Chapter

Biomimetic Superhydrophobic Materials for Environmental Applications

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Abstract

Environmental pollution has been one of the people's most significant concerns for decades. In today's industrialized and modernized society, the problem of environmental pollution has become more and more serious, directly affecting the sustainable development of each country. The unique surface properties of materials and interfaces produced by biomimetic approaches can be leveraged to create practical solutions to challenging environmental issues. Among them, superhydrophobic materials get a lot of attention because of their exceptional capacities in various environmental applications such as oil-water separation, membrane-based water purification and desalination, biofouling prevention, high-performance vapor condensation, and atmospheric water capture. This chapter reviews and discusses the fundamental principles of superhydrophobicity, recent works in preparing superhydrophobic surfaces, their potential environmental applications, and the challenges confronted in their new applications.

Keywords: superhydrophobic, biomimetic, environment, pollution treatment, application

1. Introduction

Nature inspires many scientists and engineers to create remarkable inventions for human life. Humans observe and imitate numerous natural materials, structures, and systems to design and invent new products. This creative process is known as biomimetic. One notable example of biomimetics is the superhydrophobic surface. In nature, we can find many superhydrophobic surfaces of plants and animals, such as lotus leaves and butterfly wings, with waterproof, self-cleaning, and anti-adhesion properties. These properties are studied and applied in many fields of life, such as making anti-fogging materials [1], anti-freezing materials [2], self-cleaning materials [3], or environmental treatment [4].

Recently, superhydrophobic surfaces with high applicability have received more attention from researchers. Various methods have been developed to prepare superhydrophobic surfaces, for example, the sol-gel method [5], self-assembly [6], chemical etching [7], plasma etching [8], vapor deposition [9], and so on. Moreover, there are also many studies on fabricating superhydrophobic surfaces on different substrates such as fabric [10], glass [11], silicon [6], or metal surface [5, 12] with diverse applications. The appropriate fabricating method will be chosen and developed differently based on the substrate to prepare the superhydrophobic surface successfully.

Since the nineteenth century Industrial Revolution to this day, pollution has increased quickly, directly impacting the ecosystem, including animals, plants, and human health and life. Several materials have been researched in order to deal with environmental issues. Among them, superhydrophobic materials with a unique behavior against water droplets received much attention from researchers, and they have become widespread and popular in recent years. This chapter reviews the basic contact angle science in the first part. The fabrication methods and applications of superhydrophobic materials in environmental treatment are overviewed in the following section. Some crucial issues affecting the unsuccessful wide-range applications of superhydrophobic surfaces are addressed critically in the conclusions and outlook section. Finally, some proposals are put forward for future guidance on the environmental applications of superhydrophobic surfaces.

2. Superhydrophobic surfaces in natural

Nature inspires many scientists and engineers to create remarkable inventions for human life. Humans observe and imitate numerous natural materials, structures, and systems to design and invent new products. This creative process is known as biomimicking. Biomimicking refers to designs that emulate or imitate nature's models, systems, and elements to solve complex human problems. It aims to draw inspiration from nature's engineering to solve the world's most pressing challenges and ensure a sustainable future for all life. Superhydrophobic surfaces are an essential aspect of biomimicking.

Water contact angle (WCA) is the parameter used for quantifying the wettability of a surface. The contact angle is defined as the angle created by the intersection of the liquid–solid interface and the liquid-vapor interface (geometrically obtained by making a tangent line from the contact point along the liquid-vapor interface in the droplet profile) [13]. In 1805, Young proposed the first fundamental equation that quantified the hydrophobicity/hydrophilicity of a surface based on a static contact angle [14]:

$$\cos\Theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \quad (1)$$

in which θ is the static water contact angle, γ_{SV}, $\gamma_{SL,}$ and γ_{LV} are the interfacial tensions of the solid-vapor, solid-liquid and the liquid-vapor interface, respectively. In presenting this relational equation, he is widely considered to be the pioneer of scientific research on the wettability and water contact angle.

A surface is considered hydrophilic when WCA <90 degrees ($\gamma_{SV} > \gamma_{SL}$), while it is considered hydrophobic when WCA ≥90 degrees ($\gamma_{SV} \leq \gamma_{SL}$) [13]. The pictures of hydrophilic and hydrophobic surfaces are shown in **Figure 1**.

However, Young's equation is only applicable to solids that are perfectly smooth and chemically homogeneous. The wettability of rough or chemically heterogeneous surfaces, which are more suitable, is much more complicated. Two remarkable models

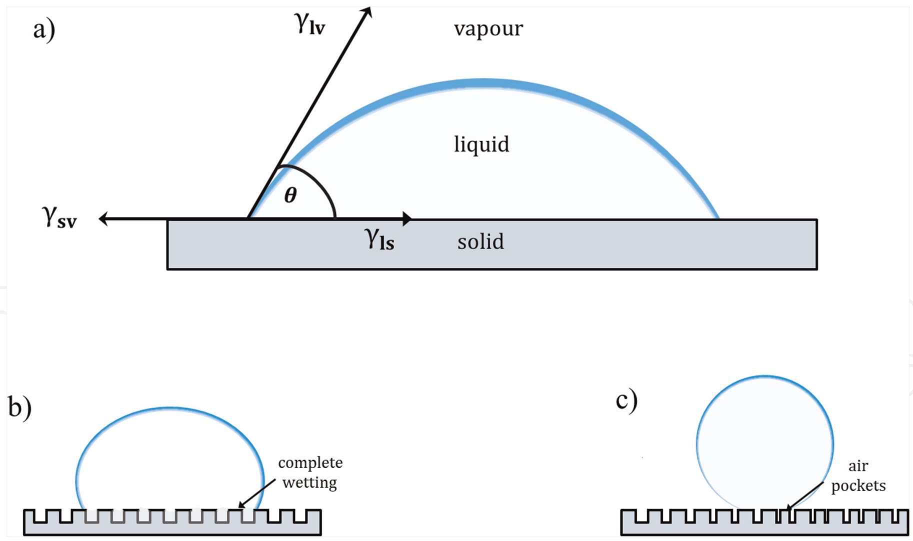

Figure 1.
Different states of the wetting behavior of solid surface.

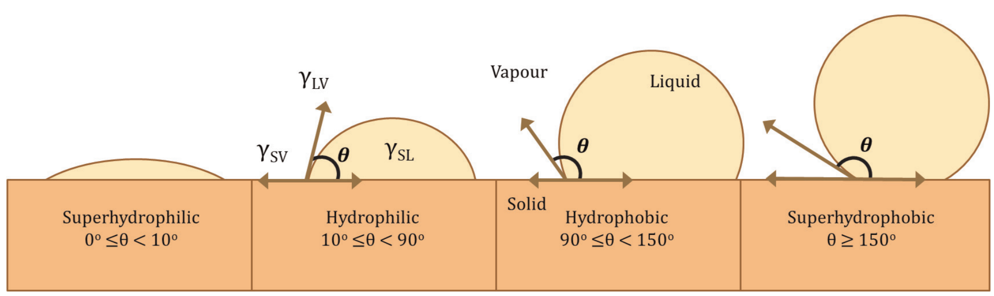

Figure 2.
Schematic of (a) Young's equation, (b) Wenzel's model, and (c) Cassie-Baxter's model.

describing the impact of surface roughness on water contact angle are the Wenzel model and the Cassie & Baxter model (**Figure 2**).

In 1936, Wenzel developed a model in which the water drop can penetrate the grooves on a rough surface. Over the course of his experiments, he discovers that roughness makes a hydrophilic surface more hydrophilic and makes a hydrophobic surface more hydrophobic. He proposed an equation showing the relationship of the water contact angle on the smooth surface and rough surface as follows:

$$\cos \Theta = \frac{r(\gamma_{SV} - \gamma_{SL})}{\gamma_{LV}} = r\, cos\Theta \qquad (2)$$

In which θ^* is the water contact angle on a rough surface, θ is the water contact angle on a similarly smooth surface, and r is the surface roughness factor, defined as the ratio of the actual area of the solid surface to the projected area (r = 1 for a perfectly smooth surface, and $r > 1$ for a rough one). The Wenzel equation indicates that the hydrophilicity is enhanced by roughness when θ is <90 degrees, whereas the hydrophobicity is increased by roughness when θ is >90 degrees.

After that, in 1944, Cassie and Baxter reported that Wenzel's equation could not accurately predict the water contact angle of droplets on rough surfaces with air pockets trapped in the rough grooves. Consequently, they proposed an alternative model in which the wetting state is considered: The grooves under the droplet are filled with vapor instead of liquid. They modified Wenzel's equation and presented another one that can predict the contact angle in these cases as follows:

$$\cos \Theta = f_1 \cos \Theta_1 + f_2 \cos \Theta_2 \tag{3}$$

in which,

$$f_1 = \frac{\text{area in contact with droplet}}{\text{projected surface area}} \tag{4}$$

$$f_2 = \frac{\text{area in contact with air beneath the droplet}}{\text{projected surface area}} \tag{5}$$

and θ_1 represents the contact angle of the smooth solid surface, and θ_2 represents the contact angle for air.

A superhydrophobic surface can be defined as the surface which have the high water contact angle (≥150degrees), low sliding angle/shedding angle (≤10 degrees), anti-sticking, anti-contamination, and self-cleaning effect. The superhydrophobic surface can be found in both natural plants and animals.

The best-known example of superhydrophobic natural surfaces is lotus leaves (*Nelumbo nucifera*), characterized by θ >150 degrees, very low water adhesion and self-cleaning properties. The self-cleaning capacity of directly removing dust and particles by displacing water droplets is derived from the Cassie–Baxter state. This property arises the from the dual (micro/nano) surface structure of Lotus leaves. Besides, in nature, numerous of plants like rice leaves and rose petals carry out the excellent hydrophobicity or superhydrophobicity. In the case of animals, insect wings' superhydrophobicity is an advantage in reducing dust/particle contamination and improving their flying capacity. Different families with highly hydrophobic wings, including dragonflies mayflies, stoneflies, lacewings, alderflies, caddisflies, butterflies, moths, etc. … have been founded. Many insects' feet are also superhydrophobic. For instance, geckos are able to climb on vertical surfaces thanks to their feet with well-aligned microscopic hairs known as setae.

Nature's mimicry is the easiest way to replicate materials with similar properties because nature has produced plants, insects, and animals that capable of repelling water over millennia. The properties of superhydrophobic surfaces are the potential for many real-world applications like the production of anti-fogging materials, anti-freezing materials, and self-cleaning materials.

3. Fabrication of superhydrophobic materials

3.1 Chemical etching method

Chemical etching is a wet method in which the surface molecules react with highly acidic or basic solutions to produce roughness. Although it only requires simple equipment and simple chemical at a low cost, it is a fast process and provides a high etching rate and selectivity. However, it still has some disadvantages. This method requires considerable amount of etching chemicals and can cause contamination to the substrates. It is also difficult to control the etching rate of the process.

Many researches using this method to fabricate superhydrophobic surfaces have been published. For example, in Qian and Shen's studies [7], the surface of aluminum, copper, and zinc surface was chemically etched with Beck's dislocation etchant, Livingston's dislocation etchant and HCl solution, respectively. Afterward, the etched surfaces were submerged in a solution of tridecafluoroctyltriethoxysilane to modify the composition of the surface. Following the procedure, static water contact angle of 156, 153, and 155 degrees was obtained for aluminum, copper, and zinc surface [7].

The study by Varshney et al.'s [15] prepared a superhydrophobic steel mesh for oil-water separation. The procedure also involved the etching step using a solution of hydrochloric acid and nitric acid and the surface chemical modification with lauric acid. It was subsequently demonstrated that the mesh produced was mechanically, chemically, and thermally stable with static water contact angle of 171 ± 4.5 degrees and sliding angle of 4 ± 0.5 degrees [15].

Lee et al. have implemented a method for reaching a superhydrophobic silicon surface with a water contact angle close to 180 degrees. The roughness of the silicon wafer was increased by immersion in a Cu plating solution, then mixing HF and H_2O_2 to form microstructure and nanostructure. Then, the silicon surface was treated with Teflon for an excellent superhydrophobic surface that can be applied in self-cleaning and microfluidic transport [16].

3.2 Sol-gel method

Sol-gel technique is considered to be the most common method for making superhydrophobic materials, which can be applied on different surfaces of solid substrate surfaces. In this method, colloidal particles of different sizes (from 1 to 100 nm) are dispersed in gels with an inter-connected rigid network with micro-/nano-pores and polymeric chains >1 μm. Here, the monomer is transformed into a colloidal solution (sol) which initiates an integrated network (gel) for polymers or particles.

Several studies on applying this method in superhydrophobic materials have been introduced. Using the sol-gel method, Fan et al. have obtained a superhydrophobic surface on the copper wafer with a water contact angle of 155.4 degrees. After roughening up the copper surface with an acidic solution, a sol-gel coating made of vinyl trimethoxylsilane, ethanol, water, and ammonia was applied. The generated sample can maintain its stability in a 3.5% NaCl solution after the operation, making it potentially useful in anticorrosion and self-cleaning applications [5].

Wang et al. also created superhydrophobic surfaces on a variety of substrates, such as silicon wafers, filter papers, glass slides, electrospun nanofiber mats, and textile fabrics (polyester, wool, and cotton). These surfaces had water contact angles exceeding 170 degrees and sliding angles under 7 degrees. The co-hydrolysis and condensation of tetraethyl orthosilicate (TEOS) and tridecafluorooctyl triethoxysilane (FAS) in NH_3-H_2O-ethanol solution produced the sol solution containing silica nanoparticles. To create a clear film, this sol solution was subsequently deposited onto several substrate surfaces [17].

A technique for producing a superhydrophobic glass surface was reported in the paper by Satapathy et al. A sol-gel SiO_2 nanoparticle solution with a linear low-density polyethylene (LLDPE) polymer matrix was used to coat the glass. Using ethanol as a non-solvent, the porosity of SiO_2 nanoparticles implanted in LLDPE was also altered. The produced SiO_2 nanoparticles embedded in LLDPE matrix, which is exceedingly impressive, had a water contact angle of 170 degrees and a sliding angle of 3.8 degrees.

The sample also had good self-cleaning abilities and was thermally, mechanically, and chemically stable [3].

3.3 Dip-coating method

The substrate is submerged in a component solution that will be placed on the substrate surface when using the dip-coating procedure. The sample is removed from the solution after the specified amount of time, resulting in the film that is then deposited on the substrate. A coating layer forms on the sample surface as a result of the solvent evaporating. This method has a number of benefits, including coating the substrate's upper and lower sides simultaneously, no material waste, application to a variety of materials, high output, and uniform, stable, and long-lasting coating. To create the coating layer, however, all of the components in this process must be submersible.

Mahadik et al. proposed a simple and low-cost dip coating method to fabricate superhydrophobic surface by using organic and inorganic silica precursor methyltrimethoxysilane (MTMS) to produce superhydrophobic silica coatings on the quartz substrate. After the coating step, the recorded water contact angle and water sliding angle were 168 ± 2 degrees and 3 ± 1 degrees, respectively. This fabricated surface had remarkable superhydrophobicity and superoleophilicity, along with high durability and optical transparency [18].

In Sun et al.'s study, superhydrophobic surfaces on zinc substrate were fabricated based on Zn's electrochemical processing under an applied electric field. This research applied an electrochemical procedure using an electrolyte mixture consisting of $NaNO_3$ and NaCl to enhance surface roughness, followed by a dip-coating process with fluoroalkylsilane-ethanol solution to modify the surface chemistry of the sample. After two-step process, the zinc surface had a maximum water contact angle of 165.3 degrees and a tilting angle of 2 degrees [19].

Sriram et al. [4] developed a fabrication method for superhydrophobic filter paper using a combination of sol-gel and dip-coating methods. First, the sol-gel solution was prepared by adding poly (methyl methacrylate-co-ethyl acrylate) polymer silicon dioxide nanoparticles to toluene under stirring, followed by adding PFOTS silane for better dispersion of nanoparticles. Then, the filter paper was coated with the solution above via dip-coating method at ambient conditions. The achieved water contact angle of the filter paper surface was >175 degrees, and the sliding angle was 3.8 degrees [4].

3.4 Electrochemical deposition method

The process of electrochemical deposition uses applied voltage to trigger chemical reactions in an aqueous electrolyte solution. This technology has the advantages of being able to apply material in any three-dimensional (3D) geometry and being suited for soft substrates because it is a low-energy process. In addition, it can be carried out at room temperature using water-based electrolytes. The main drawbacks of electrochemical deposition include its limited applicability and insufficient structural strength.

A one-step electrochemical deposition procedure was presented by Huang et al. to create a superhydrophobic surface on a copper substrate. They used a direct voltage (DC) between two copper plates that were submerged in an ethanol-stearic acid solution to carry out the procedure. The anodic copper electrode surface changed to superhydrophobicity as a result of the reaction between copper and the stearic acid solution. SEM pictures showed that the anodic copper surface was covered with copper stearate layers that resembled flowers. The water contact angle on the copper surface was 153 ± 2 degrees with the rolling-off qualities of the droplets [20].

In He and Wang's study [21], this method was utilized to prepare superhydrophobic zinc foil, in which ZnO nanorods were generated on the surface of ZnO film (oxidized zinc foil at 310°C) *via* electrochemical deposition and then spin-coated with perfluoroalkyl methacrylic copolymer to obtain superhydrophobic state. Following the method, a water contact angle of 167 degrees was obtained, demonstrating excellent potential for use in numerous applications, including anti-contamination, anti-fouling, and self-cleaning [21].

Wang et al. presented a three-step process for constructing a biomimetic hierarchical structure on aluminum surface. To create the specimens, anodized porous alumina (APA) film was first made. Nickel and copper were subsequently electrodeposited onto these specimens to create nanometer-sized pillars. To achieve a water contact angle of 152 degrees and a hysteresis angle of 6 degrees for nickel deposited and a water contact angle of 157° and a hysteresis angle of 3 degrees for copper deposited one, the roughed surface was next chemically changed with fluoroalkylsilane [21].

3.5 Plasma-etching method

Plasma-etching involves shooting a suitable gas mixture at a sample with a high stream velocity of glow discharge (plasma). The elements of the etched sample react chemically with the reactive species in the plasma during this process, producing volatile etch products that change the surface of the sample. Plasma treatment could create micro- or nanostructures. The strong points of this technique are the capability of automation, low material consumption, environmental friendliness, and low damage to photoresist. The weak points are high capital investment, difficulty in controlling parameters (surface geometry, types of gases, flow rates, system conductance, patterning, etc.), surface damage caused by plasma radiation, and toxicity of gases.

To create a superhydrophobic zinc surface with a water contact angle of 158 degrees and a sliding angle under 5 degrees, Gao et al. used a two-step plasma-etching procedure. Stearic acid was used to chemically modify the surface after it had been etched with glow discharge electrolysis plasma (GDEP) to increase surface roughness. Finally, the produced zinc surface demonstrated exceptional hydrophobicity, resilience to a range of pH levels, and resistance to prolonged environmental exposure [22].

A straightforward technique for producing superhydrophobic coating on glass was created by Ji et al. using an in-line atmospheric RF glow discharge plasma and a mixture of non-polar aromatic toluene and HMDSO. With a water contact angle of roughly 150 degrees, the fabricated glass demonstrated superhydrophobicity. The employed plasma system could be quickly scaled up for the treatment of larger substrates and continuous processing because it did not require any vacuum equipment and was appropriate for in-line operation [8].

This technique was used in the study by Psarski et al. to create a nanostructured epoxy/Al_2O_3 nanoparticle composite. First, a laser was used to create the microstructures on the metal surface. After that, a plasma source was used to etch the resulting composite in order to add nano-roughness. Once the sample had been etched, it was changed using the dip-coating procedure with 1H,1H,2H,2H perfluorotetradecyl-triethoxysilane to obtain a superhydrophobic state with a contact angle of 160 degrees and a sliding angle of 8 degrees [23].

3.6 Hydrothermal method

The hydrothermal process results in the formation of crystalline materials in a hot aqueous solution under high vapor pressure. By applying high pressure and temperature to the sample surface, this technique is typically employed to produce roughness. Crystals are produced in an autoclave during the procedure using the substrate and water that is given. Because to its simplicity, this process can produce huge crystals of excellent quality and is suitable for commercial use. The apparatus cost for this method is also significant, and the crystal formation cannot be observed or controlled during the procedure.

Shi et al. suggested using a hydrothermal process to create superhydrophobic glass. In order to increase surface roughness, the glass sample was hydrothermally treated with a solution of $Al(NO_3)_3{\cdot}9H_2O$, NaOH, and colloidal silica. This was followed by chemical modification using octyltrimethoxysilane to obtain superhydrophobicity state. Following the procedure, the prepared sample obtained a 154 degrees water contact angle and a sliding angle that was <3 degrees [11].

Wu et al. suggested using an alkaline hydrothermal process to create superhydrophobic surfaces with a ZnO micro- and nanostructure. Rose-like structures were present on the surface of the treated sample following the hydrothermal stage, which increased surface roughness. After the subsequent process, which involved spin-coating the sample with Teflon, it attained superhydrophobicity with a contact angle of 168 degrees and good stability (no change after being immersed in water for 15 days). In general, the suggested approach is easy to use, affordable, and possibly useful in a wide range of sectors [24].

The hydrothermal approach on a microstructured Ti_6Al_4V alloy surface was one of three procedures used in Shen et al. to create various nanostructures. A two-step chemical reaction, anodic oxidation, and the hydrothermal technique were used to make nanowire, nanotube, and nanomesh structures. In order to obtain the surface's extraordinary superhydrophobicity, FAS-17 was used to chemically modify it. This resulted in a water contact angle of 161 degrees and a tilting angle of 6 degrees [25].

3.7 Self-assembly method

In the self-assembly process, a disordered system of preexisting components assembles in an organized manner or a sequence thanks to interactions of local non-covalent molecules. With minimal interference, complex structures can be formed. The layer can grow using this technology at low temperatures without the need for expensive machinery or involved procedures. This type of surface treatment technique is therefore extensively applicable. Unfortunately, this procedure has a complex mechanism and takes a very long period.

Superhydrophobic copper was created by Yin et al. [26] using chemical etching and self-assembly techniques. In order to produce flower-like structures and nanoneedles of $Cu(OH)_2$ on the sample surface, the copper was first etched with a solution of sodium hydroxide and potassium persulfate. Finally, a self-assembled surface layer was created by submerging the roughed-up sample in dodecanoic acid.

When everything was finished, the prepared surface had a good superhydrophobic state with a 153 degrees WCA [26].

In the study by Song et al. [27], a technique for creating silicon with a superhydrophobic surface was presented. The aluminum-induced crystallization of the amorphous silicon technology produced the micro/nano textures on the silicon substrate surface. The next step was putting an octadecyltrichlorosilane self-assembled monolayer on silicon textured surface. The manufactured surfaces attained a 155 degrees water contact angle and a <1 degree slide angle [27].

Table 1 summarized the fabrication technique for superhydrophobic materials and their applications.

4. Applications of superhydrophobic materials in environmental treatment

Due to the unique chemical compositions and characteristics, many pollutants that are now present in water are incredibly challenging to remove. To address this problem, which has an immediate impact on both the environment and human health, scientists and researchers have put in a tremendous amount of work. The superhydrophobic surface is covered in this book chapter as a cutting-edge material that can be used in many methods of combating environmental pollution.

4.1 Oil removal

In recent years, oil spills and microplastic have become vital worldwide environmental issues. Besides different treatment methods like combustion, chemical treatment, or bioremediation, which may cause secondary pollution after being applied, the utilization of superhydrophobic material appears promising. This method can help separate the oil from the water, returning the polluted water to its original state without generating secondary pollution after pass through the superhydrophobic materials (**Figure 3**). For instance, the combustion method can help remove the oil from the water, but it also causes air pollution because it produces a large amount of CO_2 and SO_2 after the procedure.

Several published studies developed superhydrophobic surfaces and applied them in oil-water separation. For instance, Yeom and Kim proposed a dip-coating method using silica nanoparticles, hexadecyltrimethoxysilane to fabricate a superhydrophobic surface on steel mesh and sponge. The obtained water contact angles were 151.9 ± 1.6 degrees and 152.4 ± 3.2 degrees for steel mesh and sponge, respectively. Both fabricated surfaces then showed excellent performance in oil–water separation [28].

Crude oil and kerosene were often used as oil components in oil-water separation because of their close relation with oil spill pollutants, which can lead to disastrous consequences for the environment and society. Xue et al. introduced a sol-gel method with tetraethoxysilane and 1,1,1,3,3,3-hexamethyl disilazane as precursors for preparing superhydrophobic textiles. After the fabrication, the fabricated textile possessed superhydrophobic and superoleophilic properties, and it could successfully separate the crude oil from the water in an oil–water mixture [29].

Yin et al. proposed a hydrothermal method using nickel sulfide, thioacetamide, sodium hydroxide cetyltrimethylammonium bromide to fabricate superhydrophobic nickel mesh for oil-water separation purposes. The achieved WCA after modification was 158 degrees, indicating good superhydrophobicity. The fabricated mesh also

No	Substrate	Fabrication method	Properties	Application	Ref
1	Steel mesh-based material modififed with HNO_3/HCl and lauric acid	Chemical etching method	• Water contact angle: 171 ± 4.5 degrees • Sliding angle: 4 ± 0.5 degrees	Oil-water separation	[15]
2	Silicon substrate modififed with HF/H_2O_2	Chemical etching method and spin-coating	• Water contact angle: nearly 180 degrees	Structured channel for the fast transport of microfluidics and self-cleaning surfaces	[16]
3	Copper wafers modififed with vinyltrimethoxylsilane (VTMS)	Sol-gel method	• Water contact angle: 155.4 degrees	Resistance to corrosion and selfcleaning application	[5]
4	Microscope glass slides modififed with linear low density polyethylene (LLDPE) and silicon dioxide nanopowder	Sol-gel method	• Water contact angle: 170 degrees • Sliding angle: 3.8 degrees	Packaging and other industrial applications.	[3]
5	Cleaned quartz substrates modififed with methyltrimethoxysilane (MTMS), CH_3OH, and oxalic acid	Dip-coating method	• Water contact angle: 168 ± 2 degrees • Sliding angle: 3 ± 1 degrees	Material against outdoor environmental conditions	[18]
6	Filter paper modififed with poly (methyl methacrylate-coethyl acrylate) (PMMA), 1H,1H,2H,2H Perfluorooctyltrichlorosilane (PFOTS)	Sol-gel and dip-coating methods	• Water contact angle: 175 degrees • Sliding angle: 3.8 degrees	Oil-water separation	[4]
7	Copper surface	Electrochemical deposition method	• Water contact angle: 153 ± 2 degrees	Corrosion resistance application	[20]
8	ZnO film	Electrochemical deposition method	• Water contact angle: 167 degrees	Anti-contamination, anti-fouling, and self-cleaning	[21]
9	Zinc surface	Plasma-etching method	• Water contact angle: 158 degrees • Sliding angle: 5 degrees	Corrosion resistance application	[22]
10	Nanocomposite replicas of aluminum modified with 1H,1H,2H,2H perfluorotetradecyltriethoxysilane	Plasma-etching method and dip-coating	• Water contact angle: 160 degrees • Sliding angle: 8 degrees	Corrosion resistance for industrial applications	[23]
11	Glass substrate kept at 160°C and modified with octyltrimethoxysilane	Hydrothermal method	• Water contact angle: 154 degrees • Sliding angle: 3 degrees	Self-cleaning applications	[11]
12	ZnO surface kept at 180°C	Hydrothermal method	• Water contact angle: 168 degrees	Industrial applications	[24]
13	Copper plates modified with sodium hydroxide and potassium persulfate	Chemical etching and Self-assembly method	• Water contact angle: 153 degrees	Engineering metal applications	[26]
14	Silicon wafers with sodium octadecyltrichlorosilane	Self-assembly method	• Water contact angle: 155 degrees • Sliding angle: 1 degrees	Electro-mechanical system applications	[27]

Table 1.
Fabrication technique for superhydrophobic materials and their applications.

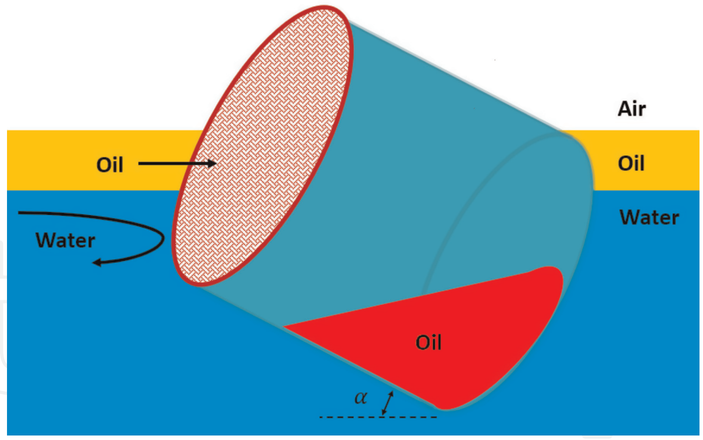

Figure 3.
Example on oil-water separation method.

showed exemplary implementation in the separation experiment of kerosene-water mixture, with an average recovery rate of over 95% [30].

Moreover, filter paper was chosen as the production substrate for superhydrophobic surfaces in other studies. Filter paper has various benefits over other substrates, including biodegradability, high flexibility, and affordability. In the study by Zhang et al., TEOS, octadecyltrichlorosilane, and polystyrene were used to create a superhydrophobic surface on filter paper. After the treatment, the paper surface's wettability changed from being superhydrophilic to being superhydrophobic, with a 156 degrees WCA. Hexan-water separation was another area where the manufactured paper excelled [31].

Teng et al. developed a coating method with nano TiO2, γ-aminopropyl-triethoxysilane, and polydimethylsiloxane (PDMS) to prepare superhydrophobic filter paper. The resulting water contact and rolling angles were 154.5 and 3.5 degrees, respectively. The prepared paper also exhibited good anti-fouling, self-cleaning, and oil-water separation ability, which was evaluated through a filtration experiment of dichloromethane-water mixture [32].

However, many hazardous chemicals are being used in these studies, such as hexadecyltrimethoxysilane, aminopropyltriethoxysilane, and octadecyltri-chlorosilane. Besides, most procedures require more than a day to fabricate superhydrophobic surface, which can be considered time-consuming. Some studies have yet to explicitly report the fabricated surface's durability and reusability. Thus, in this study, a fast and environmental-friendly method for the fabrication of superhydrophobic surface on filter paper will be developed. In addition, the applicability in oil-water separation (kerosene as oil component), durability, and reusability will also be examined after the fabrication procedure to evaluate the full potential of the fabricated filter papers.

4.2 Desalination

A useful, eco-friendly, and practical solution to the freshwater problem is solar desalination *via* interfacial evaporation. It is still difficult to create high-quality light absorber materials that can operate in a variety of tough environments and minimize heat loss while avoiding salt buildup during seawater evaporation. Due to their ability to prevent water from penetrating the pores of the absorber, superhydrophobic surfaces can be employed to circumvent this problem and open up space for vapor to pass through.

Azeem et al. created a superhydrophobic polydimethylsiloxane (PDMS) membrane using an easy and affordable technique. A surface with textures like the lotus effect can be seen on a PDMS-based membrane, which is interesting. PDMS-based textured membrane demonstrated excellent MD performance with high and sustained salt rejection at 99.99%, and permeate flux exceeding 21 kg m^2 h during a 40-hour test using very saline water (70 g/l NaCl) in air-gap membrane distillation (AGMD). Significantly, the PVDF membranes produced in this work demonstrated higher permeate flux over time as a result of a narrowing of the air gap caused by membrane stretching [33].

Superhydrophobic membranes are crucial for enhanced seawater desalination, according to a study by Ray et al. By straightforward sol-gel processing, they also achieved the successful fabrication of a three-layered membrane with a top superhydrophobic coating onto a polypropylene (PP) mat. With this membrane, a high permeate flux of roughly 6.7 liters per square meter per hour (LMH) was maintained for 16 hours, and the salt rejection level was estimated to be 99.7% [34].

An electrospun nanofibrous membrane with superhydrophobicity was used by Zhou et al. as a promising candidate for membrane distillation. With a static contact angle of 156.6 $\pm$ 1.38 degrees and a small sliding angle of 6.4 $\pm$ 0.2 degrees, the ideal membrane demonstrates superhydrophobicity. The best membrane in a laboratory-scale direct contact membrane distillation has a high permeate flux of 38.8 kg m^2 h and a salt rejection of 99.99% during the course of a 40-hour long desalination operation. With regard to wetting and fouling resistance, the superhydrophobic membrane excels.

4.3 Microplastic removal

As the world's capacity to deal with the rapidly rising output of disposable plastic goods exceeds it, plastic pollution has also emerged as one of the most urgent environmental challenges. In impoverished Asian and African countries, where rubbish collection services are either ineffective or nonexistent, plastic pollution is most noticeable. According to the report of the Environmental program of the United Nations, plastic pollution is a global problem when approximately 7 billion of the 9.2 billion tons of plastic produced from 1950 to 2017 became plastic waste, ending up in landfills or dumped [35]. Seriously, most plastics are difficult to degrade and can persist in ecological environments for many years, and they could accumulate in animal bodies and cause long-term damage. Several papers mentioning plastic (including microplastic, microplastic, and nanoplastic) removal have been published recently, showing humans' extremely high seriousness and interest in this environmental problem. These microplastics have been detected in many places, such as on land, sea, sediments, polar regions, the atmosphere, and drinking water. In the aquatic environment, the surface of microplastics is easily changed. As they get rougher and more negatively charged, they can effectively serve as a mobile surface to disperse a variety of organic contaminants, including animals and dangerous microbes. Microplastics in the environment are primarily produced at wastewater treatment facilities. But none of the water treatment techniques used today are specifically developed to get rid of microplastics. A certain quantity of microplastics can still be released into the water and continue to accumulate even though wastewater treatment plants can remove the majority of them (>90%). It is estimated that wastewater

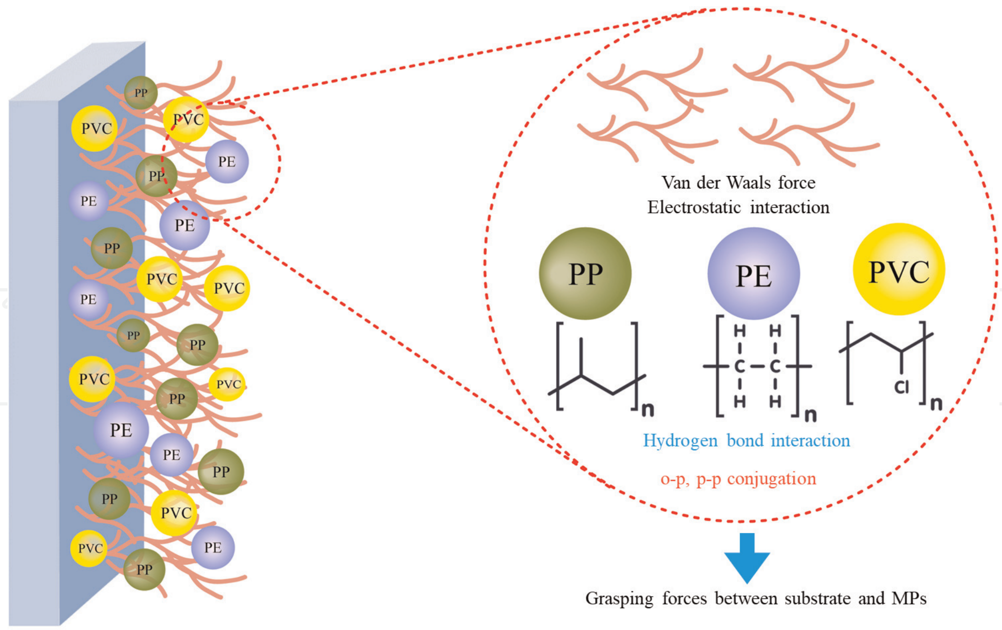

Figure 4.
Microplastics removal by adsorption process.

treatment facilities discharge between 15,000 and 4.5 million microplastic particles into surface water each day [36].

In order to provide a quick and effective method of eliminating microplastics from the environment, numerous approaches and materials have been developed. For instance, the flocculation-flocculation method may get rid of between 75.6% and 85.2% of microplastics [37]. Moreover, membrane bioreactors may remove over 95% microplastic (more than 20 m), but they are expensive to operate and membrane fouling is a possibility [38]. For the elimination of microplastics, the adsorption approach has received substantial study as an efficient, affordable, and user-friendly technique. The polluted particles can be kept in the surface of the superhydrophobic materials by the electrostatic interaction, hydrogen bonding with the microplastic particles (**Figure 4**). Electrostatic interaction, hydrogen bonding, and interaction are the main components of the adsorption process employed by Sun et al to remove polystyrene microplastics from porous materials based on chitin [39]. Several research have also suggested superhydrophobic surfaces, which can be used to adsorb microplastics from aqueous NaCl with an efficiency higher than 99%. Although there has been little study of water in natural settings and less attention paid to environmental durability, the majority of research has concentrated on simulating water trials in the lab.

Ayra et al. reported on the creation of a superhydrophobic 304 stainless steel mesh using chemical etching and lauric acid liquid-phase deposition. A 304 stainless steel mesh's surface was altered by oxidizing conditions ($FeCl_3/HCl/H_2O_2$) and liquid-phase deposition of lauric acid, which resulted in the surface achieving superhydrophobicity (169 degrees) and superoleophilicity (0 degrees). Using the superoleophilic qualities of the modified 304 SS mesh, this mesh was used to remove HDPE microplastic that HDPE migrated from the aqueous phase to the organic phase. It is explained that the repellent cloud that forms on the surface of the microplastic in water enhances dispersion. Yet, in the organic phase, van der Waals interactions cause microplastic to aggregate [40].

According to Ayra et al., superhydrophobic surfaces and functionalized surfaces for microplastics should be taken into account when choosing between different processes and methods for removing microplastics. The solid contaminants are given hydrophilic characteristics by microplastic surface functionalization (with ClO or Fe_3O_4), enhancing selectivity in the separation process. While the oil used affects selectivity when employing superhydrophobic surfaces, microplastics can also be distinguished based on their chemical makeup. The creation of safer goods and removal methods for solid contaminants will be a major problem in the future [41].

4.4 Air filter

The use of superhydrophobic nonwovens is progressively expanding, from the initial oil-water separation and self-cleaning to air filtration, waterproof self-healing, antibacterial, and other disciplines, with the advancement of society and the raising of people's standards of life. Superhydrophobicity can improve the barrier effect of masks on dust particles in the field of air filtration, particularly in the field of masks. Respiratory droplets are used to disseminate the highly infectious coronavirus. Virus-carrying droplets can adhere to the surface of modern surgical masks while being worn, placing users at risk of infection. Superhydrophobic nonwoven masks can, however, prevent the majority of droplets from sticking to their surface, boosting their ability to act as a barrier against droplets, and lowering the risk of COVID-19 infection.

A superhydrophobic, photo-sterilized, and reusable mask that may be worn for an extended period of time and used again after solar illumination was studied by Lin et al. The mask was created by ultrasonicextrusion and is based on graphene nanosheet-embedded carbon (GNEC) layer to protect COVID-19. Excellent characteristics of the GNEC mask include being superhydrophobic (water contact angle: 157.9 degrees), having a 100% BFE, and being photo-sterilizing (photothermal performance: 110.6°C). This work might encourage individuals to investigate surgical mask performance improvements to sustain global health and development [42].

Both the barrier effect of droplets and the barrier effect of particles can be improved by adding superhydrophobic characteristics. The introduction of nanoparticles into filtering nonwovens is being driven by these benefits for many researchers.

4.5 Self-healing

Polymers, metals, ceramics, and their composites are examples of self-healing materials because they can either fully or partially regain their original set of properties after being harmed during usage. Superhydrophobic nonwovens have been increasingly added to self-healing in recent years by researchers. By continuously producing the epicuticle wax layer or by allowing the micro- or nanostructure to naturally regenerate after being damaged, plant leaves, bird feathers, or insect wings can effectively preserve their ability to repel liquids in contrast to manufactured structures. Researchers have created several self-healing superhydrophobic surfaces to increase durability and extend the life of outdoor applications, drawing inspiration from the self-healing characteristics of natural plants and animals. In example, the superhydrophobic surfaces of sponge can be easily recovered after absorbing the pollutants in the aqueous solution (**Figure 5**).

Wang and colleagues imitated the Lotus leaf's structure. Using the use of an easy replica molding technique, they created a biomimetic way to create a self-healing superhydrophobic surface by integrating n-nonadecane wax into a microstructured

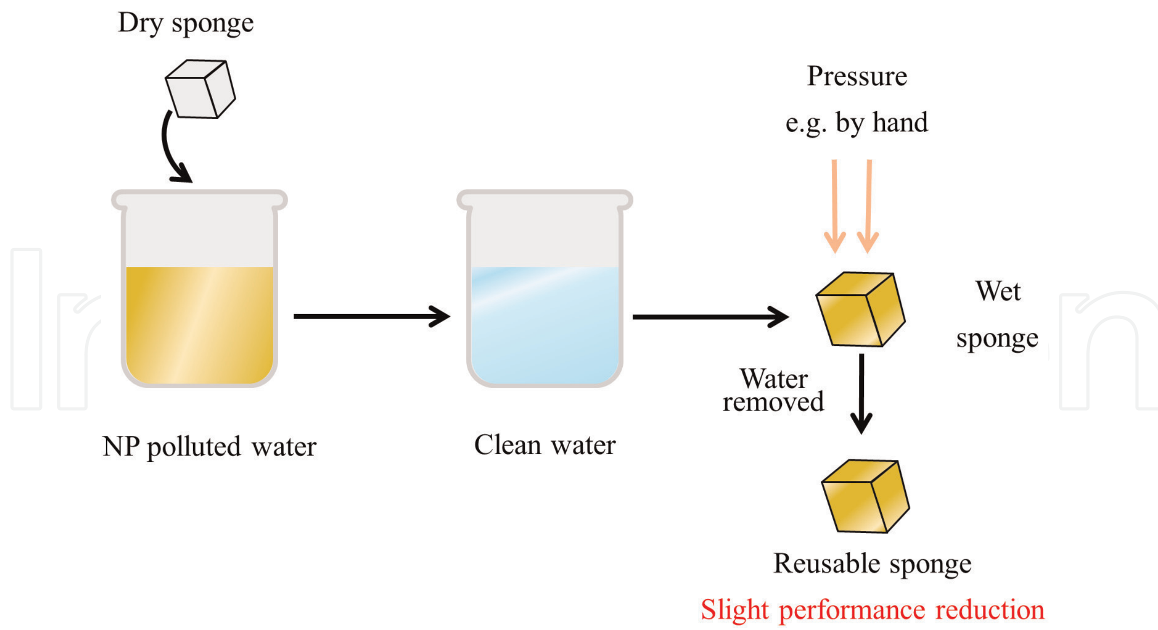

Figure 5.
Self-healing property of sponge.

PDMS matrix. Without any external stimulation, the injured surface might swiftly regain its superhydrophobicity [43].

Superhydrophobic surfaces with built-in liquid repellent qualities have a wide range of potential applications. In the study by Li et al., thermoplastic polyurethane PU/carbon nanotube (CNT) composite films were created by filtering CNT suspensions *via* electrospun thermoplastic polyurethane nonwovens. The strain-gauge sensors displayed outstanding self-restoring water repellency, high sensitivity, and durability [44].

4.6 Antibacterial

Bacterial adhesion causes financial loss, medical difficulties, and even fatalities, making it a major worry in the medical community globally. Due to the rapid emergence of bacterial resistance to the overuse and abuse of antibiotics, new approaches to combatting bacterial infections are urgently needed. Growing interest has been shown in bioinspired superhydrophobic coatings as a novel method of preventing bacterial adhesion and illnesses. In example, by depositing copper and stearic acid on cotton fabric, Suryaprabha et al. effectively created a straightforward, self-cleaning, sturdy, chemically resilient, and cost-effective antibacterial superhydrophobic coating. Gram-positive and Gram-negative bacteria were used to test the antibacterial activity of the created coating, and the inhibition zone method showed that the cotton fabric's ability to resist blood stains [45].

5. Conclusions and outlook

It is interesting to note that the quantity of papers on new superhydrophobic materials has largely held steady since 2019. Yet, the number of published works on the use of superhydrophobic materials in the environment is still constantly increasing. It demonstrates interest in the topic. Due of their numerous possible uses, biomimetic superhydrophobic materials have garnered a lot of attention during the past 10 years. The creation of superhydrophobic materials is no longer surprising given recent technical advancements. Yet, it is still difficult to create anti-corrosive coatings that are strong, resilient, affordable, and ecologically benign, and this field is still young. There are still a lot of issues that need to be solved, as well as some shortcomings and difficulties in industrial manufacturing and practical applications. Further research on superhydrophobic surfaces should concentrate on enhancing their stability and toughness. Further research is needed to better understand how to precisely manage surface structure and roughness on both microscopic and large scales. In addition, it is best to avoid using halogenated polymers or fluorine- and chlorine-containing compounds when making superhydrophobic materials. Superhydrophobic materials still have a lot of great uses in the environment, despite the fact that all the issues described above need to be resolved.

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Conflict of interest

The authors declare no conflict of interest.

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