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A REVIEW OF FABRICATION TECHNIQUES FOR SUPERHYDROPHOBIC COATINGS

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ОГЛЯД ТЕХНОЛОГІЙ ВИГОТОВЛЕННЯ СУПЕРГІДРОФОБНИХ ПОКРИТТІВ

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Superhydrophobic surfaces have emerged as a pivotal focus of modern materials science. These surfaces are notable for their unique wetting behavior and wide array of potential applications in fields such as self-cleaning coatings, anti-corrosion protection, drag reduction, anti-icing technologies, and oil-water separation. Inspired by natural models such as lotus leaves, water striders, and Salvinia molesta, these surfaces combine low surface energy materials with hierarchical micro/nanostructures to achieve water contact angles exceeding 150°. This dual scale roughness traps air pockets beneath water droplets, enabling the "lotus effect," whereby droplets roll off surfaces, removing contaminants. The development of superhydrophobic coatings is particularly important in the context of metal corrosion because economic and environmental factors have created a demand for safer, more sustainable alternatives. A wide variety of fabrication techniques have been developed, including top-down methods, such as laser ablation and etching, and bottom-up strategies, such as sol-gel deposition and chemical vapor deposition. However, many approaches are limited by complexity, cost, scalability, or environmental impact. Furthermore, the practical application of these coatings presents challenges concerning durability, material compatibility, performance under environmental stressors, and the use of fluorinated compounds, which pose ecological risks. This review critically examines current methodologies for fabricating superhydrophobic surfaces. It evaluates the underlying principles, advantages, and limitations of these methods with respect to mechanical robustness, scalability, and application-specific demands. Particular emphasis is placed on the importance of multiscale surface structuring and selecting inherently hydrophobic, low-energy materials to create functionally resilient coatings. Additionally, the work explores the limitations of current testing standards and suggests that a unified framework for evaluating mechanical wear, environmental resistance, and hydrophobic retention is essential for accelerating the transfer of technology from the laboratory to the industrial scale. The review highlights novel strategies such as biomimetic design, incorporating self-healing materials, and integrating superhydrophobic coatings with multifunctional technologies as promising future directions. Ultimately, the success of superhydrophobic surface technologies depends on a multidisciplinary effort balancing performance metrics with environmental responsibility and economic feasibility to unlock their transformative potential across diverse sectors.

Ключові слова: *superhydrophobic coatings, contact angle, surface wettability, surface roughness, water-repellent, fabrication methods.*

Introduction. Superhydrophobic surfaces have become a subject of significant interest in material science due to their wide range of applications, including self-cleaning surfaces, anti-fouling, anti-icing, drag reduction, and oil/water separation. These surfaces are inspired by numerous examples in nature, such as the water spider (Gerris remigis) that can walk on water surfaces and the Salvinia molesta leaves that resist wetting even after weeks of submersion. The most famous example is the lotus leaf, which demonstrates exceptional water-repellent properties and gave rise to the well-known "Lotus effect." The mechanism of the lotus effect was first investigated and described by Barthlott and Neinhuis in 1997 [1].

The development of corrosion-resistant superhydrophobic coatings has gained particular importance in recent years due to the economic and safety concerns associated with metal corrosion. In industrialized countries, corrosion-related costs typically amount to 1–4% of their GDP. Until recently, chromium-containing coatings were efficiently used for corrosion protection, but these have been restricted due to their harmful effects on humans and the environment. This has led to increased research in environmentally friendly alternatives, including polymeric coatings.

Superhydrophobic surfaces are characterized by their extreme water repellence, which is achieved through a combination of two key factors: the inherent hydrophobicity of the surface material (low surface energy) and surface roughness. Materials with low surface energy naturally repel water because forming a new solid-liquid interface with water is energetically unfavorable [2, 3]. However, the maximum water contact angle (WCA) that can be achieved by a flat, low surface energy material is approximately 120° [4]. To achieve superhydrophobicity, surface roughness must be introduced, which can increase the contact angle to above 150° using the same chemical composition. Furthermore, building a structure with hierarchical roughness (combining dual-scale texture) has been reported to improve both hydrophobicity and surface durability. This approach is observed in nature, such as in the Salvinia leaves and water spider legs, and is replicated in synthetic coatings through micro/nanoscale surface structuring.

The Lotus effect describes the self-cleaning mechanism observed on the lotus plant leaf surface [5]. While water droplets slide along a tilted hydrophobic surface, on a superhydrophobic surface, the near-spherical droplets roll across the surface instead. This rolling action enhances the removal of surface contaminants like dirt particles and bacteria. Examining the structure of lotus leaves reveals a waxy surface coating that repels water, combined with complex 3D microstructure textures and an additional layer of smaller-scale hair-like features covering both the surface protrusions and flat regions. These microstructures trap air underneath the water upon wetting the surface, enabling the rolling motion of water droplets. Similar structures are found in the water spider's legs, which feature micro-sized filaments with nano-grooved textures, resulting in dual-scale roughness that contributes to their water-repellent properties. These natural examples highlight the importance of hierarchical structuring in achieving superhydrophobicity, with surfaces often displaying both micro and nanoscale roughness features.

Task setting. Despite remarkable advances in laboratory-scale fabrication of superhydrophobic coatings, many existing methods remain complex, costly, or difficult to scale up. In addition, issues related to mechanical durability, environmental impact, and long-term performance still pose challenges for practical applications. Therefore, a pressing scientific and technological task is to systematize the current strategies for fabricating superhydrophobic surfaces, with a particular focus on their scalability, sustainability, and application-specific suitability. Special attention should be paid to the role of multi-scale structuring and the selection of low-surface-energy materials, which together define the effectiveness and durability of these coatings.

The aim of the work is to provide a comprehensive review of current fabrication techniques for superhydrophobic coatings, with a focus on understanding the underlying principles, advantages, limitations, and potential industrial applications of each method. Particular attention is paid to the role of surface chemistry and multi-scale roughness in achieving durable and functional superhydrophobicity.

Presentation of the main research material. Several methods are used to measure and characterize surface wettability. The most common is the water contact angle (WCA) measurement, where the angle is measured from the surface-water contact plane to the tangent line of the water-air interface. Surfaces are categorized based on their WCA values (Fig. 1): superhydrophilic ($\theta<10°$), hydrophilic ($10°<\theta<90°$), hydrophobic ($\theta>90°$), superhydrophobic ($\theta>150°$) [6]. A maximum contact angle is achieved when the droplet is completely spherical, while a minimum angle occurs when the droplet spreads to completely wet the surface.

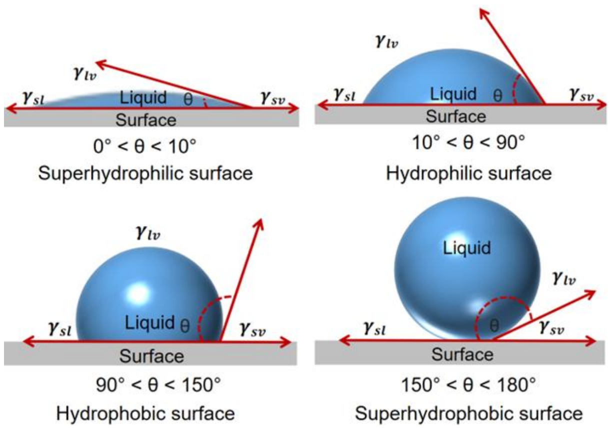

Fig. 1. Illustration of WCA values [6]

Fabrication of Superhydrophobic Surfaces. Fabrication methodologies for superhydrophobic surfaces are categorically divided into two principal approaches: top-down and bottom-up methods [7]. The top-down methodology entails the structural modification of bulk material surfaces to generate roughness. This is accomplished through various surface topography alteration techniques, including lithography, etching, and laser treatment processes. Conversely, bottom-up methodologies facilitate surface roughness through the addition of small-scale materials. Implementation occurs via deposition techniques such as chemical vapor deposition, electroplating, and sol-gel processing. It should be noted that certain deposition procedures do not inherently yield rough surfaces; consequently, supplementary treatment of precursor materials or the deposited surface may be requisite to achieve the desired roughness characteristics. The determination of appropriate fabrication approaches and specific techniques is contingent upon the selected base materials, desired surface properties, and intended application parameters. Advanced superhydrophobic surface development frequently incorporates multiple fabrication phases, integrating both top-down and bottom-up elements to attain optimal surface characteristics. Fig. 2 illustrates the two primary fabrication approaches for superhydrophobic surfaces. This section will examine these methodologies in sequence as depicted in the figure, beginning with 'top-down' techniques before exploring 'bottom-up' approaches that employ deposition to create surface roughness. Subsequently, we will briefly address deposition methods that do not require rough morphology development, highlighting general material treatment techniques that have been documented in combination with these deposition processes. It should be emphasized that this represents a simplified overview of the documented methodologies; in practice, many sophisticated fabrication techniques incorporate multiple approaches simultaneously, with their selection dependent on the specific surface design requirements and intended application.

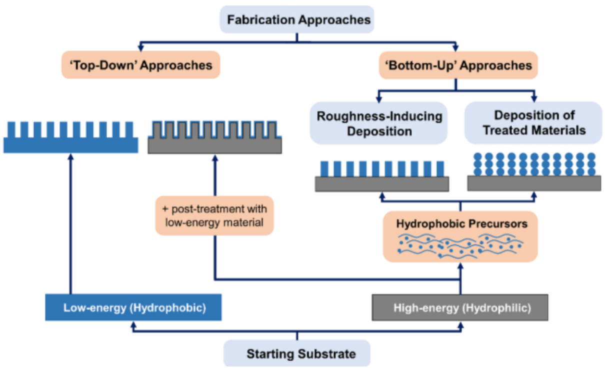

Fig. 2. Schematic illustrating the approaches for fabrication of superhydrophobic surfaces, and how this can be related to the choice of the starting materials

Top-down approaches involve structuring bulk substrates to produce rough morphology, which is essential for achieving superhydrophobicity. This can be achieved through the selective removal of hard materials or by imprinting soft materials using mold. Common top-down techniques include laser process, etching, galvanic corrosion, lithography, template imprinting [8].

Laser processing. Ultrafast lasers, particularly femtosecond lasers [9], offer a precise method for fabricating micro- and nanostructured surfaces. This technique allows for the fabrication of superhydrophobic surfaces without the need for additional coatings or surface treatments. Laser ablation can induce chemical and structural changes to the surface of materials, enhancing their water repellency [10]. Ta et al. [11] conducted a comprehensive investigation into the fabrication of superhydrophobic surfaces on 304S15 stainless steel using nanosecond fiber laser systems, showcasing a cost-effective alternative to pico- and femtosecond laser technologies. Through direct laser texturing, they achieved superhydrophobic properties, with water contact angles of approximately 154° and contact angle hysteresis as low as 4°. The study revealed that laser-induced surface roughness amplified hydrophilic behavior initially, but the surfaces transitioned to superhydrophobicity after exposure to ambient conditions for 13–18 days. This wettability change is attributed to chemical modification and decomposition processes involving carbon dioxide and magnetite. Long et al. [12] utilized femtosecond laser irradiation to fabricate superhydrophobic copper surfaces with tunable water adhesion properties, inspired by the contrasting wetting behaviors of lotus leaves and rose petals. By varying the laser scanning speed (10–200 mm/s), the researchers precisely controlled surface topographies, ranging from deep microstructures to shallower formations. Post-treatment chemical modification enhanced hydrophobicity, enabling surfaces to transition between Cassie and Wenzel wetting states based on microstructural depth. Low-speed laser treatments resulted in surfaces with minimal water adhesion, exhibiting self-cleaning properties akin to lotus leaves, while high-speed treatments created surfaces with significant water adhesion, resembling rose petals. These surfaces demonstrated adjustable water contact angles (up to 159°) and sliding angles (from <10° to 90°), alongside varied adhesion forces (10 μN to 110 μN). Applications of this technique include liquid manipulation and self-cleaning technologies, highlighting its cost-effectiveness and precision in creating functional superhydrophobic surfaces. The changes in surface morphology during laser irradiation and the resulting microstructures of the laser-treated copper surfaces at various scanning speeds (ν) are illustrated in Fig. 3.

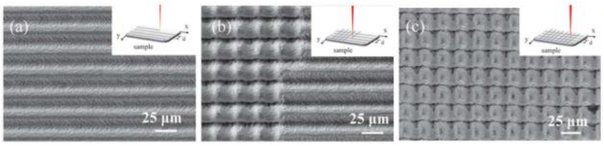

Fig. 3. The changes in surface morphology during laser irradiation process, insets on the top right show the schematics of the laser scanned paths

Etching. Etching [13] is a simple and effective approach to increase surface roughness—an essential factor in achieving superhydrophobicity. This process involves removing surface material in two primary ways: isotropically, where the removal is uniform in all directions, or anisotropically, where it occurs in specific directions. Various etching techniques exist, each with unique advantages, and they can be used alone or in combination with other fabrication methods to achieve complex, hierarchical textures. After etching, applying a low surface energy material is a common step to attain the desired superhydrophobic properties. Among various techniques, chemical etching stands out due to its simplicity and low cost. Several studies have explored its application for different substrates. These involve the removal of substrate material by exposure to harsh (acidic or basic) solutions.

Qian et al. [14] reported the synthesis of superhydrophobic surfaces on aluminum, copper, and zinc substrates by using dislocation-selective chemical etching. This process involves preferentially dissolving the dislocation sites in polycrystalline metals, creating hierarchical microstructures such as pits, grooves, and nanoparticles. After etching, the surfaces were treated with fluoroalkylsilane to enhance hydrophobicity, resulting in water contact angles exceeding 150° and roll-off angles below 10°. The study demonstrates a simple yet effective method to fabricate superhydrophobic surfaces, with potential applications for other polycrystalline materials.

Kim et al. [15] reported the synthesis of superhydrophobic stainless steel surfaces by hydrogen fluoride (HF) etching and dipping in a hot 0,1% NaCl solution, followed by fluorination treatment. The effect of the HF etching time was studied, and it was found that 20-min etching led to the highest WCA (164°) and lowest sliding angle (5°). The treatment with 0,1% NaCl solution was found to further enhance the hydrophobicity (WCA 168°, sliding angle 2°). This was due to the petal-like structures formed on the etched surface, which provided hierarchical texturing. Interestingly, extending the NaCl dipping time had negligible effect, likely due to the low concentration of the solution, which limited further surface interaction after initial etching. The surfaces showed retention of superhydrophobicity after 30 days of placing in water. Several other reports utilized chemical etching while sharing the main two-step procedure. Examples include the etching of stainless-steel substrates with sulfuric acid and ferric chloride, followed by the modification using octadecyltrichlorosilane and decyltrimethoxysilane, respectively.

Li et al. [16] proposed a similar procedure for creating superhydrophobic stainless steel surfaces while maintaining corrosion resistance. Their approach involved a three-step process: (1) etching with hydrofluoric acid (HF) to generate surface roughness through intergranular corrosion and redeposition of metallic oxides and fluorides, (2) passivation in nitric acid to restore corrosion resistance, and (3) deposition of a fluorocarbon film to reduce surface energy. This method was tested on both 304 and 316 grades of stainless steel, with significant differences observed due to their varying alloy compositions. The primary distinction being that 316 SS contains 2-3 wt. % molybdenum while 304 SS does not. Instead of adding secondary materials to create roughness, their approach utilized chemical etching to directly modify the stainless-steel surface, thereby maintaining its mechanical properties. The selective etching targeted grain boundaries through intergranular corrosion, creating micro- and sub-micrometer scale roughness. After passivation to restore corrosion resistance, a plasma-deposited fluoropolymer coating was applied to achieve high water contact angles and low hysteresis. This research addressed limitations of previous superhydrophobic stainless steel fabrication techniques, which often relied on either non-scalable process like femtosecond laser ablation or coating with materials that lacked mechanical durability.

Lee et al. [17] developed a highly efficient and reproducible approach to fabricate large-scale nanostructured polymeric and metallic surfaces with precise ratio control, utilizing anodic aluminum oxides (AAOs) or textured aluminum as replication templates, the scheme as shown in Fig. 4. The process combines photolithography, aluminum etching, and anodization with polymer replication to produce hierarchical micro- and nanostructures. Initially, photolithography using positive photoresist and square-patterned shadow masks imprints micrometer-scale patterns onto aluminum sheets. The researchers then used an etching solution to selectively transform the patterns into concave structures. Following this, anodization and AAO removal enable the formation of nanostructures, such as nanopores and nanogrooves, on both flat surfaces and within the micrometer-scale concavities. Finally, heat- and pressure-driven imprinting of thermoplastic polymers, particularly high-density polyethylene (HDPE), replicates the hierarchical designs, with HDPE being chosen for its chemical stability and resemblance to natural hydrophobic materials. The fabricated surfaces demonstrate superhydrophobic properties, attributed to the synergistic effects of the hierarchical structures and material composition. Results show a maximum static contact angle of 113° for surfaces with only micrometer-scale patterns (pitch size 25 μm) and up to 139° for flat HDPE with nanostructures. The highest contact angle of 159° was achieved on HDPE with hierarchical structures combining nanofibers and micrometer-scale papillae, demonstrating a 67% increase compared to flat surfaces. Replicas remained superhydrophobic over three months of air storage, proving the method's robustness and reliability. This technique provides a scalable and adaptable platform for producing functional and biomimetic superhydrophobic surfaces, opening avenues for applications in packaging, medical devices, and antifouling coatings.

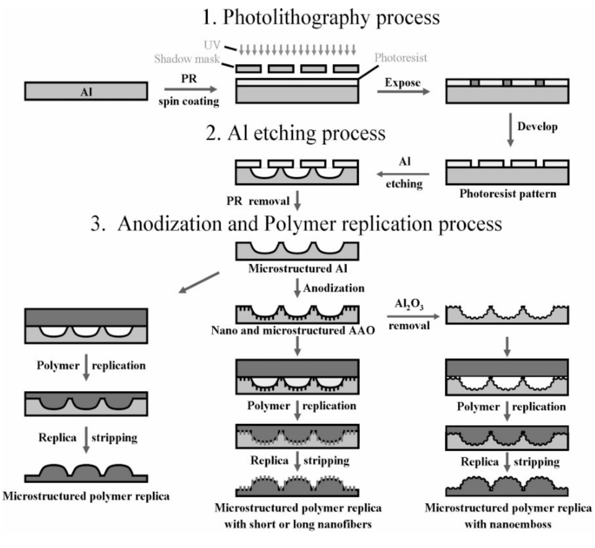

Fig. 4. Scheme of fabrication of HDPE replicas with various shapes of nanometer- and micrometer-structured surfaces [17]

Lithography. This is a technique commonly used in microelectronics to create patterns on surfaces. It involves coating a substrate with a light-sensitive material, exposing it to light through a patterned mask, and then developing the exposed areas. This method can be used to create microstructures that contribute to superhydrophobicity. Electron beam lithography is particularly precise and can be used to create complex patterns on a nanoscale [18].

Pozzato et al. [19] developed a cost-effective method for creating superhydrophobic silicon surfaces using nanoimprint lithography combined with wet chemical etching. Their process (Fig. 5) begins with creating a patterned glass mold, which is then imprinted onto a photoresist layer on a silicon substrate. This pattern is subsequently transferred to a SiO_2 layer and finally to silicon through etching techniques. The researchers employed two distinct etching approaches: 1) Isotropic etching with HNA to produce rounded channels; 2) Anisotropic etching with KOH to create rectangular channels. After etching, the surfaces were coated with octadecyltrichlorosilane (OTS) self-assembled monolayers to enhance hydrophobicity. Contact angle measurements revealed that the advancing contact angles closely aligned with Cassie model predictions, indicating the presence of trapped air beneath water droplets on these surfaces. A key advantage of this fabrication method is its tunability – the surface properties can be readily adjusted by modifying the etching method or mold parameters.

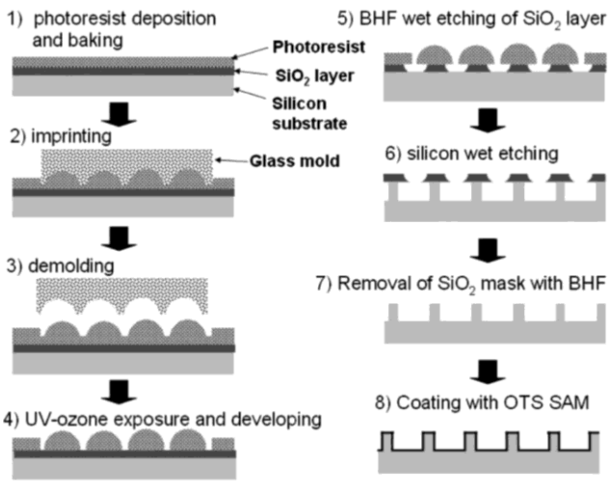

Fig. 5. Schematic of fabrication process [19]

Template imprinting. Soft lithography [20] shares the main theory with photolithography in terms of creating a replica of a previously prepared pattern [18]. Template imprinting is a versatile technique that shares the fundamental principle of photolithography in replicating patterns, unlike photolithography, which uses rigid photomasks, soft lithography employs flexible templates, typically made of polydimethylsiloxane (PDMS), to create micro- and nano-scale patterns. This method is cost-effective, environmentally friendly, and supports diverse applications, including biosensors and nanotechnology. Soft lithography offers advantages in scalability and material compatibility but faces challenges such as template deformation and defect control during the imprinting process.

Liu et al. [21] introduced a soft-lithographic imprinting technique to fabricate super-hydrophobic surfaces inspired by lotus leaves. To replicate lotus leaf-inspired microstructures, Liu et al. [21] employed a soft-lithography approach using PDMS molds, which were cast directly from natural templates. These stamps replicate microstructures and are pressed onto substrates coated with an epoxy-based azo polymer (BP-AZ-CA) in tetrahydrofuran ink, under moderate pressure (approximately 5×10^4 Nm^{-2}) for about 10 seconds. After drying the substrate in a 25 °C vacuum oven for 6 hours, the fabricated surfaces display papillary structures, achieving a water contact angle of 154,6° and a low contact angle hysteresis (3,3°). This simple, scalable method demonstrates versatility for various substrates and has potential applications in water-repellent and self-cleaning technologies.

Yun et al. [20] presented an innovative soft-lithographic approach for fabricating superhydrophobic lotus-leaf-like surfaces using reduced graphene oxide (RGO), the schematic as shown in Fig. 6. Leveraging the natural hierarchical micro/nanoscale structures of lotus leaves, polydimethylsiloxane (PDMS) stamps were prepared by replicas molding against fresh lotus leaves as the masters. Octadecylamine-modified reduced graphene oxide (ODA-RGO) was synthesized via a chemical reduction of graphene oxide (GO) with hydroquinone and octadecylamine. The resulting ODA-RGO dispersion in tetrahydrofuran (THF) served as the ink for the microcontact printing process. The PDMS stamps, coated with the ODA-RGO ink, were gently pressed onto pre-cleaned substrates such as glass slides and silicon wafers, transferring the intricate surface features of the lotus leaves. Characterization techniques, including FTIR, XPS, Raman spectroscopy, SEM, and confocal microscopy, revealed high-fidelity replication of the lotus leaf's papillary microstructures and additional nanoscale roughness derived from stacked RGO nanosheets. The fabricated surfaces demonstrated remarkable superhydrophobicity, evidenced by water contact angles exceeding 160°, and exhibited robust environmental durability under extreme conditions, such as exposure to corrosive solutions or elevated temperatures. This research highlights the potential applications of these surfaces in fields requiring durable hydrophobic and anti-corrosion properties.

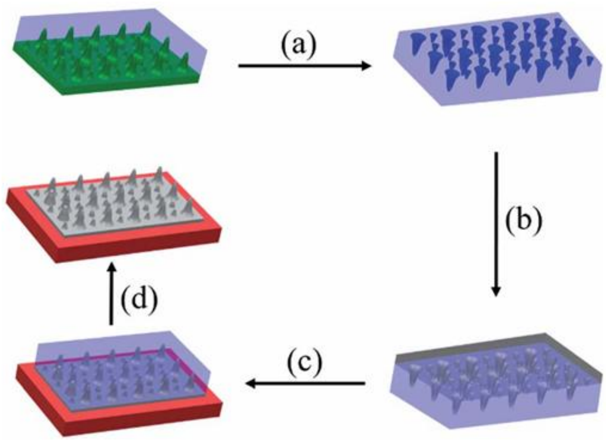

Fig. 6. Schematic diagram of the fabrication process of the ODA-RGO lotus-leaf-like surfaces:
a – preparation of the PDMS stamp through replica molding against a piece of fresh lotus leaf, b – dropping the ODA-RGO dispersion on the PDMS stamp to form a thin layer of the "ink" on the surface, c – pressing the "inked" stamp against the substrate for a few seconds, d – peeling off the PDMS stamp and vacuum drying

Bottom-up approaches refer to fabrication techniques where materials are built from their fundamental building blocks (atoms, molecules, or nanoparticles) that self-organize or are directed to assemble into more complex structures [22].

3D printing. technology represents an advanced deposition methodology for the fabrication of superhydrophobic surfaces [23]. This additive manufacturing approach shares fundamental principles with Layer-by-Layer (LbL) assembly techniques through its sequential construction of precisely controlled structural elements. However, 3D printing offers distinct advantages in the context of superhydrophobic surface engineering, including unprecedented geometric complexity, customizable hierarchical architectures, and reproducible surface topographies across multiple scales. The versatility of this manufacturing platform enables the precise implementation of biomimetic design principles while maintaining consistent quality parameters throughout the fabrication process.

It was reported [24] for the replication of the Salvinia leaf 'eggbeater' structure were fabricated by the Immersed surface accumulation three dimensional (3D) printing process. Multi-walled

CNTs were added to the liquid photo-curable resin utilized to increase surface roughness. The number of arms of the eggbeater shape (N), as well as their spacing (d), was investigated for their effect on the superhydrophobic properties (Figure 13. b-g). It was found that hydrophobicity is maximized when the spacing is kept at d=0.5. Moreover, applying N=2 resulted in a highly superhydrophobic surface (WCA = 170°), although the reduced number of arms made the structures fragile. Applying N=4 was found to be a good compromise between both strength and superhydrophobicity (152°).

Electrospinning. This is an innovative technique that uses an electrically driven jet of a polymer solution or melt to create polymer fibers with diameters ranging from nanometers to a few microns [25]. Electrospinning has emerged as a powerful technique for creating superhydrophobic coatings and surfaces, offering a versatile and efficient approach to fabricating water-repellent materials. This process involves applying a strong electric field to a polymer solution or melt, resulting in the formation of nano-scale filaments that can be collected to create non-woven webs with hierarchical structures. Recent advancements have focused on optimizing polymer blends, incorporating recycled materials like PET, and developing multi-step processes combining electrospinning with other techniques such as electrospraying and spin coating. These innovations have led to the creation of durable, self-cleaning surfaces with water contact angles exceeding 150°, capable of withstanding various mechanical stresses. Applications range from protective coatings for aerospace and solar panels to anticorrosion and anti-icing treatments. The simplicity, scalability, and eco-friendly potential of electrospinning make it a promising method for industrial-scale production of superhydrophobic materials, addressing needs in energy, infrastructure, and environmental sectors [26].

Álvarez et al. presented a novel superhydrophobic and anticorrosive coating using a three-step process involving electrospinning, spin coating, and electrospraying. They combined polytetrafluoroethylene (PTFE) with poly(acrylic acid) + β-cyclodextrin (PAA + β-CD) to create a composite coating on aluminum alloys. The electrospun PAA + β-CD layer provided adhesion and a porous network for PTFE particles, while the spin-coated PTFE layer ensured uniform distribution. The final electrosprayed layer enhanced particle bonding through heat treatments, achieving water contact angles (WCA) above 150° and excellent corrosion resistance [27].

Chemical Vapor Deposition (CVD). This is one of the most sophisticated approaches for fabricating superhydrophobic surfaces, offering exceptional control over surface morphology at the micro and nanoscale. In this gas-phase process, precursor molecules are vaporized and transported to a heated substrate where they react or decompose to form solid deposits with precisely tailored structures. For superhydrophobic applications, CVD excels at creating the dual requirements of hierarchical roughness patterns and low surface energy coatings in a single or multi-step process. The technique allows for the growth of various structures including carbon nanotubes, fluorocarbon polymers, silicon-based compounds, and metal oxides - all of which can be optimized to achieve water contact angles exceeding 150° with minimal hysteresis. What distinguishes CVD from other fabrication methods is its ability to produce highly conformal coatings even on complex geometries, excellent adhesion to substrates, and remarkable durability of the resulting superhydrophobic surfaces, making it particularly valuable for industrial and high-performance applications despite requiring specialized equipment and careful process control [28].

Lau et al. [29] were among the pioneers in fabricating superhydrophobic CNT forests by modifying vertically aligned CNTs (VACNTs) with a polytetrafluoroethylene (PTFE) coating using the chemical vapor deposition (CVD) method. The resultant surface exhibited outstanding water repellency, with advancing and receding contact angles (CAs) of 170° and 160°, respectively. This work demonstrated the effectiveness of surface functionalization in achieving high hydrophobicity by facilitating the Cassie-Baxter wetting regime, where air is trapped between the water droplet and the surface, minimizing liquid-solid contact. In another study, Sun et al. [30] explored the fabrication of three-dimensional CNT films on patterned silicon substrates, examining the effect of nanotube orientation on the surface wettability. The study revealed that the alignment of the CNT arrays had a significant influence on the surface's wetting properties, enabling a wide range of wettability, from hydrophilic (CA < 30°) to superhydrophobic (CA > 150°), depending on the CNT orientation and spacing. This work highlighted the potential of anisotropic microstructures in controlling surface energy and tuning wettability for a variety of applications. Jiang et al. [31] further refined the fabrication of ACNT films by modulating the microstructural features, such as pillar spacing, to achieve transitionable wettability states. By adjusting the pillar spacing from 6 μm to 20 μm, they produced films with varying contact angles, from hydrophilic (22,2°) to superhydrophobic (>163°), and demonstrated excellent sliding properties (sliding angles < 5°). The CNTs were grown using CVD on silicon templates and scanning electron microscopy (SEM) and atomic force microscopy (AFM) analyses revealed the nanotubes' hexagonal and honeycomb-like microstructure. This work emphasized the role of three-dimensional anisotropy and air entrapment in enhancing surface hydrophobicity, far exceeding predictions made by the Wenzel and Cassie models.

Layer by layer deposition. This technique is a highly adaptable and cost-effective method for fabricating coatings with precisely controlled chemical composition and nanostructure [32]. By sequentially depositing oppositely charged or complementary materials—such as polymers, nanoparticles, or biomolecules—this technique enables the formation of multilayer films with tunable thickness and tailored functionality. Its mild, aqueous processing conditions make it suitable for coating a wide range of substrates, including complex, non-flat, and large-area surfaces, ensuring conformal coverage even on highly irregular geometries. The modular nature of LbL allows for the incorporation of diverse materials, resulting in multifunctional coatings with applications spanning anti-corrosion, biomedical, energy, and environmental fields. Moreover, advancements in scalable deposition methods have expanded its industrial potential, making LbL assembly a powerful platform for designing advanced, sustainable coatings tailored to specific performance requirements [33]. This method involves sequentially depositing alternating layers of materials, such as polymers, nanoparticles, or other hydrophobic agents, to form hierarchical surfaces that enhance water repellency. Sutar et al. [34] the fabrication of robust self-cleaning superhydrophobic coatings by depositing polymer layers on candle soot surfaces. This approach combined the hierarchical structure of soot with a polymer layer to improve durability and self-cleaning properties, making it suitable for oil-water separation and industrial applications.

Sol-gel methods. The sol-gel methodology for fabricating superhydrophobic coatings represents a sophisticated chemical approach wherein precursors (typically metal alkoxides) undergo sequential hydrolysis and condensation reactions to transition from a colloidal solution to an interconnected network, while simultaneously incorporating both low surface energy components (such as fluoroalkylsilanes, long-chain alkyl groups, or silicone derivatives) and hierarchical surface roughness features (achieved through template-assisted processing, nanoparticle incorporation, phase separation, or layer-by-layer deposition), which can be applied via dip coating, spin coating, or spray techniques and subsequently modified through thermal curing, chemical vapor treatment, or plasma processing to enhance durability and functionality; despite challenges including mechanical resilience, long-term stability, scalability, and environmental concerns (addressed through reinforcing nanofillers, UV-resistant additives, industrial process optimization, and fluorine-free alternatives, respectively), this versatile platform continues to evolve with recent innovations in self-healing capabilities, stimuli-responsive wettability, optical transparency, and multifunctionality, thereby maintaining its position as an indispensable approach for creating surfaces with precise control over chemistry and topography at the nanoscale for applications ranging from self-cleaning surfaces to anti-icing, anti-corrosion, and anti-fouling technologies.

Lu et al. [35] explored the superhydrophobic properties of a bulk material prepared using epoxy resin and hydrogenated silicone oil (PMHS) through a sol-gel method. The material was formed by combining various reagents, followed by ultrasonic dissolution, refluxing, drying, and polishing to enhance its surface roughness. Analysis showed that nanoparticles of 50–100 nm played a key role in achieving superhydrophobicity, with polishing increasing the water contact angle from 133° to 152°. Thermal tests demonstrated durability up to 300 °C, with optimal hydrophobic properties achieved at 100 °C, where the contact angle reached 161°. The material also displayed excellent repairability, regaining hydrophobicity after surface damage and polishing. With its durability, recoverability, and hydrophobic performance, this material has promising applications in fields like self-cleaning, corrosion protection, and oil-water separation.

Covalent functionalization. This is a critical strategy in the development of durable superhydrophobic coatings, enabling chemical bonding between hydrophobic agents and substrate surfaces. This approach enhances the mechanical, chemical, and thermal stability of coatings while ensuring long-term functionality under harsh conditions.

Zhang et al. [36] prepared carbon nanotubes (CNTs) grafted with silica nanoparticles to create CNTs-SiO_2 hybrids, which were incorporated into an epoxy matrix using a one-step spraying method. The resulting superhydrophobic coating achieved a water contact angle of 159,3° when the ratio of CNTs to SiO_2 was 1:3. The entwined CNTs-SiO_2 hybrids created a micro-nano hierarchical structure, enhancing water repellency and providing good mechanical durability and chemical stability. Additionally, the coating demonstrated significant photothermal conversion capabilities, delaying water freezing and efficiently melting ice under laser irradiation

Physical treatment. Physical treatments for superhydrophobic coatings involve methods to enhance surface roughness, durability, and functionality [37]. Abrasion followed by heating can restore hydrophobicity through self-healing mechanisms, with coatings regaining high contact angles and low sliding angles after degradation cycles. Micropatterning via physical friction, combined with annealing and chemical modifications, creates multifunctional superhydrophobic surfaces with enhanced anti-corrosion and anti-adhesive properties [26]. Liquid Flame Spraying (LFS) efficiently produces nanostructured coatings on large surfaces using eco-friendly processes. Electrochemical anodization generates nanotube structures that improve hydrophobicity when combined with surface chemical modifications. Additionally, integrating physical structuring with chemical repair techniques enables the development of self-repairing surfaces resistant to environmental damage [38]. These treatments are essential for applications such as medical devices, corrosion protection, and self-cleaning technologies.

Combination of bottom-up and top-down approaches. The integration of bottom-up and top-down approaches in the fabrication of superhydrophobic coatings provides an effective strategy to address the inherent limitations of each method when applied independently, enhancing the overall performance and applicability of the resulting surfaces. Bottom-up techniques, such as sol-gel processing and layer-by-layer assembly, enable precise control over chemical composition and nanoscale structuring, forming a foundation of finely tuned surface properties. In contrast, top-down methods, including laser texturing and plasma etching, introduce controlled micro- and macro-scale roughness, essential for achieving the hierarchical surface topography critical to superhydrophobicity. By combining these approaches, such as applying sol-gel coatings onto pre-textured substrates or employing physical structuring as a post-treatment to chemically assembled layers, researchers can engineer surfaces with multi-scale roughness, significantly improving water repellency, durability, and functional efficiency. This hybrid methodology also allows for tailored material compatibility and optimized process parameters, though it requires careful consideration of sequencing, substrate selection, and scalability to ensure practical implementation [39].

Fabrication and Scalability Challenges. Despite significant progress in the development of superhydrophobic coatings, their widespread application is limited by technological, operational and environmental factors. Although high-precision top-down methods such as laser ablation are reliable, they are expensive and have a low throughput. Bottom-up approaches (e.g. sol-gel) are more scalable but often have inferior structural integrity [40]. Material incompatibility remains a significant barrier, as the need for specialized substrate preparation and the use of adhesives that increase surface energy can reduce hydrophobicity [41].

Financial barriers include the high cost of initial components and inefficient processes such as photolithography. Under real-world conditions, coatings lose effectiveness when in contact with oils or surfactant-containing solutions, and when condensation occurs below the dew point, destroying the air gap. The lack of uniform testing standards for wear, penetration and weatherability makes it difficult to compare data [42].

Environmental risks are associated with the use of fluorine-containing compounds that are toxic and have low biodegradability [43], as well as with waste generation when coatings are applied using non-uniform methods. Over 50% of commercial products are designed for materials with natural roughness, such as fabric, wood and paper, while coatings for metals and glass remain rare. Additionally, the temperature instability of most coatings limits their versatility [44].

Conclusion. Addressing the durability challenges of superhydrophobic surfaces requires a multifaceted approach that integrates several innovative strategies. Self-healing capabilities utilizing responsive polymers and microcapsule-based healing agents offer promising solutions to maintain surface integrity despite mechanical damage. Biomimetic engineering principles, particularly those derived from resilient natural models such as Salvinia molesta, provide valuable design insights for creating more robust water-repellent structures. The establishment of a cross-sector collaborative framework with standardized testing protocols has proven essential for bridging the gap between laboratory innovations and commercial applications. Ultimately, the widespread adoption of superhydrophobic technologies hinges on achieving an optimal balance between performance metrics, production economics, and environmental sustainability. A challenge that requires continued interdisciplinary cooperation among materials scientists, engineers, and industry stakeholders to overcome current limitations and unlock the full potential of these remarkable surfaces. Superhydrophobic surfaces represent a transformative technology with applications spanning multiple industries. Ongoing research continues to advance, and the integration of superhydrophobic surfaces with other technologies promises to unlock even greater possibilities, driving progress in fields from healthcare to energy. Future developments may include surfaces that adjust their properties in response to environmental changes, such as temperature or pH. This adaptability could open new possibilities in fields like medicine and advanced manufacturing. Combining superhydrophobic surfaces with sensors or energy harvesting devices could create multifunctional materials. For instance, a surface that repels water while also generating electricity from environmental vibrations offers exciting possibilities for smart technologies.

References

1. Barthlott W., Neinhuis C. Purity of the sacred lotus, or escape from contamination in biological surfaces. Planta. 1997. Vol. 202, no. 1. P. 1–8. URL: https://doi.org/10.1007/s004250050096
2. Ma M., Hill R. M. Superhydrophobic surfaces. Current opinion in colloid & interface science. 2006. Vol. 11, no. 4. P. 193–202. URL: https://doi.org/10.1016/j.cocis.2006.06.002
3. Xiang S., Liu W. Self-Healing superhydrophobic surfaces: healing principles and applications. Advanced materials interfaces. 2021. P. 2100247. URL: https://doi.org/10.1002/admi.202100247
4. Cassie A. B. D. Contact angles. Discussions of the faraday society. 1948. Vol. 3. P. 11. URL: https://doi.org/10.1039/df9480300011
5. Superhydrophobicity in perfection: the outstanding properties of the lotus leaf / H. J. Ensikat et al. Beilstein journal of nanotechnology. 2011. Vol. 2. P. 152–161. URL: https://doi.org/10.3762/bjnano.2.19
6. The challenges, achievements and applications of submersible superhydrophobic materials / Y. A. Mehanna et al. Chemical society reviews. 2021. Vol. 50, no. 11. P. 6569–6612. URL: https://doi.org/10.1039/d0cs01056a
7. Crick C., Parkin I. Preparation and characterisation of super-hydrophobic surfaces. Chemistry - A european journal. 2010. Vol. 16, no. 12. P. 3568–3588. URL: https://doi.org/10.1002/chem.200903335
8. Superhydrophobic surfaces: a review on fundamentals, applications, and challenges / J. Jeevahan et al. Journal of coatings technology and research. 2018. Vol. 15, no. 2. P. 231–250. URL: https://doi.org/10.1007/s11998-017-0011-x
9. Guo Y., Zhao H. Femtosecond laser processed superhydrophobic surface. Journal of manufacturing processes. 2024. Vol. 109. P. 250–287. URL: https://doi.org/10.1016/j.jmapro.2023.12.005
10. Ultrafast laser processing of materials: a review / K. C. Phillips et al. Advances in optics and photonics. 2015. Vol. 7, no. 4. P. 684. URL: https://doi.org/10.1364/aop.7.000684
11. Laser textured superhydrophobic surfaces and their applications for homogeneous spot deposition / V. D. Ta et al. Applied surface science. 2016. Vol. 365. P. 153–159. URL: https://doi.org/10.1016/j.apsusc.2016.01.019
12. Superhydrophobic surfaces fabricated by femtosecond laser with tunable water adhesion: from lotus leaf to rose petal / J. Long et al. ACS applied materials & interfaces. 2015. Vol. 7, no. 18. P. 9858–9865. URL: https://doi.org/10.1021/acsami.5b01870
13. Bayer I. S. Superhydrophobic coatings from ecofriendly materials and processes: a review. Advanced materials interfaces. 2020. Vol. 7, no. 13. P. 2000095. URL: https://doi.org/10.1002/admi.202000095
14. Qian B., Shen Z. Fabrication of superhydrophobic surfaces by dislocation-selective chemical etching on aluminum, copper, and zinc substrates. Langmuir. 2005. Vol. 21, no. 20. P. 9007–9009. URL: https://doi.org/10.1021/la051308c
15. Facile fabrication of superhydrophobic surfaces from austenitic stainless steel (AISI 304) by chemical etching / J.-H. Kim et al. Applied surface science. 2018. Vol. 439. P. 598–604. URL: https://doi.org/10.1016/j.apsusc.2017.12.211
16. Li L., Breedveld V., Hess D. W. Creation of superhydrophobic stainless steel surfaces by acid treatments and hydrophobic film deposition. ACS applied materials & interfaces. 2012. Vol. 4, no. 9. P. 4549–4556. URL: https://doi.org/10.1021/am301666c
17. Fabrication of hierarchical structures on a polymer surface to mimic natural superhydrophobic surfaces / Y. Lee et al. Advanced materials. 2007. Vol. 19, no. 17. P. 2330–2335. URL: https://doi.org/10.1002/adma.200700820
18. Manoharan K., Bhattacharya S. Superhydrophobic surfaces review: functional application, fabrication techniques and limitations. Journal of

micromanufacturing. 2019. Vol. 2, no. 1. P. 59–78. URL: https://doi.org/10.1177/2516598419836345

19. Superhydrophobic surfaces fabricated by nanoimprint lithography / A. Pozzato et al. Microelectronic engineering. 2006. Vol. 83, no. 4-9. P. 884–888. URL: https://doi.org/10.1016/j.mee.2006.01.012
20. Superhydrophobic lotus-leaf-like surface made from reduced graphene oxide through soft-lithographic duplication / X. Yun et al. RSC advances. 2020. Vol. 10, no. 9. P. 5478–5486. URL: https://doi.org/10.1039/c9ra10373b
21. Fabricating Super-Hydrophobic Lotus-Leaf-Like Surfaces through Soft-Lithographic Imprinting / B. Liu et al. Macromolecular rapid communications. 2006. Vol. 27, no. 21. P. 1859–1864. URL: https://doi.org/10.1002/marc.200600492
22. Superhydrophobic perpendicular nanopin film by the bottom-up process / E. Hosono et al. Journal of the american chemical society. 2005. Vol. 127, no. 39. P. 13458–13459. URL: https://doi.org/10.1021/ja053745j
23. Application of 3D printing for fabrication of superhydrophobic surfaces with reversible wettability / W. Zhao et al. RSC advances. 2024. Vol. 14, no. 25. P. 17684–17695. URL: https://doi.org/10.1039/d4ra02742f
24. 3D-Printed biomimetic super-hydrophobic structure for microdroplet manipulation and oil/water separation / Y. Yang et al. Advanced materials. 2017. Vol. 30, no. 9. P. 1704912. URL: https://doi.org/10.1002/adma.201704912
25. Doshi J., Reneker D. H. Electrospinning process and applications of electrospun fibers. Journal of electrostatics. 1995. Vol. 35, no. 2-3. P. 151–160. URL: https://doi.org/10.1016/0304-3886(95)00041-8
26. Superhydrophobic electrospun nanofibers / N. Nuraje et al. J. Mater. Chem. A. 2013. Vol. 1, no. 6. P. 1929–1946. URL: https://doi.org/10.1039/c2ta00189f
27. Novel design of superhydrophobic and anticorrosive PTFE and PAA + β − CD composite coating deposited by electrospinning, spin coating and electrospraying techniques / A. Vicente та ін. Polymers. 2022. Т. 14, № 20. С. 4356. URL: https://doi.org/10.3390/polym14204356
28. Superhydrophobic fabrics produced by electrospinning and chemical vapor deposition / M. Ma et al. Macromolecules. 2005. Vol. 38, no. 23. P. 9742–9748. URL: https://doi.org/10.1021/ma0511189
29. Superhydrophobic carbon nanotube forests / K. K. S. Lau et al. Nano letters. 2003. Vol. 3, no. 12. P. 1701–1705. URL: https://doi.org/10.1021/nl034704t
30. 3D carbon nanotube network based on a hierarchical structure grown on carbon paper backing / X. Sun et al. Chemical physics letters. 2004. Vol. 394, no. 4-6. P. 266–270. URL: https://doi.org/10.1016/j.cplett.2004.07.014
31. Superaligned carbon nanotube arrays, films, and yarns: a road to applications / K. Jiang et al. Advanced materials. 2011. Vol. 23, no. 9. P. 1154–1161. URL: https://doi.org/10.1002/adma.201003989
32. Boinovich L., Emelyanenko A. Principles of design of superhydrophobic coatings by deposition from dispersions. Langmuir. 2009. Vol. 25, no. 5. P. 2907–2912. URL: https://doi.org/10.1021/la803806w
33. Li Y., Liu F., Sun J. A facile layer-by-layer deposition process for the fabrication of highly transparent superhydrophobic coatings. Chemical communications. 2009. No. 19. P. 2730. URL: https://doi.org/10.1039/b900804g
34. Fabrication of robust self-cleaning superhydrophobic coating by deposition of polymer layer on candle soot surface / R. S. Sutar et al. Journal of applied polymer science. 2020. Vol. 138, no. 9. P. 49943. URL: https://doi.org/10.1002/app.49943
35. Study on the superhydrophobic properties of an epoxy resin-hydrogenated silicone oil bulk material prepared by sol-gel methods / K. Zheng et al. Materials. 2021. Vol. 14, no. 4. P. 988. URL: https://doi.org/10.3390/ma14040988
36. A durable and photothermal superhydrophobic coating with entwinned CNTs-SiO2 hybrids for anti-icing applications / F. Zhang et al. Chemical engineering journal. 2021. Vol. 423. P. 130238. URL: https://doi.org/10.1016/j.cej.2021.130238
37. Parvate S., Dixit P., Chattopadhyay S. Superhydrophobic surfaces: insights from theory and experiment. The journal of physical chemistry B. 2020. Vol. 124, no. 8. P. 1323–1360. URL: https://doi.org/10.1021/acs.jpcb.9b08567
38. Barthwal S., Uniyal S., Barthwal S. Nature-Inspired superhydrophobic coating materials: drawing inspiration from nature for enhanced functionality. Micromachines. 2024. Vol. 15, no. 3. P. 391. URL: https://doi.org/10.3390/mi15030391
39. Modifying flexible polymer films towards superhydrophobicity and superoleophobicity by utilizing water-based nanohybrid coatings / F. Krasanakis et al. Nanoscale. 2023. URL: https://doi.org/10.1039/d2nr06780c
40. Challenges and strategies for commercialization and widespread practical applications of superhydrophobic surfaces / L. Li et al. Science advances. 2023. Vol. 9, no. 42. URL: https://doi.org/10.1126/sciadv.adj1554
41. Modification of commercial polymer coatings for superhydrophobic applications / S. S. Cassidy et al. ACS omega. 2024. URL: https://doi.org/10.1021/acsomega.3c09123
42. Bioinspired surfaces for turbulent drag reduction / K. B. Golovin et al. Philosophical transactions of the royal society A: mathematical, physical and

engineering sciences. 2016. Vol. 374, no. 2073. P. 20160189. URL: https://doi.org/10.1098/rsta.2016.0189
43. Environment-Friendly antibiofouling superhydrophobic coatings / S. M. R. Razavi et al. ACS sustainable chemistry & engineering. 2019. Vol. 7, no. 17. P. 14509–14520. URL: https://doi.org/10.1021/acssuschemeng.9b02025
44. Recent progresses of superhydrophobic coatings in different application fields: an overview / Y. Bai et al. Coatings. 2021. Vol. 11, no. 2. P. 116. URL: https://doi.org/10.3390/coatings11020116

Юн Ц., Баклан Д.В. Огляд технологій виготовлення супергідрофобних покриттів

Супергідрофобні поверхні стали ключовим напрямком сучасного матеріалознавства. Ці поверхні вирізняються унікальною поведінкою при змочуванні та широким спектром потенційних застосувань у таких сферах, як самоочисні покриття, антикорозійний захист, зменшення лобового опору, технології боротьби з обмерзанням та розділення нафти і води. Натхненні природними моделями, такими як листя лотоса, водорізи та Salvinia molesta, ці поверхні поєднують матеріали з низькою поверхневою енергією з ієрархічною мікро/наноструктурою для досягнення кутів контакту з водою, що перевищують 150°. Ця двошарова шорсткість утримує повітряні кишені під краплями води, забезпечуючи «ефект лотоса», коли краплі скочуються з поверхні, видаляючи забруднення. Розробка супергідрофобних покриттів особливо важлива в контексті корозії металів, оскільки економічні та екологічні фактори створили попит на безпечніші та стійкіші альтернативи. Було розроблено широкий спектр технологій виготовлення, включаючи низхідні методи, такі як лазерна абляція і травлення, і висхідні стратегії, такі як золь-гель осадження і хімічне осадження з газової фази. Однак багато підходів обмежені складністю, вартістю, масштабованістю або впливом на навколишнє середовище. Крім того, практичне застосування цих покриттів пов'язане з проблемами довговічності, сумісності матеріалів, продуктивності під впливом екологічних стресів та використання фторованих сполук, які становлять екологічні ризики. У цьому огляді критично проаналізовано сучасні методології виготовлення супергідрофобних поверхонь. Оцінюються основні принципи, переваги та обмеження цих методів з точки зору механічної міцності, масштабованості та вимог до конкретних застосувань. Особливий акцент зроблено на важливості багатомасштабного структурування поверхні та вибору гідрофобних, низькоенергетичних матеріалів для створення функціонально стійких покриттів. Крім того, в роботі досліджуються обмеження поточних стандартів тестування і припускається, що уніфікована система оцінки механічного зносу, стійкості до навколишнього середовища і гідрофобного утримання має важливе значення для прискорення передачі технології від лабораторії до промислового масштабу. Огляд висвітлює нові стратегії, такі як біоміметичний дизайн, використання матеріалів, що самовідновлюються, та інтеграція супергідрофобних покриттів з багатофункціональними технологіями як перспективні майбутні напрямки. Зрештою, успіх технологій супергідрофобних поверхонь залежить від міждисциплінарних зусиль, що збалансовують показники продуктивності з екологічною відповідальністю та економічною доцільністю для розкриття їхнього трансформаційного потенціалу в різних секторах.

Ключові слова: *супергідрофобні покриття, кут змочування, змочуваність поверхні, шорсткість поверхні, водовідштовхувальні властивості, методи виготовлення.*

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