Research progress on low surface energy superhydrophobic coating materials

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Abstract

Superhydrophobicity is a phenomenon where the contact angles of various water droplets with low surface tension on a solid surface are larger than 150°. In the past few years, there has been much growing interest in the design and application of superhydrophobic surfaces. Such surfaces have great significance for both fundamental research and a variety of practical applications. This paper mainly discusses research progress on low surface energy superhydrophobic coating materials, including superhydrophobic theoretical basis, various superhydrophobic materials and methods. Although many significant advances have been achieved, superhydrophobic surfaces are still in their "toddler stage" of development. The current challenges and outlook of this fast-growing field of superhydrophobicity are discussed.

Keywords

Superhydrophobic coating; fluorine material; silicon material.

1. Introduction

Generally, the surface of the superhydrophobic material has a stable contact angle of more than 150° and a rolling contact angle of less than 10°. In the natural world, many famous botanical professors of the University of Bonn, W. Barthlott, observed the microscopic structure of the plant leaf surface and found that this self-cleaning feature is composed of a certain roughness, micron-structured mastoid on the rough surface and surface wax. The existence of the joint [1]. Insects also have water rafts on their feet. Mosquitoes can walk on water without scratching the surface because of the superhydrophobic material on them [2-3]. The manufacture of artificial superhydrophobic surfaces and their wide application in the fields of waterproofing, snow prevention, oxidation resistance, corrosion prevention, self-cleaning, drag reduction and selective absorption have become hot topics today.

2. Superhydrophobic theoretical basis

The wettability of a solid surface is determined by the surface chemical composition of the solid and the three-dimensional microstructure of the surface. The wetting characteristics of the droplet on the solid surface are often described by Young's equation (Young's Eq.). The contact angle between the droplet and the solid surface is large, the wettability is poor, and the liquid repellency is strong.

$$\text{Young's } Eq: \cos\theta_s = (\gamma_{SV} - \gamma_{SL}) / \gamma_{LV}$$

$$\text{Dupre's Eq:} \cos\theta_s = [2\phi(\gamma_{SV} - \gamma_{SL})^{1/2}] - 1$$

$$\text{Wemze's Eq:} \cos\theta_r = r(\gamma_{SV} - \gamma_{SL}) / \gamma_{LV} = \cos\theta_s$$

$$\text{Cassie's Eq:} \cos\theta_r = f\cos\theta_s + f - 1$$

Where: γ_{SV}, γ_{SL}, γ_{LV} are the interfacial tension between solid-gas, solid-liquid and gas-liquid, respectively ; Φ is the correlation coefficient; θ_s is the contact angle of the smooth surface; θ_r is the contact angle of the rough surface; r is rough Degree factor; f is the area fraction of the liquid contact solid surface [4-5].

The coating film of the lotus effect must have three characteristics at the same time:

(1) a hydrophobic surface having a low surface energy

(2) suitable surface roughness

(3) Low roll angle.

The lotus leaf effect can be achieved by two methods: one is to add super hydrophobic agent, such as fluorosilicone surfactant, so that the surface of the coating film has ultra-low surface energy, the dust is not easy to adhere; the other is to simulate the surface of the lotus leaf. The concave and convex microstructure design of the surface of the coating film reduces the contact area between the contaminant and the coating film, so that the contaminant cannot adhere to the surface of the coating film, and can only be loosely accumulated on the uneven surface of the surface, so that it is easily washed away by rain.

3. Superhydrophobic theoretical basis

3.1 Fluorine / silicon material

Fluorine has the strongest electronegativity, small atomic radius, low atomic polarizability, large C-F bond energy in organofluorine compounds, and spiral distribution of fluorine atoms along carbon bonds, with shielding effect. The force is small and the surface energy is very low. The introduction of F atoms in silanes or polysiloxanes can further reduce the surface energy. In typical hydrophobic fluorosilicon materials, fluoroalkylsilanes (FAS) are commonly used surface hydrophobic treatment materials, and one end of the molecule is perfluoro or fluoroalkane. The other end is a group of 1 to 3 functional groups of a hydrolyzable reaction such as a halogen, an alkoxy group or the like, such as $C_8F_{17}CH_2CH_2SiCl_3$, $C_8F_{17}SiCl_3$, $C_8F_{17}CH_2CH_2$-$Si(OCH_3)_3$, $C_{10}F_{21}SiCl_3$, $CF_3(CF_2)_5(CH_2)_2$-$(CH_3)_2SiCl$, $C_6F_{13}(CH_2)_2Si(OC_2H_5)_3$ [6-8]. The fluorine-containing resins used for coating mainly include Teflon series, PVDF, FEVE, and PVF resins. The silicone resin is an organopolysiloxane having a highly branched structure, and commonly used silicone monomers are: organochlorosilane monomers, organoalkoxysilane monomers, organoacyloxysilane monomers, organosilyl alcohols, and A silicone monomer or the like containing an organic functional group. In practical applications, different silicone monomers can be selected according to actual needs, and different organic groups are introduced into the silicone resin. An SiO_2 aerogel prepared by a lyotropic method under subcritical conditions, and a silicon aerogel prepared by a simpler route [9-10].

3.2 Other hydrophobic materials

Other synthetic polymers such as polyene, fluorine-free acrylate, amphiphilic PVA nanofibers, etc., can also achieve super hydrophobicity in combination with certain process technologies. Recently, a team of researchers from the Institute of Nanotechnology and Nano-Bionics of the Chinese Academy of Sciences, Zhang Wei, constructed a multi-walled carbon nanotube (MWCNT)/thermoplastic elastomer (TPE) composite superhydrophobic smart coating with multi-level micro-nano composite structure. The layer also has super-hydrophobicity and excellent strain sensing performance, which can effectively resist the interference of water, acid, lye, sweat in the environment [11].

4. Preparation of superhydrophobic surface

4.1 Template method

This method produces a rough coating on a substrate having nano or micro-methylene pores on its surface. The super-hydrophobic coating prepared by the template method has the advantages of simple operation, good repeatability and controllable nanowire diameter ratio.

The template method further includes a stencil printing method, a template extrusion method, and the like. Sun et al. [12] used the lotus leaf as the original template to obtain the concave template of PDMS, and then used the concave template to obtain the PDMS convex template, which is a replica of the lotus leaf, which has the same surface structure as the lotus leaf, thus showing good superhydrophobicity and very low roll angle. This process is similar to "printing" and is therefore referred to as stencil printing. Feng Lin et al. [13] prepared a superhydrophobic surface with a hydrophilic polyvinyl alcohol material by template extrusion, and the contact angle can reach 171.2°.

4.2 Sol-gel method

The sol-gel method belongs to the "wet chemical" synthesis method and is a commonly used method for preparing porous materials and organic-inorganic hybrid materials. Hydrolysis is carried out by using a compound containing a highly chemically active component as a precursor to obtain a condensation reaction, a stable gel is formed in the solution, and finally the gel is dried. After solvent removal, some micro-nanopores are sometimes left behind, and these micro-nanoporous structures impart certain properties to the material, including superhydrophobicity. For example, silicone aerogels are called "fourth generation materials" because they have a well-structured pore structure, which has a very high specific surface area, the lowest density among known materials, very low thermal conductivity, and other characteristics [14]. In combination with sol-gel method and chemical modification method, lotus leaf copper-ferrite film was prepared on ordinary copper alloy. The sol-gel method has certain advantages for the preparation of inorganic superhydrophobic materials such as ZnO, TiO2 and Al2O3, but has the disadvantages of long process route, solvent pollution and high cost. The preparation of superhydrophobic biomimetic materials on copper substrates is also a common method.

4.3 Steam induced phase separation method

During the evaporation of the polymer solution, the thermodynamic state of the solution is unstable, and the polymer chains are prone to self-aggregation, forming a polymer aggregate phase. When the polymer chain is aggregated to a certain extent, a phase separation process occurs between the polymer aggregation phases, and a surface having a micro-nano-scale roughness structure is formed. This film formation method is called a vapor-induced phase separation method. Yuan Zhiqing et al. directly dissolved polypropylene (PP) [15] or polystyrene [16] pellets in xylene or tetrahydrofuran, dissolved, added appropriate amount of ethanol and mixed, and applied the solution to a clean glass slide to obtain coating with good hydrophobic properties, and the method is simple, efficient and reproducible.

4.4 Laser and plasma etching

Etching is the use of modern physical chemistry to produce a rough, fine-grained appearance on the surface of the coating. Plasma polymerization and photo etching are mainly used. Polydimethylsiloxane is laser etched to make it surface-modified with hydrophobicity without changing its original surface properties [17].

There are many other methods, such as nanoarray method, phase separation method, etc., which are not enumerated here.

5. Conclusions and outlooks

This paper gives a brief review of recent progress in low surface energy superhydrophobic coating materials. The low adhesion superhydrophobic surface has been widely used in production practice due to its excellent properties such as self-cleaning and corrosion resistance. The application of superhydrophobic coating materials in the fields of oil transportation, biosensors, microfluidic controls and intelligent separation membranes has become a hot topic in current research. However, the wettability of a solid surface is a complex property that affects all other surface properties of the solid. At present, the research on the wettability control of solid materials is still limited. How to ensure stability and how to commercialize is still a problem to be solved. The intelligentization of nano-superhydrophobic materials has become the future trend. It is believed that the combination of super-hydrophobic materials, smart materials and flexible intelligent systems will become a focus in the future. Meanwhile, further efforts should concentrate on the application of low surface energy superhydrophobic coating materials to textiles, coatings, gene delivery, microfluidic channels, and non-wetting liquid transfer.

References

[1] W. Barthlott, C. Niehues, Planta 1997, 20-21.
[2] D. L. Hu, B. Chan, J. W. M. Bush, Nature 2003, 424, 663.
[3] X. F. Gao, L. Jiang, Nature 2004, 432-436.
[4] WENZELRN. J. Phys. Colloid Chem., 1949, 53: 1466-1467.
[5] CASSIEABD. Discuss. Faraday Soc., 1948, 3:11-16.
[6] SCHONDELMAIERD, CRAMMS, KLINGELERR, et al. Langmuir, 2002, 18: 6242-6245.
[7] TADANAGAK, KITAMUROK, MATSUDAA, et al. Sol2GelSci.Technol., 2003, 26: 707-708.
[8] HANJT, ZHENGY, CHOJH, et al. J. Phys. Chem. B., 2005, 109: 20773-20778.
[9] Rao A V, Kulkarni M M, Amalnerkar D P, et al. Superhydrophobic silica aerogels based on methyltrimethoxysilane precursor[J]. Journal of Non-Crystalline Solids, 2003, 330(1-3): 187-195.
[10] Rao A V, Kulkarni M M, Bhagat S D. Transport of liquids using superhydrophobic aerogels[J]. Journal of colloid and interface science, 2005, 285(1): 413-418.
[11] Li L, Bai Y, Li L, et al. A Superhydrophobic Smart Coating for Flexible and Wearable Sensing Electronics[J]. Advanced Materials, 2017, 29(43): 1702517.
[12] Sun M, Luo C, Xu L, et al. Artificial lotus leaf by Nano casting[J]. Langmuir, 2005, 21(19): 8978-8981.
[13] Feng L, Song Y, Zhai J, et al. Creation of a superhydrophobic surface from an amphiphilic polymer[J]. Angewandte Chemie International Edition, 2003, 42(7): 800-802.
[14] Huang Z, Zhu Y, Zhang J, et al. Stable biomimetic superhydrophobicity and magnetization film with Cu-ferrite nanorods[J]. The Journal of Physical Chemistry C, 2007, 111(18): 6821-6825.
[15] Yuan Zhiqing, Chen Hong, Tang Jianxin et al. Preparation and blood compatibility of superhydrophobic polypropylene surface[J]. Journal of Functional Materials, 2007, 38(8):13592-1361
[16] Yuan Z, Chen H, Tang J, et al. Facile method to fabricate stable superhydrophobic polystyrene surface by adding ethanol[J]. Surface and Coatings Technology, 2007, 201(16-17): 7138-7142.
[17] Khorasani M T, Mirzadeh H, Sammes P G. Laser induced surface modification of polydimethylsiloxane as a super-hydrophobic material[J]. Radiation Physics and Chemistry, 1996, 47(6): 881-888.