Preparation and Application of Superhydrophobic Surface Materials

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Abstract. Superhydrophobic materials have attracted wide attention due to their special wettability on the surface. In this paper, the basic definition, principle, and several common wetting models of superhydrophobic are summarized firstly. Then, the advantages and disadvantages of commonly used methods for preparing superhydrophobic materials are briefly analyzed, including dip coating method, spraying method, template method, chemical vapor deposition method, etching method, electrospinning method, phase separation method, and layer-by-layer assembly method. Finally, the application of superhydrophobic materials in oil-water separation, moisture-proof packaging, self-cleaning, and other fields is summarized and elaborated. The application of smart superhydrophobic materials which can respond to external stimuli such as pH, light, and temperature is also introduced. The purpose is to provide reference for the development of superhydrophobic materials. Preparing excellent superhydrophobic materials in a simple and environmentally friendly way is the key to meet the requirements of current industrial production.

Keywords: Superhydrophobic surface · Nanostructures · Chemical modification · Moisture-proof packaging

1 Introduction

With the development of industrialization, superhydrophobic surfaces have attracted extensive attention and research. In nature, many plant leaves and animal feathers are superhydrophobic, the most classic of which is the lotus leaf effect. Inspired by the lotus leaf effect, superhydrophobic surfaces are usually constructed by combining micro and nano multilevel structures with low surface energy chemical composition. The superhydrophobic material generally refers to the material whose water contact angle on static surface is greater than 150° and rolling angle is less than 10° [1–4]. Superhydrophobic materials generally have excellent self-cleaning and anti-pollution properties due to their good non-wettability to water. Therefore, they have broad application prospects in daily life and many industrial fields [5–7].

In this paper, the current research status of superhydrophobic materials is briefly described, and some problems that need to be solved are also put forward. It aims to bring help to the future research and promote the further research of superhydrophobic materials.

1.1 Definition of Superhydrophobic

The wettability of liquid on solid surface is characterized by contact angle. The contact angle is the angle between the solid-liquid interface and the tangent of the gas-liquid interface along the solid-liquid-gas three-phase contact point. It can be expressed by Young's equation, which describes the wettability of liquids on smooth solid surfaces. The contact angle of 90° is the critical angle for judging the wettability between droplets and solid surfaces. When theta is greater than 90°, it shows that the surface is hydrophobic and vice versa. In fact, there is almost no absolutely smooth surface in nature. The wetting state of liquid on rough solid surface is characterized by Wenzel model and Cassie-Baster model. Wenzel model considers that the apparent contact angle between droplet and solid surface is larger than the intrinsic contact angle due to the increase of surface roughness. While the Cassie-Baster model considers that the droplets are suspended on the concave and convex grooves on the solid surface, and the droplets fall on the solid-liquid-gas three-phase composite interface (Fig. 1).
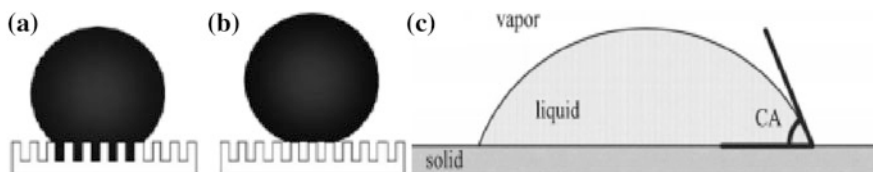

Fig. 1. **a** Wenzel model, **b** Cassie-Baster model, **c** schematic diagram of contact angle

2 Preparation Method of Superhydrophobic Surface

It has been shown that the superhydrophobic property of material surface is determined by its surface energy and surface roughness. Therefore, the superhydrophobic surface can be constructed by using the materials with low surface energy and constructing rough structure. At present, the methods used to construct superhydrophobic surface mainly include dip coating method, spraying method, template method, chemical vapor deposition method, etching method, electrostatic spinning method, phase separation method, and layer by layer self-assembly method. The related methods will be summarized below.

Dip Coating Method. At present, the dip coating method is considered to be the most commonly used method to construct the superhydrophobic surface. This method can be applied to the preparation of superhydrophobic surfaces with large substrates and does not require much time. In general, the substrate needs to be impregnated in the prepared superhydrophobic coating for treatment, and then it should be dried and

cured. Superhydrophobic coatings contain solid particles, adhesives, and hydrophobic components that increase surface roughness. Wang et al. [8] firstly prepared silica nanoparticles by sol-gel method, and then the cotton fabric was soaked into a mixture of hydrophobic particles and dopamine hydrochloride for superhydrophobic treatment. The strongly adhered micro/nanoscale roughness with low surface energy imparted the fabric with excellent hydrophobicity and durability. Wang et al. [9] formed a super-hydrophobic surface by soaking the paper into the prepared silica sol. The superhy-drophobic paper had excellent mechanical properties and the functions of acid and moisture resistance.

Spraying Method. Superhydrophobic coating can be constructed on the surface of the substrate by spraying method. Hydrophobic nanoparticles are usually mixed with organic reagents and the resulting suspension is sprayed onto the substrate surface. This method is simple, efficient, and has a good application prospect. Lu et al. [10] prepared a coating by mixing two different size ranges of TiO_2 nanoparticles in an ethanol solution containing perfluorooctyltriethoxysilane. And then the coating was sprayed onto the filter paper or glass surface. The modified filter paper or glass obtained good hydrophobicity and self-cleaning ability.

Template Method. Template method is to fabricate superhydrophobic surface quickly by self-made template or duplicating existing micro-and nano-structures. This method has the advantages of simplicity, efficiency, and large area replication, but the service life of the template is not long. Liu et al. [11] fabricated a transparent super-hydrophobic surfaces by calcining candle-soot-coated polydimethylsiloxane (PDMS) films. The network structures were created on glass. The substrate exhibited a water contact angle of 163° and a high thermal stability.

Chemical Vapor Deposition. Chemical vapor deposition involves the chemical reaction of two or more gaseous materials and then the resulting new material is deposited onto the surface of the substrate. Bao et al. [12] proposed a method for fabricating superhydrophobic surfaces, which was developed by coating metal oxide nanoparticles, including ZnO, Al_2O_3 and Fe_3O_4, on various substrates followed by treatment with PDMS via chemical vapor deposition (CVD) method. Lau et al. [13] prepared hydrophobic vertical array carbon nanotubes (VACNTs) by chemical vapor deposition technology.

Etching Method. The etching method is to change the structure of solid surface by physical or chemical methods to form regular or irregular micro-nano size roughness. Then the wetting state of solid surface will be changed. The surface hydrophobicity can be regulated by the method through the operation and design of the surface structure, but the cost is high and it is not suitable for large area preparation. Sung-Woon et al. [14] obtained a superhydrophobic Si surface with a contact angle of 165° via plasma etching by combining the fabrication of microscale rod structures and the deposition of fluorocarbon films on the Si surface.

Electrostatic Spinning Method. Electrostatic spinning is a unique fiber manu-facturing process in which polymer solution or its melt is placed in a high-voltage electrostatic field and doped with nanoparticles to form micro-nanofibers under the action of electric field force. It has the advantages of simple manufacturing device, various spinnable materials, and controllable process, which can be used alone or in combination with other methods. Lim et al. [15] used methyltriethoxysilane (MTES) as

an ORMOSIL precursor to prepare silica (SiO_2) sol containing methyl groups by sol-gel method. And then the superhydrophobic surface with multifunctionalities and thermal stability was obtained by creating hierarchically electrospun fibrous structures.

Phase Separation Method. Phase separation process usually utilizes the different solubility or thermal properties of mixtures to initiate the separation of two or more phases in the system, resulting in micron or nanometer rough structure. The method can be used to prepare uniform and large area superhydrophobic films due to the easy control of experimental conditions and simple operation. It has great practical value, but volatilization of solvents will cause certain environmental pollution. Zhang et al. [16] obtained the poly(vinylidene fluoride) (PVDF) membrane with thermal stability and mechanical stability by using phase separation method and adding ammonia water into the N-methyl-2-pyrrolidone (NMP) solution of PVDF. Obeso et al. [17] precipitated poly(hydroxybutyrate) (PHB) on the surface of cellulose fibers of papers using a phase separation process to obtain a superhydrophobic surface with rough texture at both micro and nano length scales.

Layer-by-layer Assembly Method. Layer-by-layer (LBL) assembly method is to assemble nanoparticles or polymer electrolytes onto the substrate by layer-by-layer deposition under the action of electrostatic, coordination bond. This method has the advantages of simple operation, easy control of assembly degree and structure. Shang et al. [18] fabricated highly transparent porous silica coatings on glass substrate through LBL assembly of raspberry-like polystyrene@silica (PS@SiO_2) microparticles. Under the action of low surface energy materials, the prepared coatings showed superhydrophilic and superhydrophobicity properties. Gomes et al. [19] proposed a simple technique of LBL of applying polycation chitosan (CH) and polyanion alginates (ALG) to prepare CH/ALG multilayers on cotton samples.

3   Application of Superhydrophobic Materials

The special wettability of superhydrophobic materials can make them combine with different substrates so that they can be widely used in oil-water separation, self-cleaning, moisture-proof packaging, and responsive materials.

Oil-Water Separation. More and more oily wastewater is produced by modern industrial activities. The consequent environmental problems and the waste of water resources have aroused wide attention. At present, there are many methods for separating oil-water mixture, such as gravity method, centrifugal method, ultrasonic method, adsorption method, and filtration method. But low efficiency and poor stability are the biggest drawbacks of these methods. Oil-water separation is essentially an interfacial problem, so materials with special wettability have been extensively studied. Xu et al. [20] prepared hydrofluoric acid-titanium dioxide (HFA-TiO_2) sol by mixing silica nanoparticles (SiO_2) with ethanol solution. Then the porous substrates including polyester fabric and polyurethane sponge were coated with the coating solution by a simple dip coating method. The modified coatings showed unusual capabilities for controllable filtration of an oil–water mixture and selective removal of water from bulk oil. Dang et al. [21] fabricated a superhydrophobic polymer that can be applied to cotton fabric, filter paper, and PU by a simple random copolymerization. The wetting

state of the coating can be changed by in situ and ex situ treatment. Thus, the coating can be applied in highly controllable oil/water separation such as continuous separation of oil/water/oil three phase mixtures (Fig. 2).
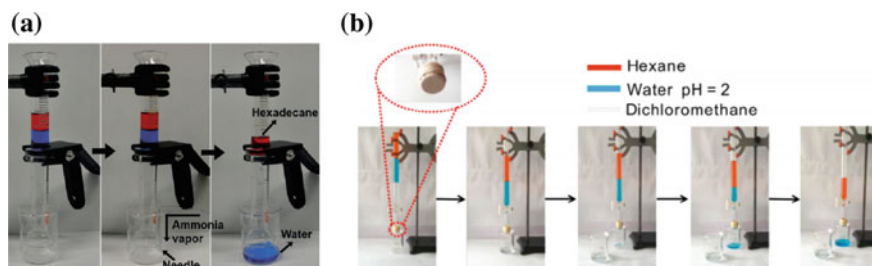

Fig. 2. a Schematic diagram of continuous separation of oil/water/oil three phase systems, **b** oil-water separation by the functionalized polyester fabric

Responsive Function. In order to expand the application field of superhydrophobic materials, more and more researches have been conducted on smart materials that can respond to external stimuli such as temperature, pH, and light [22–25]. Xu et al. [26] prepared superhydrophobic coatings by mixing SiO_2 with TiO_2 modified by decanoic acid. The superhydrophobic coating presented hydrophobic properties in air and neutral water environment and hydrophilic properties in alkaline solution or ammonia vapor. Xu et al. [27] reported a template lamination method to fabricate multifunctional TiO_2-high-density polyethylene (HDPE) nanocomposite surfaces with superhydrophobicity, UV-induced reversible wettability, and selfcleaning properties. Geissler et al. [28] prepared superhydrophobic paper with cellulose stearyl ester (CSE) solution and nano-particles, which could be responded to temperature. The paper would become hydro-philic after heat treatment at 70 °C for 5 min. Cao et al. [29] fabricated thermo and pH dual-controllable mesh by photo initiated free radical polymerization. The coated mesh showed superhydrophilicity and underwater superoleophobicity at certain temperature and pH. While the water resistance of poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) hydrogel decreased when the temperature reached above 55 °C or pH was larger than 13 (Fig. 3).

Moisture-Proof Packaging. The mechanical properties of paper will be degraded due to the easy absorption of moisture by its fibers when it is used for storage and transportation. In order to widen the application field of paper, the superhydrophobic coating can be combined with paper, so that paper can be used in the field of moisture-proof packaging. A superhydrophobic paper was fabricated by precipitating TiO_2 nanoparticles/sodium alginate (ALG) multilayers on paper surface layer-by-layer fol-lowed by an adsorption treatment of colloidal carnauba wax. The prepared superhy-drophobic paper with excellent moisture-proofing property and high strength stability had a great potential in moisture-proof paper packaging [30]. Li et al. [31] developed a simple method to fabricate superhydrophobic paper which had excellent moisture resistance by depositing carnaubawax onto the surface of cellulose fibers via a phase separation method (Fig. 4).
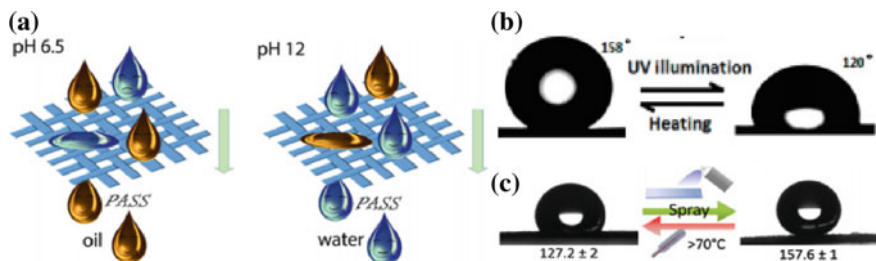
Fig. 3. Schematic diagram of **a** surface wettability at different pH, **b** wettability transition of TiO$_2$-polymer nanocomposite surface, **c** wettability transition of superhydrophobic paper treated at different temperatures
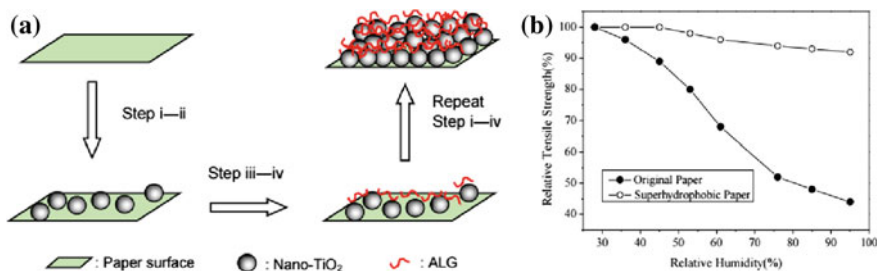
Fig. 4. **a** Schematic diagram illustration of the preparation process of TiO$_2$/ALG multilayers on paper surface, **b** relative tensile strength of original paper and superhydrophobic paper under different relative humidity

Self Cleaning. The water droplets can roll freely on the surface of the substrate when the contact angle between water droplets and superhydrophobic surface is greater than 150° and the rolling angle is less than 10°, which can realize the self-cleaning characteristics of the material surface. Fu et al. [32] synthesized the quaternary ammonium salts (QAS) functionalized fluorinated copolymer tethered hydroxyl groups. And then the superhydrophobic nanocomposite coatings with self-cleaning properties were prepared by crosslinking fluorine copolymers and poly(urea-formaldehyde) nanoparticles (PUF NPs) nanoparticles with hexamethylene diiso-cyanate. The self-cleaning properties of nano-composite coatings were studied by using copper chloride dihydrate powder as pollutant. Excellent self-cleaning performance was achieved by adding PUF NPs into the copolymer. Chen et al. [33] prepared self-repairing superhydrophobic coatings based on TiO$_2$ with photocatalysis and micro-capsules, which was against UV irradiation and chemically stable. The coatings showed good self-cleaning property to the powder dirt (Fig. 5).
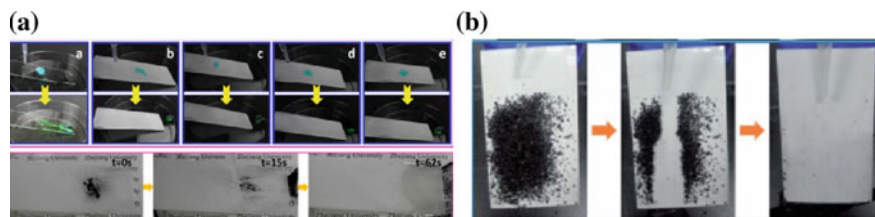
Fig. 5. **a** Self cleaning test by copper chloride dihydrate particles, **b** self cleaning ability of the pH-capsules based superhydrophobic surface

4 Conclusions

In this paper, the preparation methods and applications of superhydrophobic materials are reviewed in order to provide some reference for the future research of superhydrophobic materials. At present, superhydrophobic materials have been extensively studied, and some achievements have been achieved. However, there are few superhydrophobic materials in the actual production. Actually, there are still some problems to be solved urgently. For example, the preparation of superhydrophobic materials mostly involves fluorine-containing materials, which does not meet the current needs of green development. Although fluorine-containing substances can promote the hydrophobicity, the pollution to the environment and the harm to human health can not be ignored. Therefore, it is a challenge to develop economically and environmentally friendly superhydrophobic materials with excellent superhydrophobic performance, and it is also of great significance for the advancement of superhydrophobic research.

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