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Interfacial Effects of Superhydrophobic Plant Surfaces: A Review

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Abstract

Nature is a huge gallery of art involving nearly perfect structures and properties over the millions of years of development. Many plants and animals show water-repellent properties with fine micro-structures, such as lotus leaf, water skipper and wings of butterfly. Inspired by these special surfaces, the artificial superhydrophobic surfaces have attracted wide attention in both basic research and industrial applications. The wetting properties of superhydrophobic surfaces in nature are affected by the chemical compositions and the surface topographies. So it is possible to realize the biomimetic superhydrophobic surfaces by tuning their surface roughness and surface free energy correspondingly. This review briefly introduces the physical-chemical basis of superhydrophobic plant surfaces in nature to explain how the superhydrophobicity of plant surfaces can be applied to different biomimetic functional materials with relevance to technological applications. Then, three classical effects of natural surfaces are classified: lotus effect, salvinia effect, and petal effect, and the promising strategies to fabricate biomimetic superhydrophobic materials are highlighted. Finally, the prospects and challenges of this area in the future are proposed.

Keywords: interfacial effects, superhydrophobicity, plant leaves, contact angle, bionics

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1 Introduction

Nature is the creation of aesthetic functional system, where many natural organisms have vagarious structures through millions of years of evolution, giving rise to the best adaption to the environment[1]. In the past decades, scientists have shown great interest in superhydrophobic surfaces and done a lot of studies, especially the opal structure of butterfly wings, the nano-papillae morphology of lotus leaf, and the needle-shaped seta of water strider become a focus of current research[2]. Meanwhile, their surface special wettability, such as superhydrophobicity, is also attractive due to wide applications, such as anti-icing, drag-reduction, self-cleaning, anti-sticking, *etc*[3]. Superhydrophobicity is defined as that the Contact Angle (CA) of a drop on the surface is larger than 150° and an important characteristic of superhydrophobic surface is its repelling to water[4]. In this review, we mainly focus on the superhydrophobic plants in nature. Our survey shows that there is a rapid increase in the published papers about superhydrophobic surfaces in the past decade, seen from Fig 1. The chemical compositions of cuticle wax and surface structure play an important part in the wettability to reduce surface free energy. However, compared with the surface structure, the impact of chemical composition of wax on the wettability is relatively smaller[5]. Generally, the surface structures of superhydrophobic plants in nature are rough, and most of them are at least two different scales (micro- and nano-scales). It is well-known that the lotus leaf is a typical superhydrophobic example with a high contact angle and a low sliding angle due to the cooperative effect of surface roughness, low surface-energy coatings, and micro/nanostructures on the surfaces, which endows the lotus leaves with a unique self-cleaning property, called "lotus effect". However, it should be noted that the high contact angle of the surface does not have to mean a high water resistance. For example, the red rose petal is also super water-repellent, whose nanostructure has no wax crystals, but has nano-folds[6]. Meanwhile, the petal surface shows a strong adhesive force, which is different

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from the lotus leaf with a low adhesion, and this phenomenon is defined as "petal effect". In nature there exists another fern with super water-repellency, whose surface can hold an air layer for a long time underwater, called "salvinia effect" for short[7]. It is indicated that a larger fraction of air among each hair results in the hydrophobicity of the surface. The surface structures play a very important role in achieving a hydrophobic surface.

Some classical models and corresponding formulae about the surface wettability were established to understand the mechanism of superhydrophobic phenomena from a theoretical viewpoint, *e.g*. Young's model[8], Wenzel model[9], and Cassie model[10]. Based on these models, scientists not only theoretically explained superhydrophobic mechanism, but also calculated the CAs of the corresponding surface and paved the way for an improved knowledge of the conduction of superhydrophobic surfaces. Studying the superhydrophobic plant surfaces aims at fabricating functional materials with similar properties used for human daily life. Importantly, natural structures offer ideal models for us to obtain excellent biomimetic materials since these structures in nature show a large number of functions, such as special wettability, high adhesive force, lower friction under water, structural colors, anti-reflection and so on[11]. However, even though nature has successful solutions, some structures are not necessarily optimal for technical performance. Thus it is important to figure out the principle of nature's solutions and artificial systems rather than simply copying nature[12]. In addition, inspired by the natural surface structures, various smart methods about achieving super water-repellency surfaces were employed, such as chemical vapor deposition[13], electrochemical deposition[14], phase separation[15], sol–gel processing[16,17], crystallization control[18], lithography[19] and so on[20,21]. A variety of artificial materials with hierarchical surface structures were constructed by these methods by virtue of inorganic and organic molecules[22], such as ZnO, TiO_2, silyl compound, or fluorocarbons, *etc*. However, current procedures for the fabrication of superhydrophobic surface are also difficult for large-scale industrial manufacture. Therefore, the comprehensive understanding of the functions provided by objects and processes found in nature can guide us to bionic nano-materials, nano-devices and so forth.

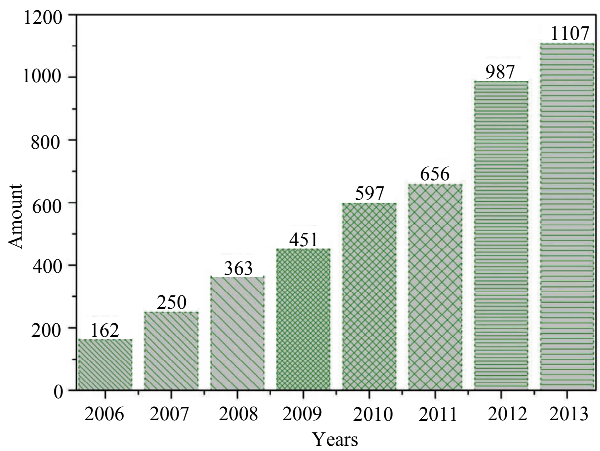

Fig. 1 The scheme of published papers about "superhydrophobic surface" in "web of science".

To this end, this review is classified into four parts to discuss the interfacial effects of the superhydrophobicity in plant leaves. The first section is the brief introduction about this review, and in section **2**, the chemical compositions of leaf surfaces are briefly summarized. In the following part, an overview of three different effects are given: the lotus effect shows self-cleaning property with a high contact angle and a low hysteresis; the petal effect has a high adhesive force, and the drop on such surface can stay stable even when it is turned upside down; the salvinia surface has the capability of holding an air film under water for a long time (days to months), although the pin of surface is hydrophilic, called "salvinia effect" for short. Finally, the prospects and progress of superhydrophobic surfaces in nature are briefly proposed.

2 The chemical composition of plant surfaces

For superhydrophobic plant leaves, micro/nano-hierarchical structure of the cuticle is common in plant surfaces, which is comprised of two levels of different scales. But the sculptures of more than two orders can be found in some plant species[23,24]. The cuticle is the main interface between plant and environment, and the primary microstructure of plant surfaces can be divided into the following four sections, originating from four different modifications of the epidermal cells, as shown in Fig. 2[25–27]. Fig. 2a illustrates that the first structure is coves and it is a folding cuticle, which derives from the coves of the cell wall. In the second case, the sub-cuticular inserts of mineral crystals, such as silicon oxides (Fig. 2b), cause tubercular or verrucate surface sculptures. In the third case, the folding cuticle itself (Fig. 2c) creates the structures. The fourth kind of surface