

Feature Article

Recent advances in designing superhydrophobic surfaces

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ARTICLE INFO

Article history:

Received 5 February 2013

Accepted 26 March 2013

Available online 10 April 2013

Keywords:

Biomimeticism

Bioinspiration

Superhydrophobic

Wetting

Surfaces

ABSTRACT

The interest in superhydrophobic surfaces has grown exponentially over recent decades. Since the lotus leaf dual hierarchical structure was discovered, researchers have investigated the foundations of self-cleaning behavior. Generally, surface micro/nanostructuring combined with low surface energy of materials leads to extreme anti-wetting properties. The great number of papers on this subject attests the efforts of scientists in mimicking nature to generate superhydrophobicity. Besides the thirst for knowledge, scientists have been driven by the many possible industrial applications of superhydrophobic materials in several fields. Many methods and techniques have been developed to fabricate superhydrophobic surfaces, and the aim of this paper is to review the recent progresses in preparing manmade superhydrophobic surfaces.

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1. Introduction

Nature is an inexhaustible source of functional surfaces. Since millennia, plants and animals have developed surfaces with special wettability ranging from very high slippery to high sticky surfaces. The surface wettability, as regards to water, is measured by the contact angle which a water droplet forms when it is put on a

surface. Among many intriguing phenomena happening in nature, self-cleaning has excited the scientist's curiosity. Self-cleaning surfaces exhibit special non-wetting properties owing to a water contact angle greater than 150° and an effortless rolling off of water droplets. The interest on superhydrophobic surfaces has risen after the discovery of the self-cleaning properties of lotus leaves depending on its hierarchical roughness. Actually, it has been found out that the micro/nanostructures combined with the low surface energy bring superhydrophobic properties. On a slippery surface, the water droplets do not penetrate into the asperities of surface, and the interactions with the surfaces are lowered. On

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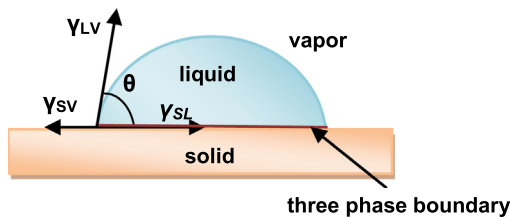


Fig. 1. Diagram showing the forces at the three-phase contact line of a liquid droplet on a solid.

the other hand, superhydrophobic surfaces showing high sticky behavior have also fascinated scientists. These surfaces exhibit high water contact angle ($>150^\circ$), and high roughness and water droplet are less prone to roll off on them. In this case, the water droplet penetrates into cavities of surface, the high roughness increases the contact area, and as consequence, the liquid–solid interactions are increased. Mimicking the nature, scientists have developed many methods to fabricate superhydrophobic surfaces. The efforts were focused on surface texturing, in order to create a suitable micro/nano-roughness able to generate the superhydrophobic properties. The huge literature reveals the great interest for both fundamental research and practical applications [1–6]. The main challenge is to fabricate robust and durable superhydrophobic surfaces suitable for application in many fields ranging from barrier, anti-icing/fogging, water/oil separation, anti-bioadhesion materials.

1.1. Basics of superhydrophobicity

When a droplet of water rests on a surface, there is a contact angle measured at the edge of the droplet. It can be defined as the tangent angle of the liquid–vapor interface at the three-phase boundary (Fig. 1). For a smooth surface, the contact angle is described by the Young Eq. (1) [7]:

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

where γ_{LV} relates to the interfacial tension between liquid and vapor, γ_{SL} is the interfacial tension between solid and liquid, and γ_{SV} is the interfacial tension between solid and vapor.

For contact angles less than 90° , the surface is conventionally described as hydrophilic, if the contact angle varies between 90° and 150° , the surface is hydrophobic, and if water contact angle is greater than 150° , the surface is conventionally described as superhydrophobic.

Hydrophobic surfaces can be enhanced to superhydrophobic by addition of roughness or more accurately by a certain type of morphology. This amplification of surface wettability can be viewed as a physical amplification of surface chemistry. Actually, two models have been elaborated which describe the behavior of a droplet on rough hydrophobic surfaces (Fig. 2). According to the first model, the droplet maintains contact with the surface and penetrates the asperities, and the surface contact area is increased (the Wenzel case) [8,9]. Alternatively, according to the second model, the

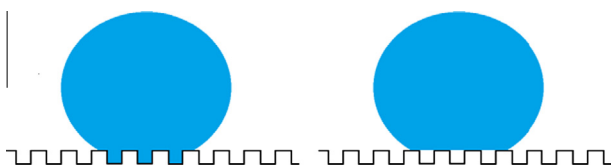


Fig. 2. Behavior of a liquid droplet on a rough surface. Left, Wenzel state; right, Cassie-Baxter state.

droplet is suspended on the asperities, the droplet rests on a composite phase made of both solid–liquid and solid–vapor interfaces (the Cassie-Baxter case) [10,11].

The Wenzel equation takes into account that the droplet follows the roughness surface and fills the asperities. Therefore, the surface area associated with the contact angle is increased by a factor r , the roughness factor.

$$r = \text{roughness factor} = \frac{\text{actual surface area}}{\text{planar area}} \quad (2)$$

The equation describing the Wenzel state is the following:

$$\cos \theta_w = r \cos \theta \quad (3)$$

The roughness factor r emphasizes the effect of the surface chemistry determined by the term $\cos \theta$. When $\theta < 90^\circ$, an increase in roughness factor r reduces θ_w , but if $\theta > 90^\circ$, an increase in roughness leads to an increase in θ_w .

In the Cassie-Baxter state, the droplet is suspended on the surface asperities. The liquid does not penetrate into the protrusions of the surface features. In the Cassie-Baxter equation, the apparent contact angle is the result of all contributions of different phases:

$$\cos \theta_{CB} = f_1 \cos \theta_1 + f_2 \cos \theta_2 \quad (4)$$

where f_1 and f_2 are the surface fraction of the phase 1 and 2, respectively, and θ_1 and θ_2 the contact angle of phase 1 and 2, respectively. If only one type of protrusion is present, given f the fraction of asperities, $(1 - f)$ is the air fraction. Water droplet has a 180° contact angle with air, so the equation becomes:

$$\cos \theta_{CB} = f(1 + \cos \theta_w) - 1 \quad (5)$$

Surfaces that are wetted in the Wenzel manner are usually sticky, while surfaces in the Cassie-Baxter state are slippery. The two equations describe two limit behaviors, and surfaces may show intermediate Wenzel-Cassie state. In this case, apparent contact angle depends on both solid-surface fraction f and roughness factor r . The equation that describes this situation is the following:

$$\cos \theta_{CW} = fr \cos \theta + f - 1 \quad (6)$$

For many surfaces, a transition from Cassie-Baxter to Wenzel state was observed. Many factors can determine this change such as surface heterogeneity, both chemical heterogeneity and roughness [12–14], and the interaction at the contact line seems to play a crucial role in giving rise to adhesion hysteresis [15,16].

Young equation is valid for ideal, smooth, and homogeneous surfaces; water contact angle is measured at the equilibrium and it is unique. In practice, chemical heterogeneity and roughness can engender a contact angle hysteresis (H) between the water front advancing across a surface and receding from the surface. Generally, advancing contact angle (θ_A) exceeds receding contact angle (θ_R). There are different methods to measure contact angle hysteresis. By the sessile drop method, advancing contact angle is determined by increasing the droplet volume and measuring the contact angle just before the wetting line advances. Afterward, the receding contact angle is determined by decreasing the volume of the water droplet. We can also measure contact angle hysteresis of a liquid droplet stuck on a tilted plane, measuring the difference between the contact angle at the front and at the rear of the droplet just before it starts to slide down. Generally, the front angle is larger than the rear angle. If the water droplet cannot remain stuck on a tilted plane, the tilting angle (α) just before the droplet rolls off measures the slippery character of the surface. When a water droplet is deposited on a superhydrophobic surface, and it is in a Cassie-Baxter state, it tends to form near-spherical droplets, to roll on the surface and, if the surface is slightly inclined, to collect all foreign

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