is driven by changes in the hox gene ultrabithorax. Plos Genetics 2009; 5(7): e1000583.
5. Barthlott W, Neinhuis C. Purity of the sacred lotus, or escape from contamination in biological surfaces. Planta 1997; 202: 1–8.
6. Xiao, Tian J, Zhang B, *et al.* Research progress of superhydrophobic self-cleaning coatings. Modern Paint & Finishing 2017; 20(3): 32–35.
7. Minehide Y, Naoki N, Hiroyuki M, *et al.* Theoretical explanation of the lotus effect: superhydrophobic property changes by removal of nanostructures from the suface of a lotus leaf. Langmuir the Acs Journal of Surfaces & Colloids 2015; 31(26): 7355–7363.
8. Meng LY, Soo JP. Superhydrophobic carbon -based materials: a review of synthesis, structure, and applications. Carbon Letters 2014; 15(2): 89–104.
9. Yang M, Zhang L, Jiang H, *et al.* Effect factors and fabrication of superhydrophobic surface. Science & Technology in Chemical Industry 2016; 24(4): 78–82.
10. Young RN. The bakerian lecture: experiments and calculations relative to physical optics. London: Philosophical Transactions of the Royal Society of London; 1804. p. 1–16.
11. Wenzel RN. Resistance of solid surfaces to wetting by water. Industrial and Engineering Chemistry 1936; 28: 988–994.
12. Cassie ABD, Baxter S. Wettability of porous surfaces. Transactions of the Faraday Society 1944; 40: 546–551.
13. Chen J, Wang J, Wang W, *et al.* Preparation and Application of Hyperhydrophobic Surface Materials. China Materials Progress 2013; 32(7): 399–405.
14. Gao L, Mccaetgy TJ. How wenzel and cassie were wrong. Langmuir 2007; 23: 3762–3765.
15. Chen H, G T, Zhang X, *et al.* Research progress of superhydrophobic surface. Chemical Research 2013; 24 (4): 434–440.
16. Wang B, Nian J, Tie L, *et al.* Theoretical advances in stable hyper-hydrophobic surfaces. Physical Journal 2013; 62 (14): 1–15.
17. Yu M, Chen S, Zhang B, *et al.* Why a lotus-like superhydrophobic surface is self-cleaning? An explanation from surface force measurements and analysis. Langmuir the Acs Journal of Surfaces & Colloids 2014; 30(45): 13615–13621.
18. Cao M, Guo D, Yu C, *et al.* Water-repellent properties of superhydrophobic and lubricant-infused “slippery” surfaces： a brief study on the functions and applications. Acs Applied Materials & Interfaces 2016; 8(6): 3615–3623.
19. Spori DM, Drobek T, Zurcher S. *et al.* Beyond the lotus effect: roughness infuences on wetting over a wide surface-energy range. Langmuir the Acs Journal of Surfaces & Colloids 2008; 24(10): 5411–5417.
20. Zheng J. Feng J, Zhong M. Polymer superhydrophilic/superhydrophobic surfaces were prepared by the $CaCO_3$ particle template method. Polymer Journal 2010; 1 (10): 1186–1192.
21. Liu X, Xu Y, Ben K, *et al.* Transparent, durable and thermally stable PDMS-derived superhydrophobic surfaces. Applied Surface Science 2015; 339(1): 94–101.
22. Peng P, Ke Q, Zhou G, *et al.* Fabrication of microcavity-array superhydrophobic surfaces using an improved template method. Journal of Colloid and Interface Science 2013; 395: 326–328.
23. Qi Y, Cui Z, Liang B, *et al.* A fast method to fabricate superhydrophobic suefaces on zinc substrate with ion

assisted chemical etching. Applied Surface Science 2014; 305(7): 716–724.

24. Cho SW, Kim JH, Lee HM, *et al.* Superhydrophobic Si surfaces having microscale rod structures prepared in a plasma etching system. Surface and Coatings Technology 2016; 306: 82–86.
25. Liu J, Xiao X, Shi WL, *et al.* Fabrication of a superhydrophobic surface from porous polymer using phase separation. Applied Surface Science 2014; 297(4): 33–39.
26. Liu J, Xiao X, Cai X. Preparation of superhydrophobic porous polymer coating via phase separation. Polymer Materials Science and Engineering 2013; 29 (10): 113–117.
27. Tao D, Varanasi KK, Ming H, *et al.* Nonwetting of impinging droplets on textured surfaces. Applied Physics Letters 2009; 94(13): 3109.
28. Jiang L, Wang L, Zhao Y, *et al.* Superhydrophobic TiO_2 nanofiber mesh membranes were prepared by electrospinning (in Chinese). Journal of Higher Chemistry 2009; 30(4): 731–734.
29. Huang W, Lin CS. Robust superhydrophobic transparent coatings fabricated by a low-temperature sol-gel process. Applied Surface Science 2014; 305(3): 702–709.
30. Li F, Jia K, Li Q, *et al.* Farbrication of superhydrophobic and superoleophilic PVDF nanofibers with hollow beads structure by electrospinng for the separation of separation of oil and water. New chemical materials 2016; 44(3): 223–225.
31. Zhang Q. Preparation and characterization of super-hydrophobic surface of micro-nanocomposite (in Chinese). Ningbo: Ningbo University; 2012.
32. Shang Q, Zhou Y. Fabrication of transparent superhydrophobic porous silica coating for self-cleaning and anti-fogging. Ceramics International 2016; 42: 8706–8712.
33. Sanjay S, Latthe IH. Porous superhydrophobic silica films by sol-gel process. Microporous and Mesoporous Materials 2010; 130(1-3): 115–121.
34. Wei W, Lu XM, Jiang D, *et al.* A novel route for synthesis of UV-resistant hydrophobic titania-containing silica aerogels by using potassiumtitanate as precursor. Dalton Transactions 2014; 43(25): 9456–9467.
35. Zheng Y, He Y, QingY, *et al.* Preparation of a SiO_2/polytetrafluoroethylene hybrid superhydrophobic coatings. Chemical Industry and Engineering Progress 2012; 31(7): 1562–1566.
36. Su F, Yao K. Facile fabrication of superhydrophobic surface with excellent mechanical abrasion and corrosion resistance on copper substrate by a novel method. ACS Applied Materials & Interfaces 2014; 6(11): 8762–8770.
37. Ding Y, Li Y, Yang L, *et al.* The fabrication of controlled coral-like Cu_2O films and their hydrophobic property. Applied Surface Science 2013; 266: 395–399.
38. Xu L, Tong F, Lu X, *et al.* Multifunctional polypyrene/silica hybrid coatings with stable excimer fluorescence and robust superhydrophobicity derived from electrodeposited polypyrene films. Journal of Materials Chemistry C 2015; 3(9): 2086–2092.
39. Huang Y, Sarker DK, Chen XG. Superhydrophobic nanostructured ZnO thin films on aluminum alloy substrates by electrophoretic deposition process. Applied Surface Science 2015; 327: 327–334.
40. Li L, Huang T, Jie J, *et al.* Robust biomimetic-structural superhydrophobic surface on aluminum alloy. Acs Applied Materials & Interfaces 2015; 7(3): 1449–9457.
41. Cao Z, Xiao D, Kang L, *et al.* Superhydrophobic pure silver surface with flower-like structures by a facile galvanic exchange reaction with $[Ag(NH_3)_2]OH$. Chemical Communication 2008; 23(23): 2692–2694.
42. Yang T, Tian H, Chen Y. Preparation of superhydrophobic silica films with honeycomb like structure by emulsion method. Journal of Sol-Gel Science and Technology 2009; 49: 243–246.
43. Liu Y, Liu J, Li S, *et al.* One-step method for fabrication of biomimetic superhydrophobic surface on aluminum alloy. Colloids and Surfaces A: Physicochemical and Engineering Aspects 2015; 466: 125–131.
44. Xue C, Li Y, Zhang P, *et al.* Washable and wear-resistant superhydrophobic surfaces with self-cleaning property by chemical etching of fibers and hydrophobization. ACS Applied Materials & Interfaces 2014; 2014(6): 10153–10161.
45. Ji H, Gang C, Hu J, *et al.* Preparation and properties of monodisperse poly(ethyl methacrylate). New

Chemical Materials 2011; 39(8); 106–108.

46. Yang C, Wang F, Li W, *et al.* Anti-icing properties of superhydrophobic ZnO/PDMS composite coating. Applied Physics A 2015; 122(1): 1–10.
47. Shang Q, Zhou Y. Fabrication of transparent superhydrophobic porous silica coating for self-cleaning and anti-fogging. Ceramics Inter-national 2016; 42(7): 8706–8712.
48. Hou L, Fang L. Preparation and application development of superhydrophobic surface. Chemistry 2016; 79(10): 897–904.
49. Zhou Y. Preparation and properties of artificial bionic superhydrophobic functional surfaces [PhD thesis]. Beijing: University of Science and Technology of China; 2012.
50. Li H, Gu X, Liu L, *et al.* Advances in studying hyperhydrophobic surfaces (in Chinese). Applied Chemical Industry 2016; 45(12): 2347–2350.
51. Guo H, Zhang, Z, Li G, *et al.* Super-hydrophobic molecular film on the inner wall surface of steel for natural gas pipelines and its corrosion resistance. Oil & Gas Storage and Transportation 2011; 30(10): 781–784.
52. Xue C, Li Y, Zhang P, *et al.* Super-hydrophobic molecular film on the inner wall surface of steel for natural gas pipelines and its corrosion resistance. Oil & Gas Storage and Transportation 2011; (10): 781–784, 717.
53. Wang Z, Ou J, Wang Y, *et al.* Anti-bacterial superhydrophobic silver on diverse substrates based on the mussel-inspired polydopamine. Surface & Coatings Technology 2015; 280: 378–383.
54. Xu W, Song J, Sun J, *et al.* Progress in fabrication and application of superhydrophobic surfaces on metal substrates. Journal of Materials Engineering 2011; 1(5): 93–98.
55. Liang W, Zhang Y, Wang B, *et al.* Biological applications of biomimetic superhydrophobic surfaces. Acta Chimica Sinica 2012; 70(23): 2393–2403.