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Bioinspired Design, Preparation Technologies and Applications of Superhydrophobic Materials: From Theoretical Fundamentals to Industrial Prospects

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ABSTRACT

Since Barthlott et al. revealed the microscopic mechanism of lotus leaves' "self-cleaning" superhydrophobicity in 1997, superhydrophobic materials (with water contact angle > 150° and rolling angle < 10°) have become a research hotspot in interface science and materials engineering. However, they face critical bottlenecks: laboratory preparation methods (e. g., precise templating) are hard to scale up, mechanical durability is insufficient (contact angle decreases significantly after sandpaper friction), and traditional low-surface-energy materials containing fluorine or silicon pose environmental risks and cost issues. This paper reviews superhydrophobic materials from four dimensions: theoretical basis, preparation technology, performance regulation, and application scenarios, while analyzing challenges and proposing prospects. The theoretical basis integrates classical wetting theories (Young equation, Wenzel model, Cassie-Baxter model) and the biomimetic binary synergistic complementary principle (cooperation of multi-scale rough structures and low-surface-energy chemistry). Preparation technologies include the biomimetic template method (replicating natural structures), phase separation method (constructing porous rough structures via polymer-solvent separation), and spraying/coating method (rapidly building rough coatings with low-surface-energy materials and nanoparticles). Performance regulation is achieved by optimizing microscopic structures (e.g., "micrometer-nanometer" hierarchical design) and modifying surface chemistry (e.g., plasma treatment, sol-gel method) to control contact angle, rolling angle, and stability. Applications span self-cleaning (e.g., architectural glass coatings), oil-water separation (e.g., superhydrophobic-superhydrophilic netting), and dry-style antifogging (via biomimetic hierarchical structures). Current challenges (e. g., insufficient mechanical durability) are discussed, and future prospects are proposed: innovating surfactants for efficient CO_2 utilization in emulsions, applying 3D printing to fabricate precise biomimetic microstructures, and integrating multifunctionality (e. g., superomniphobicity, high-temperature resistance, antifouling). This work aims to provide a framework for advancing superhydrophobic materials' research and industrialization.

KEYWORDS

Superhydrophobic materials; Wetting theory; Biomimetic mechanism; Preparation technology; Performance regulation; Application; Mechanical durability

1 Introduction

Since Barthlott et al. revealed the microscopic mechanism of the "not being tainted by the mud" of lotus leaves in 1997, superhydrophobic materials (with water contact angle > 150° and rolling angle < 10°) have become a research hotspot in the fields of interface science and materials engineering [1]. The surface of the lotus leaf is composed of many papillae, with the average diameter of the papillae being 5-9 μm. The contact angle and rolling angle of water on this surface are (161.0 ± 2.7)°/ and 2° respectively. Each papilla is composed of a nanoscale structure branch with an average diameter of (124.3 ± 3.2 nm). Additionally, nanoscale structures can also be found on the lower layer surface of the lotus leaf, which can effectively prevent the lower layer of the lotus leaf from being wetted. These nanoscale structures, especially those on the micrometer papillae, play an important role in superhydrophobicity [1]. This biomimetic inspiration provides a core idea for the design of artificial superhydrophobic materials.

Currently, the research on superhydrophobic materials has expanded from basic theory to practical applications, but still faces key bottlenecks: on one hand, laboratory preparation methods (such as precise template method) are difficult to scale up production, and the mechanical durability of the materials is insufficient (the contact angle significantly decreases after sandpaper friction); on the other hand, traditional low surface energy materials containing fluorine and silicon have environmental risks and cost issues [2]. Therefore, systematically reviewing the theoretical system of superhydrophobic materials, optimizing the preparation process, and expanding the green application paths are of great significance for promoting their industrialization in fields such as architecture, environmental protection, and biomedicine.

This paper discusses from four dimensions: theoretical basis, preparation technology, performance regulation, and application scenarios, analyzes current challenges and proposes prospects, aiming to provide a framework reference for further research on superhydrophobic materials.

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2 Theoretical Basis of Superhydrophobic Materials

The wetting behavior of superhydrophobic materials is jointly determined by the surface chemical composition and the microscopic geometric structure. The classical wetting theory and the biomimetic mechanism together constitute its theoretical core.

2.1 Classical Wettability Theory

2.1.1 Young Equation (Smooth Surface)

In 1805, Thomas Young proposed the fundamental equation describing the wetting property of a smooth solid surface, revealing the relationship between the interfacial tension of the solid-liquid-gas three-phase interface and the contact angle:

$$\cos\theta_Y = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}$$

Here, (θY) represents the intrinsic contact angle of the solid surface, and (γSV), (γSL), (γLV) are the interfacial tensions of the solid-gas, solid-liquid, and liquid-gas interfaces respectively [3]. This equation clearly states that (θY> 90°) indicates a hydrophobic surface, (θY< 90°) indicates a hydrophilic surface, but it cannot explain the superhydrophobic phenomenon of rough surfaces.

2.1.2 Wenzel Model (Complete Wetting of Rough Surfaces)

In 1936, Wenzel introduced the "roughness factor" r (actual surface area / apparent surface area, (r > 1)), which modified the Young equation to describe the situation where a liquid completely wets a rough surface:

$$\cos\theta_W = r\cos\theta_Y$$

This model states that: The rough structure can "amplify" the surface wetting property - for a hydrophobic surface (θ> 90°), as the roughness increases, the apparent contact angle (θ) further increases; for a hydrophilic surface, it becomes more hydrophilic [3]. However, when the surface roughness is extremely high, the liquid cannot completely wet the surface, and the model fails.

2.1.3 Cassie-Baxter Model (Composite Contact State)

In 1944, Cassie and Baxter proposed the "composite contact" mechanism, suggesting that when a liquid comes into contact with a rough surface, the air is trapped in the microstructure gaps, forming a "solid-gas-liquid" three-phase composite interface. The equation is: $\cos\theta_C = f_S\cos\theta_Y + f_V\cos\theta_V$

Here, f_S and f_V represent the area ratios of the solid and air at the contact interface ($f_S + f_V = 1$), ($\theta_V = 180°$) (the contact angle between the liquid and air), and after simplification, it becomes:

$$\cos\theta_C = f_S\cos\theta_Y - f_V$$

When (f_V) approaches 1, (θ_C) approaches 180°, which is the ideal superhydrophobic state [3]. This model successfully explains the superhydrophobic mechanisms of materials such as lotus leaves and carbon nanotube membranes.

2.2 Biomimetic Mechanism: Binary Synergistic Complementary Principle

The common mechanism of natural superhydrophobic surfaces is the "binary synergistic complementary principle" - the cooperative effect of multi-scale rough structures and low surface energy chemical compositions. Typical examples are as follows:

Lotus leaf surface:The relationship between the contact angle and the diameter of the lotus leaf surface is that when the contact angle is 160°, the diameter of the lotus leaf is 128 nm [1]. (Figure 1).

Cactus spines: The gradient structure of the conical spines generates a Laplace pressure difference, driving the directional transportation of droplets; the combination of surface micron grooves and nano protrusions enables efficient fog collection [4].

Spider silk: the unique structural features of wet-rebuilt spider silk enable forces arising from Laplace pressure differences and from surface energy gradients to combine so that hysteresis effects can be overcome and micrometre-sized water drops moved [5].

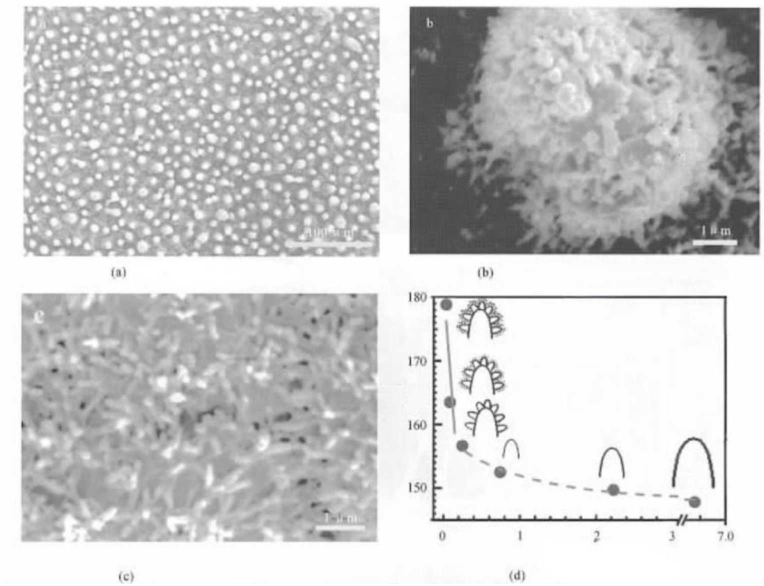

Figure 1

Figure 1 Relationship between the microstructure of the lotus leaf surface and the contact angle

(a) Large-area SEM images of the surface of lotus leaves; (b) The high-magnification SEM image of a single papilla in Figure; (c) SEM photo of the lower surface of the lotus leaf; (d) The relationship between the contact angle and the diameter [1].

3 Main Preparation Techniques of Superhydrophobic Materials

The core of preparing superhydrophobic materials is "constructing rough structures" and "reducing surface energy". The existing technologies can be classified as biomimetic template method, phase separation method, spraying and coating method, etc. The process characteristics and performance of each method are shown in Table 1.

3.1 Biomimetic Template Method

Superhydrophobicity is achieved by replicating the surface structures of natural organisms or fabricating bio - like structures. Typical cases include:

Arrayed Carbon Nanotube (ACNT) Films: Li Huanjun et al. used metal - phthalocyanine complexes as precursors to prepare vertically aligned ACNT films through high - temperature pyrolysis. The surface of the film features a "micro - papillae + nanotube" structure, with a water contact angle of 161°. After being modified with fluorosilane, the contact angle increased to 172°, and the rolling angle was less than 1° [6]. Scanning Electron Microscopy (SEM) results show that the carbon nanotubes have a uniform diameter (approximately 60 nm) and a length of about 4 μm, which conforms to the Cassie - Baxter model [6].

Polyacrylonitrile (PAN) Nanofibers: Feng Lin et al. prepared PAN nanofibers using the template extrusion method. The ends of the fibers are needle - shaped (with a diameter of approximately 100 nm), and a contact angle of 173.8.± 1.3° can be achieved without low - surface - energy modification. After that, an ultra-hydrophobic surface composed of nanofibers made of amphiphilic polyvinyl alcohol (PVA) was prepared (with a contact angle of 171.2°). PVA nanofibers were prepared. PVA nanofibers were fabricated. This phenomenon is attributable to the rearrangement of PVA molecules during the initial stage of the extrusion process, which is accompanied by the reorientation of hydrophobic groups (—CH2—)at the air / solid interface. This method can be extended to prepare super-hydrophobic surfaces using many types of materials [7].

3.2 Phase Separation Method

Constructing a porous and rough structure through the phase separation of polymers and solvents is a simple operation and suitable for large - area preparation:

PMMA/PS Composite Film: Ma Ying et al. prepared polymer films by spin-coating PMMA and PS within the range of PMMA/(PS + PMMA) 15% - 35% (i.e., the mass ratio of PMMA to PS was within 1/5 to 1/2). When the proportion of PMMS/PS on the polymer film was appropriate, a superhydrophobic surface could be obtained after treatment with cyclohexane.

Surfaces obtained with either too large or too small proportions of the two components could not achieve superhydrophobicity. The water contact angle of the film was greater than 150°, indicating superhydrophobicity. When the PMMA ratio is too small, the PS on the film is dissolved, and the proportion of PS on the substrate is too small to cover enough substrate, so the film is difficult to show superhydrophobic. The second is when the PMMA ratio is too large, that is, the proportion of PS is too small, then PS is dispersed in PMMA phase in the form of dispersed phase. Therefore, after PS dissolves, many shallow pits of different sizes are left on the surface of the film, which makes it difficult to achieve superhydrophobicity [8].

3.3 Spraying and Coating Method

Rapidly constructing a rough coating by spraying a composite system of low - surface - energy materials and nanoparticles shows significant potential for industrial applications:

Organic Polysilazane (OPSZ)/Nano - SiO_2 Composite Coating: Wang Qi et al. mixed and sprayed OPSZ and nano - SiO_2 in different proportions. As the SiO_2 content increased, the coating surface changed from disordered micron protrusions to a regular micro - nano pore structure. The embedding effect of SiO_2 on micron diatomite enhanced the adhesion. After rubbing with 360 - cm sandpaper, the contact angle still remained above 150°, indicating excellent friction resistance [9].

4 Performance Control of Superhydrophobic Materials

The performance (contact angle, rolling angle, stability) of superhydrophobic materials depends on the microstructure and surface chemical state. The main control paths are as follows:

4.1 Microscopic Structure Optimization: Hierarchical Structure Design

"The micrometer-nanometer" hierarchical structure can significantly enhance hydrophobicity and stability, the core of which lies in increasing the air retention rate (fV) and reducing the solid-liquid contact area:

Lotus-like layered structure: Jiang Lei et al. prepared a kind of ACNT membrane with both high contact angle and low rolling angle. The average diameter of the papillae and the average distance between them were (2.89 ± 0.32) μm and (9.61 ± 2.92) μm respectively. The research results also showed that the contact angle of this membrane surface was approximately 160° and the rolling angle was approximately 3°. This indicates that the lotus-like ACNT membrane has both high contact angle and low rolling angle, and these two aspects play equally important roles in the superhydrophobic surface. In contrast, the rolling angle of the lotus-like ACNT membrane is much smaller than that of the closely arranged ACNT membrane. This is because a discrete contact is established between the solid and the liquid, which directly affects the shape, length and continuity of the three-phase contact line, thereby significantly reducing the rolling angle [1].

Carbon nanotube membrane structure: The porous array carbon nanotube membrane prepared by the high-temperature decomposition of phthalocyanine metal complexes has an extremely hydrophobic effect. Its contact angle with water is 161°. After being treated with fluorosilane, this array carbon nanotube exhibits a better hydrophobic effect, with the contact angle with water reaching up to 172°[6].

4.2 Plasma Treatment Method

Wu used perfluoroalkyl silane as the gas source and controlled the gas phase pressure and the substrate temperature to obtain different surface roughness of the deposited film, thereby fabricating superhydrophobic films. Additionally, superhydrophobic films were also prepared by depositing a mixture of methyl silane (TMS) and fluorosilane (FAS-7), with the contact angle between the film and water reaching up to 160° at its maximum [10].

Sol-Gel Method: Rao et al. prepared silica sol with Si-CH3 groups covering its surface by the sol-gel method using methyltrimethoxysilane as the precursor and ammonium hydroxide as the catalyst. The water contact angle of this silica sol reached as high as 173°[10].

5 Applications of Superhydrophobic Materials

5.1 Self-Cleaning Applications

Superhydrophobic materials can remove surface contaminants by allowing water droplets to roll off. Typical applications include:

Architectural Glass: The OPSZ-PFMA-TMOS composite coating prepared by Wang Qi et al. allows water droplets to remove over 95% of methylene blue on the surface. Red wine and cola form spherical shapes on the coating surface, indicating that the coating has strong anti - fouling properties against these contaminants. This coating features advantages such as low process cost and convenient operation, and can be used for large - scale development of super - hydrophobic coatings with high practical value. For example, it can be applied as anti - corrosion/anti - fouling paint in ship and marine engineering structures, including offshore engineering (offshore platforms, drilling, oil extraction, storage and transportation), coastal engineering (steel structures, reinforced concrete), and warships, etc., providing a new solution for the development of new high - hydrophobic/super - hydrophobic coatings [9].

5.2 Oil-Water Separation Applications

Superhydrophobic - superhydrophilic materials can achieve efficient separation by taking advantage of the difference in wetting properties:

Netting materials: Ma Xiaomeng prepared an ultra-hydrophobic-ultra-hydrophilic net. The ultra-hydrophobic stainless steel net fabricated by the etching method achieved an oil-water separation efficiency of 98% for cyclohexane, thereby achieving the ultra-hydrophobic effect [11].

5.3 Other Applications

Dry-Style Antifogging Applications: Gao et al. found that mosquito compound eyes have hexagonal close-packed micro/nano-papilla hierarchical structures, which can prevent microscale fog droplets from condensing on the surface (remaining dry even after long-term moisture exposure, while surrounding hydrophobic hairs nucleate droplets). They fabricated artificial analogues via soft lithography, replicating such hierarchical structures with PDMS micro-hemispheres and silica nanopillars. These artificial structures show superhydrophobic properties, realizing a "dry-style" antifogging effect—microscale fog droplets are inhibited from nucleating on the surface, achieving antifogging by preventing droplet condensation instead of traditional wetting-dependent strategies [12].

6 Challenges and Prospects

6.1 Current Challenges

Insufficient mechanical durability: Most superhydrophobic materials rely on micro - nano rough structures. After being rubbed with sandpaper, the contact angle generally decreases. These materials also exhibit deficiencies in thermal stability, chemical stability, and mechanical durability [9].

6.2 Future Prospects

(1) New developments in surfactants: Based on the synthesized macromolecular chain transfer agent PVAc-Br and PVAc-alt-PDBM-Br, and in combination with various acrylic monomers other than DMAEMA for ATRP polymerization, a new type of amphiphilic surfactant was designed. This surfactant can form C/W emulsions with a higher CO_2 volume fraction and longer stability time, promoting the efficient utilization of CO_2 in the emulsion system [13].

(2) 3D Printing Technology Application: The authors utilized 3D printing to prepare eggbeater-headed superhydrophobic microstructures inspired by Salvinia molesta leaf, with a feature precision at the micrometer level, showing superhydrophobic properties, and applicable for microdroplet manipulation and oil/water separation [14].

(3) Multifunctional Integration: Fabricating "superomniphobic - high-temperature tolerant - biofouling-resistant" integrated surfaces, like the doubly re-entrant structured SiO_2 surface, which repels all tested liquids (including fluorinated solvents) without any hydrophobic coating, endures temperatures over 1000° C, and resists biofouling, achieving synergistic multi-performance [15].

7 Conclusion

In summary, superhydrophobic materials, inspired by natural surfaces (e. g., lotus leaves) and guided by classical wetting theories (Young equation, Wenzel, and Cassie-Baxter models) and the biomimetic binary synergistic principle, have been developed via techniques like biomimetic templating, phase separation, and spraying/coating to construct micro-nano rough structures with low surface energy. Their performance (contact angle, stability, etc.) is tunable through microstructure optimization and surface chemical modification, enabling applications in self-cleaning, oil-water separation, and dry-style antifogging. Despite challenges in mechanical durability, future prospects lie in innovating surfactants, advancing 3D printing for precise biomimetic structures, and integrating multifunctionality (e. g., high-temperature tolerance, antifouling) to drive industrialization.

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