ISSN: 2414-1895 DOI: 10.6919/ICJE.202201_8(1).0055

# Recent Progress in 2-Step Fabrication and Practical Application of Superhydrophobic Surface on Metals: a Review

Shuchun Gou

Pittsburgh Institute, Sichuan University, Chengdu, 610225, China

*E-mail:2018141522040@stu.scu.edu.cn

## Abstract

**This review investigates the fabrication process and recent practical application of superhydrophobic surfaces on metals. Based on Young's equation, Wenzel model, and Cassie-Baxter model, the fabrication is usually divided into two steps: construction and modification. By improving the 2-step preparation method, practical superhydrophobic materials have been produced to meet various needs.**

## Keywords

**Metals, Superhydrophobic, Fabrication, Applications.**

## 1. Introduction

On a flat solid surface, when a water droplet spread naturally and the solid-liquid-gas phase system reached equilibrium, plotting a tangent line is made along with the liquid-gas interface at the three-phase junction. The angle between the tangent line and the solid-liquid interface is contact angle θ, as shown in Fig. 1. Surface wettability can be measured by the contact angle. The surface with a contact angle below 90° is hydrophilic and the hydrophobic surface has the angle above 90°. The contact angle of the superhydrophobic surface is above 150°.

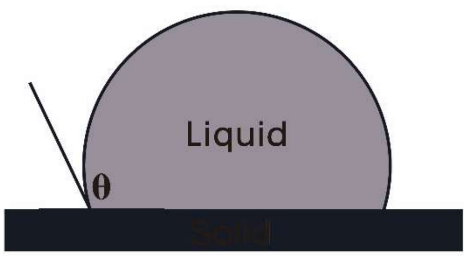


**Fig. 1.** Illustration of contact angle.

In the 19th century, Young proposed a equation to combine the contact angle with the surface energy:

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

Where, θ is the contact angle, γSA , γSL and γLA are the interfacial surface tension of solid-air, solid-liquid and liquid-air. Young's equation is the essential equation for surface wettability but applies

Volume 8 Issue 1, 2022
DOI: 10.6919/ICJE.202201_8(1).0055

strictly to ideal smooth surfaces. To analysis the surface wetting behavior of rough surfaces, Wenzel and Cassie&Baxter proposed new models.

In Wenzel's model, the water droplet entirely fills the roughness grooves of the rough surface like Fig. 2(b). In this regime, Wenzel defined a roughness factor, which is defined as the ratio of actual surface area between projected surface area, to relates apparent contact angle to Young's contact angle as follows:

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

Where, θw is the apparent contact angle, r is the roughness factor. This regime shows that increasing the roughness makes the hydrophobic surface more hydrophobic and makes a hydrophilic surface more hydrophilic.

In the Cassie-Baxter model, the water droplet is suspended on the surface asperities and does not fill them because of capillarity like Fig. 2(c). The liquid interface consists of two different phases, solid and air, which influence the apparent contact angle as shown in Eq. (3):

$$\cos\theta_C = f_1\cos\theta_1 + f_2\cos\theta_2 \tag{3}$$

Where θc is the apparent contact angle in the model, $f1$ and $f2$ are the fraction of liquid-solid and liquid-air interface, θ1 and θ2 are the contact angle of solid and air phase. Since $f1+f2=1$ and θ2=180°, Eq.(3) can be simplified as follows:

$$\cos\theta_C = f_1\cos\theta_1 + f_2 = f_1\cos\theta_1 + f_1 - 1 \tag{4}$$

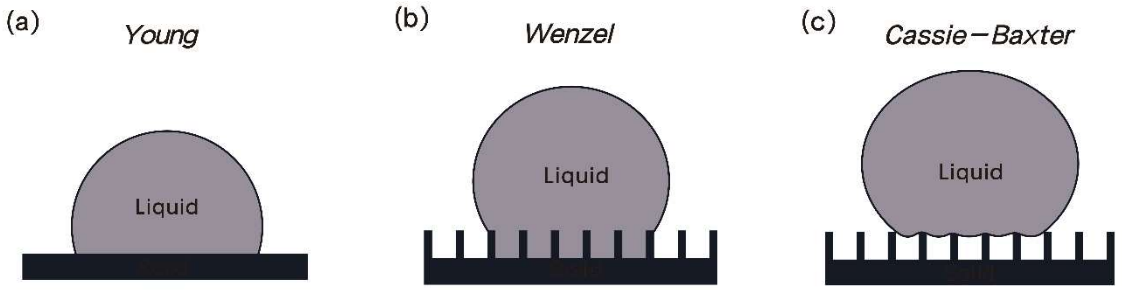


**Fig. 2.** Schematic diagram of the different models: (a)Young, (b)Wenzel, (b) Cassie-Baxter

Metals are important materials for human society. Producing superhydrophobic surface on metals can increase the characteristics of them to meet human needs. According to the models, the preparation is usually divided into two steps: constructing a special rough surface and modifying the low surface energy substance on the rough surface. At present, metal-based superhydrophobic materials have shown excellent application prospects in self-cleaning, anti-corrosion, anti-icing and others.

## 2. Method for Preparation of Superhydrophobic Surface on Metals

According to Young's equation, a surface with lower surface energy has a greater contact angle. In addition, Wenzel and Cassie-Baxter model show that a rough surface with a special structure can have a greater contact angle. Therefore, the preparation is usually divided into two processes:

ISSN: 2414-1895 DOI: 10.6919/ICJE.202201_8(1).0055

constructing a rough surface with micron-nanoscale structures(construction) and modifying the surface with some low surface energy substances(modification).

## 2.1 Construction

### 2.1.1 Etching

Etching is widely used to construct a rough structure of superhydrophobic surface on metals. Wet etching and electrochemical etching are common methods in recent progress.

Wei et al. [1] used a 0.3 M HCl aqueous solution to etch the treated AZ31 alloy sheet (15 mm × 18 mm × 1.0 mm). The etched sample has a rough surface with special micron-nano structures. Wet etching has the advantages of simple operation, low cost, and high efficiency. However, the corrosive waste liquid will cause serious environmental pollution.

Compared with wet etching, the solution used in electrochemical etching is less corrosive and easier to handle. In addition, electrochemical etching usually has a faster etching rate. Ma et al. [2] designed an electrochemical etching process to more easily fabricate superhydrophobic GH4169 surfaces. In the process, the treated GH4169 sheet was used as the anode in sodium nitrate solution and the cathode in sodium chloride solution was a copper plate. The anode and the cathode were parallelly set and their distance is 10 mm. By controlling current density, etching time, electrolyte concentration, and temperature, rough surfaces with different microstructures were fabricated.

### 2.1.2 Laser Ablation

This method uses one or more laser pulses to remove the material from the substrate with a little deformation in the surrounding area. The features of the rough surface depend on laser characteristics such as laser pulse width, pulse energy, repetition rate, and the properties of the material used.

Xin et al. [3] ablated TC4 alloy sheets at room temperature by nanosecond laser and got a rough surface to fabricate superhydrophobic surface. The sheets were ablated by nanosecond laser scanning vertically line-by-line.

Laser ablation had the problem of high cost in the past. However, with the development of nanosecond laser research, this problem has been primarily solved. Lei et al. [4] proposed a new low-cost method to fabricate superhydrophobic surface on aluminum alloy based on large spot diameter nanosecond laser ablation and demonstrated the feasibility of this method for industrial application.

### 2.1.3 Deposition

The rough surface is formed by the deposition of micro and nano particles on the surface of the matrix through displacement reaction or cathodic reduction reaction in this method. It mainly includes chemical deposition and electrodeposition.

The Chemical deposition is simple and the reaction conditions are controllable. This approach is often constrained by the cost of the reaction solution. Pi et al. [5] constructed a composite film ($Cu_2S@Cu_2O$) with a micro-nano structure on the copper surface by a simple chemical bath deposition method. In detail, the pretreated copper sheets and copper meshes were vertically placed in the solution containing 0.1 M $CuSO_4$ and 0.1 M $Na_2S_2O_3$ at 50°C.

Electrodeposition is usually carried out under normal temperature and pressure, with low cost and a simple and controllable preparation process. However, the micro-nano structures formed are usually not stable because of stress. Li et al. [6] used a three-electrode deposition system(1 mM $AgNO_3$, 3 mM CitNa, 0.1 M $KNO_3$) at room temperature to deposit Ag nanoparticles onto stainless-steel 304 meshes. The stainless-steel mesh, platinum plate and saturated calomel electrode were used as working electrode, counter electrode and reference electrode.

### 2.1.4 Hydrothermal Treatment

Hydrothermal treatment takes water as the solvent and makes the crystals grow on the surface of the substrate under the condition of high temperature or high pressure, forming a micro-nano rough structure. Li et al. [7] constructed ZnO nanoflake arrays on Al substrates. The treated Al substrates were suspended in the mixed solution of 16 mM $Zn(NO_3)_2 \cdot 6H_2O$ and 16 mM $C_6H_{12}N_4$ at 90 ℃

ISSN: 2414-1895 DOI: 10.6919/ICJE.202201_8(1).0055

for 2 h. The microstructure formed by hydrothermal treatment is uniform in size, but it usually requires high temperature or high pressure. Therefore, equipment is usually the main reason for limiting this method.

### 2.2 Modification

According to Wenzel's model, for the surface with a contact angle less than 90°, the increase of roughness will lead to the decrease of apparent contact angle. Therefore, modification is an important process for fabricating superhydrophobic surfaces of metals with high surface energy. Modifiers are usually classified as fluorine-containing and fluorine-free.

#### 2.2.1 Fluorine-Containing Modifiers

The surface energy of a hydrocarbon decreases when hydrogen is replaced by fluorine. Therefore, organic fluorine compounds have low surface energy and are commonly used modifiers.

Guo et al. [8] modified the treated 7055 aluminum alloy with 1H, 1H, 2H, 2H- -Perfluorooctyltriethoxysilane and successfully fabricated a superhydrophobic surface(167.3°). In the process, some treated samples with rough surfaces were placed in 1 vol.% Perfluorooctyltriethoxysilane/anhydrous alcohol solution for 10 min and then heated at 120℃ for 10 min.

#### 2.2.2 Fluorine-Free Modifiers

The surface energy of fluorine-free silanes is generally higher than that of fluorine-containing silanes. The fluorine-free modifiers are usually alkyl-containing methyl and ethyl groups. Compared with fluorine-containing modifiers, fluorine-free modifiers have the advantages of being environmentally friendly and low cost.

Barthwal et al. [9] used polydimethylsiloxane to modify the aluminum surface with micro-nano structure through a thermal vapor deposition method and obtained the superhydrophobic surface (161±1°). In the progress, the polydimethylsiloxane prepolymer and curing agent were mixed at a weight ratio of 10:1 and cured for 2 h at 120 ℃ to prepare the polydimethylsiloxane stamp. The stamp was heated at 230 ℃ for 5 min and then place the aluminum simple 5 cm above on the stamp for 10 min to modify the surface.

## 3. Practical Application

By studying the principle of the two-step preparation method and adjusting the fabrication process, practical superhydrophobic materials have been produced to meet various needs.

Li et al. [10] fabricated a zinc coating with ZnO film on a steel substrate through electrodeposition and hydrothermal treatment and modified it with pentadecafluorooctanoic acid (C8HF15O2, 90%) to obtain a superhydrophobic surface with excellent self-cleaning performance and stability. Compared with common 2-step fabrication, they used both electrodeposition and hydrothermal treatment in the construction part. The ZnO films obtained by hydrothermal treatment improve the effect of the modification process and make the superhydrophobic surface more stable.

He et al. [11] prepared a superhydrophobic surface with corrosion resistance by hydrothermal treatment, annealing, and modification (stearic acid, C18H36O2). By hydrothermal treatment and annealing treatment, they prepared nano-needle shaped Fe2O3 on micro-sized Fe3O4 octahedral particles in the construction part. In the annealing process, the nanoneedles grew out vertically on the facets of octahedral particles and the optimal processing has produced a micro-nano structure in accord with the Cassie-Baxter model, showing great corrosion resistance.

Tang et al. [12] prepared a superhydrophobic surface with micro-nano layered wrinkle structure on AZ31 alloy by ultrasonic-acid synergistic corrosion method and 1H, 1H, 2H, 2H-perfluorodecyltriethoxydsilane modification. The surface showed excellent repellency and durability towards the water and viscous oil, indicating superior oleophobicity. In analysis, they find that the

ISSN: 2414-1895 DOI: 10.6919/ICJE.202201_8(1).0055

superhydrophobic surface with medium roughness had the best performance in ice resistance which means it is possible to minimize ice adhesion force by designing the structure.

## 4. Conclusion

Inspired by natural things such as lotus leaves and cicada wings, superhydrophobic surfaces have received extensive attention in recent years. In this review, the 2-step fabrication and practical application of metal-based superhydrophobic surfaces are discussed. Compared with one-step fabrication, the 2-step fabrication seems complicated. However, the two steps, construction, and modification are based on rough surface and low energy, the keys of Young's equation and Cassie-Baxter model, and they studying them help people design practical superhydrophobic surfaces that meet the demands. Although many efforts have been devoted to fabricating practical superhydrophobic surfaces, there is still a long way. In the future, the following challenges should be solved:

1) Stability. Although many researchers showed stability of the superhydrophobic surface, it is only tested in the laboratory, such as impacting with gravel or water, setting in solution with different pH. The real use environment is far worse than theirs. To fabricate a stable superhydrophobic surface for practical application, researchers need to detect the stability in a more rigorous environment.

2) Design of different metals. Different properties of different metals make the same preparation method have different results so it is hard to design a process to fabricate the desired surface. To simplify the design process, researchers may need to systematically study the effects of various methods on common metals.

3) Environmentally friendly and consumption. The waste liquid in the preparation process of superhydrophobic materials is extremely harmful to the environment, such as fluorine-containing modifiers, etching residual liquid, electrochemical residual liquid. Researchers need to weigh the consumption of waste materials in the production process so that practical superhydrophobic surfaces in the laboratory can be fabricated industrially.

## References

[1] Dongsong Wei, Jinguo Wang, Yan Liu, Dawei Wang, Shuyi Li, Huiyuan Wang, Controllable superhydrophobic surfaces with tunable adhesion on Mg alloys by a simple etching method and its corrosion inhibition performance, Chemical Engineering Journal, Volume 404, 2021, 126444, ISSN 1385-8947.

[2] Ning Ma, Dan Cheng, Jingqiang Zhang, Shuguo Zhao, Yao Lu, A simple, inexpensive and environmental-friendly electrochemical etching method to fabricate superhydrophobic GH4169 surfaces, Surface and Coatings Technology, Volume 399, 2020, 126180, ISSN 0257-8972.

[3] Guoqiang Xin, Congyi Wu, Haiyin Cao, Weinan Liu, Bo Li, Yu Huang, Youmin Rong, Guojun Zhang, Superhydrophobic TC4 alloy surface fabricated by laser micro-scanning to reduce adhesion and drag resistance, Surface and Coatings Technology, Volume 391, 2020, 125707, ISSN 0257-8972.

[4] Zhenglong Lei, Ze Tian, Xi Chen, Yanbin Chen, Jiang Bi, Shibo Wu, Haoran Sun, Large spot diameter nanosecond laser treatment of aluminum alloy sheets for high-speed superhydrophobic hierarchical micro- and nanostructured surface preparation, Surface and Coatings Technology, Volume 361, 2019, Pages 249-254, ISSN 0257-8972.

[5] Pihui Pi, Kun Hou, Cailong Zhou, Guidong Li, Xiufang Wen, Shouping Xu, Jiang Cheng, Shuangfeng Wang, Superhydrophobic Cu2S@Cu2O film on copper surface fabricated by a facile chemical bath deposition method and its application in oil-water separation, Applied Surface Science, Volume 396, 2017, Pages 566-573, ISSN 0169-4332.

[6] Shuyi Li, Yan Liu, Zhuangzhuang Tian, Xin Liu, Zhiwu Han, Luquan Ren, Biomimetic superhydrophobic and antibacterial stainless-steel mesh via double-potentiostatic electrodeposition and modification, Surface and Coatings Technology, Volume 403, 2020, 126355, ISSN 0257-8972.

ISSN: 2414-1895 DOI: 10.6919/ICJE.202201_8(1).0055

[7] Hong Li, Hongyan Lu, Shulong Liu, Qiang Li, Qinzhuang Liu, SiO2 shell on ZnO nanoflake arrays for UV-durable superhydrophobicity on Al substrate, Materials Research Bulletin, Volume 114, 2019, Pages 85-89, ISSN 0025-5408.

[8] Fuqiang Guo, Shuwei Duan, Dongting Wu, Kenji Matsuda, Tao Wang, Yong Zou, Facile etching fabrication of superhydrophobic 7055 aluminum alloy surface towards chloride environment anticorrosion, Corrosion Science, Volume 182, 2021, 109262, ISSN 0010-938X.

[9] Sumit Barthwal, Si-Hyung Lim, A durable, fluorine-free, and repairable superhydrophobic aluminum surface with hierarchical micro/nanostructures and its application for continuous oil-water separation, Journal of Membrane Science, Volume 618, 2021, 118716, ISSN 0376-7388.

[10] Hao Li, Sirong Yu, Jinhui Hu, Enyang Liu, A robust superhydrophobic Zn coating with ZnO nanosheets on steel substrate and its self-cleaning property, Thin Solid Films, Volume 666, 2018, Pages 100-107, ISSN 0040-6090.

[11] Shijun He, Jiakun Shi, Jianying Huang, Jun Hu, Yuekun Lai, Zhong Chen, Rational designed structured superhydrophobic iron oxide surface towards sustainable anti-corrosion and self-cleaning, Chemical Engineering Journal, 2020, 127768, ISSN 1385-8947.

[12] Lingling Tang, Nan Wang, Zhenyi Han, Haohan Sun, Dangsheng Xiong, Robust superhydrophobic surface with wrinkle-like structures on AZ31 alloy that repels viscous oil and investigations of the anti-icing property, Colloids and Surfaces A: Physicochemical and Engineering Aspects, Volume 594, 2020, 124655, ISSN 0927-7757.