International Journal of Scientific Research in Science, Engineering and Technology
Print ISSN: 2395-1990 | Online ISSN : 2394-4099 (www.ijsrset.com)
doi : https://doi.org/10.32628/IJSRSET

Advancing Superhydrophobic Materials: Theoretical Insights, Synthesis Techniques, and Engineering Applications

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Article Info
Volume 9, Issue 1
Page Number : 197-201
Publication Issue :
January-February-2022
Article History
Accepted : 11 Feb 2022
Published: 22 Feb 2022

ABSTRACT

Superhydrophobic materials, defined by water contact angles over 150° and minimal sliding angles, have gained significant interest due to their exceptional water-repellent characteristics. These properties make them suitable for a wide range of applications, including self-cleaning surfaces, corrosion-resistant coatings, and anti-icing technologies. This paper presents a comprehensive overview of superhydrophobic materials, emphasizing their theoretical foundations, synthesis techniques, and diverse applications in mechanical engineering.

The study begins with an exploration of the fundamental principles underlying superhydrophobicity, followed by an examination of the methods employed to enhance the durability of these surfaces. The synthesis of superhydrophobic materials is discussed in detail, highlighting various fabrication techniques and materials used to achieve the desired properties. The paper also delves into the wide range of applications in mechanical engineering, where the unique properties of superhydrophobic materials—such as self-cleaning, anti-icing, and drag reduction—offer significant benefits. Despite the promising applications, the paper identifies key challenges, including durability, scalability, and environmental concerns, which must be addressed for broader adoption. Finally, the paper outlines future directions in the field, suggesting avenues for research and development to overcome these challenges and unlock the full potential of superhydrophobic materials.

Keywords: Superhydrophobic materials, Synthesis, Material Science.

1. Introduction

Nanostructured materials have recently attracted significant attention due to their distinct properties, which differ considerably from those of their bulk counterparts. Nowadays, coatings based on nanomaterials are not only used for protection against mechanical damage or for aesthetic purposes but also serve as multifunctional smart materials [1-3]. According to various studies [4-13], these smart coatings can be employed for a wide range of applications, including anti-corrosion, anti-wear, antibacterial, antifungal, self-cleaning, superhydrophobic, solar reflective, photocatalytic, radar-absorbing, and electrically conductive polymeric uses.

The inspiration for superhydrophobic materials originates from nature, where surfaces like lotus leaves exhibit water repellency due to their micro/nano-structured surfaces combined with a hydrophobic waxy coating. This phenomenon, known as the "lotus effect," has driven extensive research into replicating these properties in synthetic materials. The potential applications of superhydrophobic surfaces are vast, ranging from everyday items like self-cleaning windows to specialized applications in aerospace and medicine. Furthermore, the superhydrophobic surfaces have recently gained attention as a promising method [14] to combat corrosion and biofouling. As discussed in [14-16], the development of superhydrophobic (SH) materials and coatings has led to innovative technologies with broad applications across various industries, including construction, automotive, transportation, aerospace, healthcare, energy, and textiles. While the primary focus has been on their use in terrestrial or in-air applications, the potential of superhydrophobic surfaces in underwater or submerged environments is particularly remarkable. In these settings, SH surfaces could significantly improve vessel hydrodynamic efficiency, reduce maintenance requirements for equipment and platforms, and enhance the overall performance of underwater infrastructure. The versatility of SH materials offers exciting opportunities to advance technology in multiple sectors.

However, the structures that enhance superhydrophobicity often lead to mechanical and chemical weaknesses [14]. When subjected to mechanical stress or chemical exposure, the actual contact areas become significantly smaller, leading to increased contact pressure that can surpass the material's mechanical limits. Consequently, superhydrophobic surfaces are vulnerable to losing their water-repellent properties due to damage to the surface features from mechanical or chemical factors. In summary, these mechanical and chemical vulnerabilities present significant challenges for the practical application of superhydrophobic surfaces [17].

The objective of this review is to provide a comprehensive overview of the recent developments in the synthesis and application of superhydrophobic materials. The paper is structured to cover the theoretical foundations of superhydrophobicity, various synthesis techniques, and key applications. Additionally, it addresses the current challenges faced in the field and suggests potential future research directions.

2. Theoretic Background

Grasping the principles of superhydrophobicity is crucial for understanding the failure mechanisms of superhydrophobic surfaces, developing strategies for creating long-lasting superhydrophobic surfaces, and manufacturing durable superhydrophobic materials for practical use.

2.1 Fundamentals of Superhydrophobicity

Superhydrophobicity represents a unique form of wettability, which is often characterized by the contact angle (CA). The contact angle (θ) serves as an intuitive measure of the wetting behavior of solid surfaces. For a smooth solid surface, the contact angle is determined by the equilibrium between the solid, liquid, and gas phases of a water droplet on the surface. The surface tension is a key factor in this balance, as illustrated in Fig. 1a. The size of the contact angle is generally calculated using the Young equation (θCA) (1), which provides the following relationship:

$$P_{VL}\ \mathrm{Cos}\,\theta = P_{VS} - P_{IS} \quad (1)$$

P_{VL} = tension of liquid

P_{VS} = tension of solid-vapor PVL is the tension-liquid–vapor

P_{IS} = solid-liquid tention

The contact angle of water on a smooth surface is often referred to as the Young contact angle. The model describing the behavior of water on a smooth surface is known as the Young model.

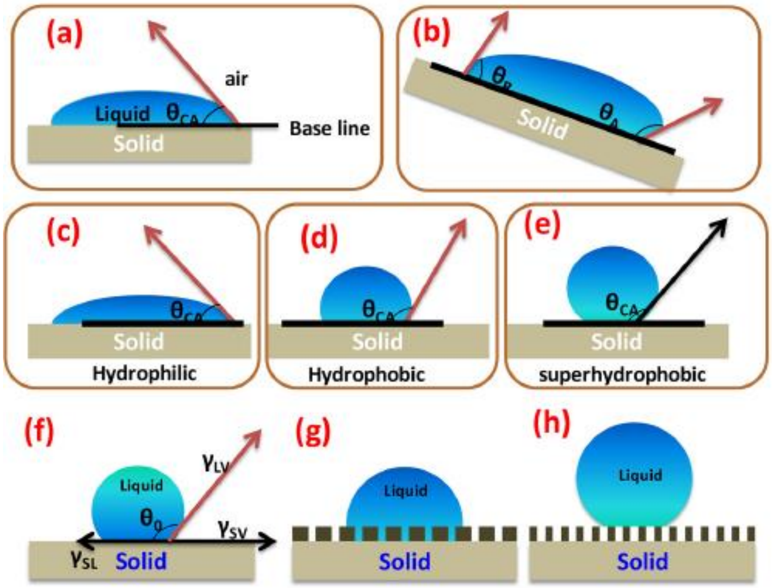

Figure 1. Diagram [18], [19] **(a):** Show the contact angle between a liquid droplet and a solid surface, **(b):** Illustrate the advancing and receding angles. **(c):** Depict a hydrophilic surface with a low contact angle. **(d):** Show a hydrophobic surface with a high contact angle. **(e):** Illustrate a superhydrophobic surface with an extremely high contact angle. **(f):** Present the Young's model, showing a liquid droplet on a smooth surface. **(g):** Depict the Wenzel model, illustrating a rough surface with a modified contact angle. **(h):** Show the Cassie-Baxter model, representing a composite surface with air pockets.

The coefficient of spreading can be represented as:

$$Q_{SVL} = P_{VS} - P_{LS} - P_{VL} \quad (2)$$

The spreading coefficient (SSLV) is a measure of the relative forces between a liquid, a solid, and a vapor. It's calculated as the sum of the interfacial tensions between the liquid and gas, the solid and gas, minus the interfacial tension between the solid and liquid.

If SSLV is greater than or equal to zero, the liquid will completely wet the solid surface, spreading out to form a thin film. This occurs when the forces promoting spreading (liquid-gas and solid-gas interfacial tensions) outweigh the forces opposing spreading (solid-liquid interfacial tension). Conversely, if SSLV is less than zero, the liquid will form a lens on the solid surface with a specific contact angle. This happens when the forces opposing spreading are stronger than those promoting it, resulting in a partial wetting effect.

The contact angle of a liquid on a solid surface is defined as the angle formed between a tangent to the liquid surface and the solid surface at their point of intersection as seen in Fig. 1(a). This angle provides insight into the wettability of the solid surface by the liquid.

A distinction between hydrophilic and hydrophobic materials can be made based on the Young contact angle, which is typically considered to be 90 degrees. This distinction is rooted in the relationship between the water contact angle (WCA) and capillary penetration, as well as the sign of the numerator in a specific equation (Equation 1).

Surfaces with a water contact angle (WCA) ranging from 10 to 90 degrees ($P_{VS} > P_{VL}$) are generally classified as hydrophilic Fig.1 (c). These surfaces exhibit a strong affinity for water and tend to be easily wetted. On the other hand, surfaces with a WCA ranging from 90 to 150 degrees ($P_{VS} < P_{VL}$) are considered hydrophobic as illustarated in Figure 1 (d). These surfaces have a weaker affinity for water and are less likely to be wetted. Extreme wettability states are categorized as superhydrophilic when the water contact angle (WCA) is less than 10°, and superhydrophobic represented by Figure 1 (e). When the WCA exceeds 150°. Superhydrophobicity is characterized by an almost complete non-wetting condition, meaning that a surface with this property should also exhibit very low contact angle hysteresis (less than 10°), allowing water droplets to easily roll off the surface [20].

The hydrophilic surfaces have WCA $< 65^{\circ}$ and water adhesion tension, $T > 30$ Mnm^{-1} based on the investigational long range attractive forces where water adhesion tension is formulated as [21]:

$$T = P_{VL} \operatorname{Cos} \theta \tag{3}$$

Table 1 Technique for Creating Durable Superhydrophobic Surfaces [14]

Material	Method	Modifier	Chemical durability	Mechanical durability
PSS-ODA Complexes	LbL assembly	PAH–SDS complexes	Flame retardant	Withstanding 200 cycles of cotton fabric abrasion
Cotton fabrics	Self-assembly	DTPMP and PDMS		Withstanding 12 laundering cycles
Cotton fabrics	Dip-coating process	Silica nanoparticles and TEOS		Withstanding 20 abrasion cycles
CNT	Spray-coating process	Soy-based polyether polyol	Withstanding 3.5% NaCl solution of 72 h	
APTES	Sol–gel process	TEOS	Withstanding 3.5% NaCl solution of 72 h	
Al	Wet etch process	Composites of PDMS and ZnO		Withstanding mechanical abrasion
PDMS	3D printing	Nanosilica		Withstanding mechanical damage tests under ultrasonication

The advancing angle is the maximum contact angle observed just before a droplet begins to move, whereas the receding angle is the minimum contact angle as the droplet retracts. Contact angle hysteresis is the difference between the advancing angle (θ_A) and the receding angle (θ_R) (Fig. 1b) [20]. Another key parameter for characterizing superhydrophobicity is the sliding angle, also known as the roll-off angle. The sliding angle refers to the minimum tilt angle required for a water droplet to roll off a superhydrophobic surface. This parameter is closely related to contact angle hysteresis, as illustrated in the following equation [22].

$$m \cdot g \cdot \mathrm{Sin}\,\alpha = \beta \cdot P_{VL} \left(\mathrm{Cos}\,\theta_R - \mathrm{Cos}\,\theta_A \right) \tag{4}$$

m = mass of the droplet

g=acceleration because of gravity

α = sliding angle

β = diameter of the wetting area

2.2 Methods for Durable Superhydrophobic Surfaces

As seen in Table 1 [14], [23-29], A variety of methods exist for constructing superhydrophobic surfaces that are resistant to wear and can automatically repair themselves, making them suitable for real-world applications.

3. Synthesis of Superhydrophobic Materials

Superhydrophobic surfaces can be fabricated through various methods. The choice of technique depends on the desired surface properties, the material used, and the application.

3.1 Chemical Vapor Deposition

The Chemical Vapor Deposition (CVD) [30], [31] is a technique widely used to create thin films on substrates by depositing material from vapor-phase precursors through chemical reactions at elevated temperatures. The diagram of CVD system is presented in Figure 1. This method is particularly valuable in the synthesis of superhydrophobic materials, where it allows precise control over surface roughness and composition, crucial for achieving water contact angles above 150°. CVD processes, such as Plasma-Enhanced CVD (PECVD), are used to create durable, uniform coatings on various substrates, making them ideal for applications like anti-corrosion coatings, self-cleaning surfaces, and anti-icing technologies.

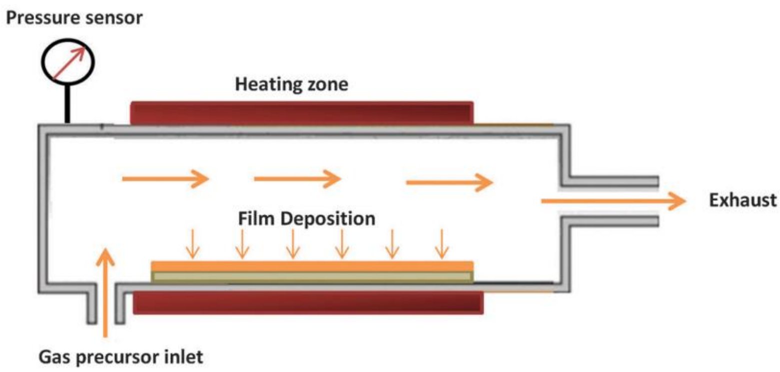

Figure 2: Diagram of CVD system [31]

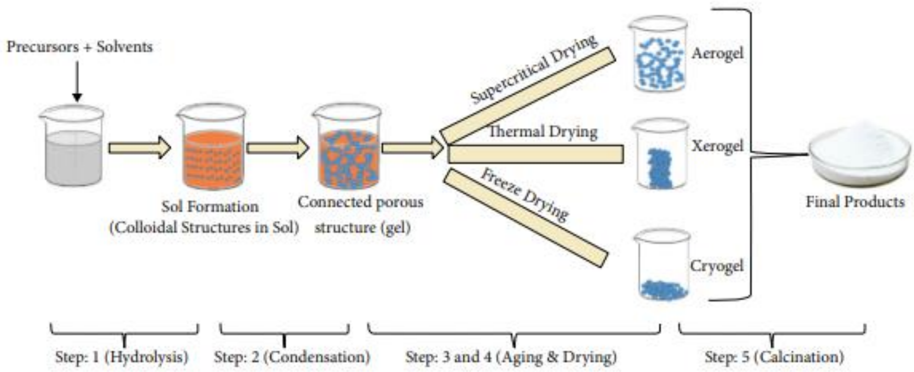

Figure 3: Different level of sol-gel process [34]

3.2 Sol-Gel Process

The sol-gel process [32-34] is a versatile method used to create superhydrophobic coatings by transitioning a liquid sol into a solid gel through hydrolysis and condensation reactions. This technique involves preparing a colloidal solution of metal alkoxides or silica precursors, which is then applied to a substrate. Upon aging and heat treatment, the sol transforms into a gel that forms a thin, porous network with high surface area, crucial for achieving superhydrophobicity. The resulting coatings can exhibit excellent water repellency and durability, making them suitable for self-cleaning surfaces, anti-corrosion applications, and protective coatings in harsh environments. The different level stages can be seen in Figure 3 for sol-gel process.

3.3 Electrospinning

Electrospinning [35], [36] is a technique used to create superhydrophobic surfaces by spinning a polymer solution or melt into fine fibers using an electric field. In this process, a high-voltage electric field is applied to a polymer solution, which causes it to form a charged jet that elongates and solidifies into nanometer to micrometer-sized fibers as it travels toward a collector. These fibers are then assembled into a non-woven mat or coating, which can be engineered to exhibit superhydrophobic properties through subsequent treatments or modifications. The high surface area and porous structure of the electrospun fibers enhance the surface roughness and reduce surface energy, resulting in effective water repellency and applications in filters, textiles, and protective coatings.

3.4 Plasma Treatment

Plasma treatment [37] is a technique used to enhance the superhydrophobic properties of surfaces by modifying their chemical and physical characteristics through exposure to plasma. In this process, a substrate is exposed to a low-pressure plasma generated from gases like oxygen, nitrogen, or argon. The plasma treatment can etch micro- or nano-scale features onto the surface and introduce functional groups that lower the surface energy, leading to enhanced water repellency. This method is particularly useful for creating durable superhydrophobic coatings on a variety of substrates, including polymers and metals, which can be critical for applications such as anti-corrosion, self-cleaning surfaces, and protective coatings.

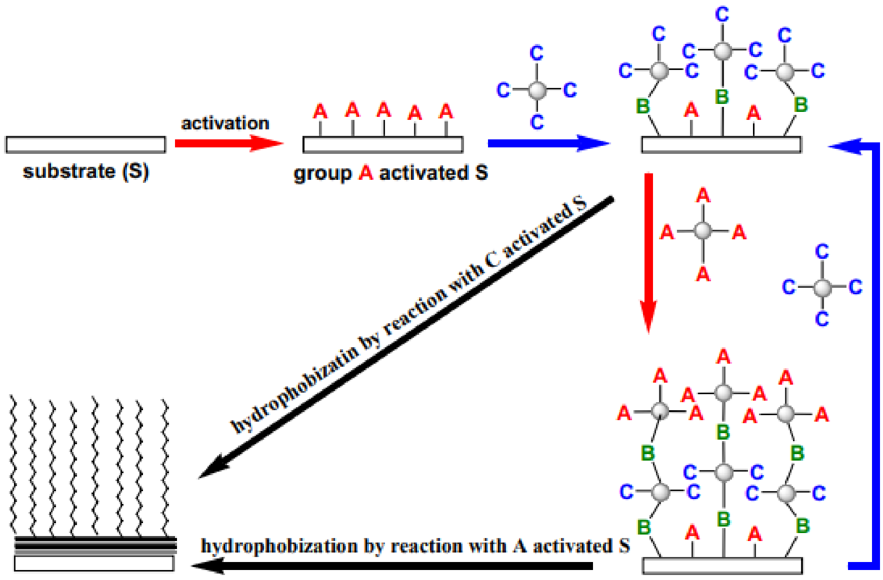

Figure 4: Steps Involved in the Covalent Layer-by-Layer Assembly of Functional Particles [39]

3.5 Layer-by-Layer Assembly

Layer-by-Layer (LBL) [38], [39] Assembly is a method used to fabricate superhydrophobic coatings by sequentially depositing alternating layers of different materials onto a substrate. This technique involves the deposition of oppositely charged polyelectrolytes or nanoparticles from aqueous or organic solutions onto a substrate, creating a multilayered film with tailored properties. Each layer is carefully controlled to achieve the desired surface roughness and chemical composition, which are crucial for imparting superhydrophobic characteristics. The LbL process allows for precise control over the thickness and uniformity of the coating, enabling the creation of superhydrophobic surfaces with high water repellency and various applications, including in protective coatings, textiles, and biomedical devices.

Table 2: Properties and applications of superhydrophobic materials [1]

Utilization	Products	Requirements
Aerospace	Reflective paints	High mechanical and thermal resistance
	Anti-icing paints	Low surface energy, low toxic
	Self-cleaning paint	High CA, excellent mechanical and thermal resistance
Automobile	Self-cleaning paints	High CA, high weather resistance
	Self-cleaning glasses	Good adhesion with glasses, high weather and mechanical resistance, transparent
	Transparent coatings for solar cells	High weather and mechanical resistance, transparent, water resistance
Coating industry	Antibacterial coatings	High biological activity and weather resistance
	Anti-icing coatings	Low surface energy, low toxic

	Antifouling coatings	Non-toxic metallic nanoparticles, high durability
Construction	Self-cleaning glasses	Good adhesion with glasses, high weather and mechanical resistance, transparent
	Photo catalysis walls	High sensibility to UV, high transformation effi
Energy	Transparent coatings for solar cells	High weather and mechanical resistance, transparent, water resistance
	Batteries	High chemical resistance
Textile industry	Self-cleaning textiles	Mechanical and detergent resistance, flexible
	Antibacterial textiles	High biological activity, low human toxic, flexible
	Filtration membranes	High efficient, recyclability, flexible

4. Applications of Superhydrophobic Materials in Mechanical Engineering

Superhydrophobic materials, characterized by their extreme water repellency, have found diverse applications in mechanical engineering. Their unique properties, such as self-cleaning, anti-icing, and reduced drag, make them highly valuable in various engineering fields [1-13].

One significant application of superhydrophobic materials is in self-cleaning surfaces. These materials can repel water droplets, preventing the accumulation of dirt, dust, and other contaminants. This is particularly beneficial in industries such as construction, automotive, and textiles. For example, superhydrophobic coatings can be applied to building facades to reduce maintenance costs and improve aesthetics. This ability to maintain cleanliness without the need for harsh chemicals or extensive manual labor contributes not only to reduced operational expenses but also to environmental sustainability.

Another important application lies in anti-icing. Superhydrophobic surfaces can prevent ice formation, which is crucial in industries like aviation, transportation, and energy. By minimizing ice buildup on surfaces, these materials can enhance safety and efficiency. For instance, superhydrophobic coatings can be applied to aircraft wings to reduce the risk of icing during flight. In the energy sector, these materials are employed in wind turbines and power lines to mitigate the detrimental effects of ice accumulation, thereby ensuring consistent energy production and transmission even in harsh winter conditions.

In the field of fluid mechanics, superhydrophobic materials have the potential to reduce drag. By creating a textured surface with microscopic air pockets, these materials can minimize the contact area between the fluid and the surface, leading to reduced frictional forces. This is particularly advantageous in applications such as pipelines, ships, and turbines. The reduction in drag not only enhances the efficiency of fluid transport systems but also contributes to significant energy savings, making these materials an attractive option for industries aiming to improve their energy efficiency and reduce operational costs.

Moreover, superhydrophobic materials have found applications in microfluidics. These materials can be used to create devices with precise control over fluid flow on a small scale. By manipulating the wetting properties of the surfaces, researchers can design microfluidic channels with unique characteristics, enabling various applications in fields like biotechnology and medical diagnostics. This precision in fluid control is crucial for the development of lab-on-a-chip devices, which are revolutionizing the fields of healthcare and biological research by allowing for the rapid, low-cost analysis of small fluid samples.

In conclusion, superhydrophobic materials offer a wide range of benefits in mechanical engineering. Their self-cleaning, anti-icing, drag-reducing, and microfluidic applications demonstrate their versatility and potential to address various engineering challenges. As research and development in this field continue to advance, we can expect to see even more innovative applications of these remarkable materials. Future innovations may include more durable and scalable production methods, enabling the widespread adoption of superhydrophobic surfaces in everyday applications, further solidifying their role in modern engineering solutions. Table 1 shows the essential properties according to the utilization.

5. Challenges and Future Directions

Superhydrophobic materials, despite their numerous benefits, face significant challenges that need to be addressed before they can achieve widespread commercial and industrial application. One of the primary challenges is the durability of these materials. Superhydrophobic surfaces often rely on delicate micro- and nanostructures to achieve their water-repellent properties. These structures can be easily damaged by physical wear, abrasion, or chemical exposure, leading to a loss of superhydrophobicity. This fragility limits their use in environments where the surfaces are subjected to harsh conditions or mechanical stress, such as in automotive or aerospace applications.

Another challenge is the scalability and cost-effectiveness of producing superhydrophobic materials. While laboratory-scale production methods have demonstrated the feasibility of creating these surfaces, translating these methods to large-scale manufacturing remains difficult. The precise fabrication of micro- and nanostructures often requires expensive equipment and materials, driving up the cost. Additionally, the reproducibility of these structures over large areas remains a concern, as inconsistencies can lead to variations in performance. For superhydrophobic materials to be economically viable, more efficient and scalable production techniques must be developed.

Environmental and health concerns also pose challenges for the widespread adoption of superhydrophobic materials. Some of the chemicals and materials used in the fabrication of superhydrophobic surfaces, such as fluorinated compounds, are known to be harmful to the environment and potentially to human health. The use of such materials could lead to regulatory hurdles, limiting their applicability in consumer products. Therefore, there is a pressing need to develop environmentally friendly and non-toxic alternatives that can provide the same or better performance without compromising safety.

Looking to the future, research in superhydrophobic materials is likely to focus on enhancing their durability and developing more sustainable fabrication methods. One promising direction is the exploration of self-healing materials, which can repair damage to their micro- and nanostructures autonomously, thereby extending the lifespan of the superhydrophobic surface. Additionally, advances in material science, such as the development of new polymers or hybrid materials, may lead to the creation of superhydrophobic surfaces that are both robust and environmentally friendly. These innovations could open up new applications for superhydrophobic materials in fields ranging from renewable energy to healthcare.

In conclusion, while superhydrophobic materials hold immense potential, overcoming the challenges of durability, scalability, and environmental impact is essential for their broader adoption. Future research and development efforts will likely focus on creating more resilient and sustainable superhydrophobic surfaces, paving the way for their integration into a wider range of industrial and consumer applications. As these challenges are addressed, superhydrophobic materials could become a cornerstone of advanced material science, driving innovation in numerous fields.

6. CONCLUSION

Superhydrophobic materials represent a remarkable advancement in material science, with the potential to revolutionize various sectors of mechanical engineering. This paper has provided an in-depth analysis of the theoretical background, synthesis methods, and practical applications of these materials. The fundamental principles of superhydrophobicity, coupled with innovations in surface durability, lay the groundwork for their effective use in challenging environments. Through the synthesis of these materials, researchers have developed a wide array of techniques to tailor their properties for specific applications. The diverse applications in mechanical engineering, from self-cleaning surfaces to drag-reducing coatings, demonstrate the versatility and utility of superhydrophobic materials. However, the challenges associated with durability, large-scale production, and environmental impact must be addressed to fully realize their potential. As research progresses, future advancements in material science, sustainable practices, and scalable production methods will be critical to overcoming these obstacles. The continued development of superhydrophobic materials holds the promise of significant technological advancements, driving innovation and efficiency across multiple engineering domains.

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