

Edited by  
Mehmet Gürsoy and Mustafa Karaman

# Surface Treatments for Biological, Chemical and Physical Applications





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Chemical, and Physical  
Applications**



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*Edited by Mehmet Gürsoy and Mustafa Karaman*

**WILEY-VCH**

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## Preface

Solids are composed of a bulk material covered by a surface. The surface acts as an interphase to the surrounding and it is usually the surface phase that determines if a material is suitable for an intended application or not. Hence, treatment of a surface through either chemical or physical routes has been an important topic that has attracted the attention of both researchers and industry because of the endless application possibilities. Surface modification techniques are now being used extensively in the textile, aerospace, automotive, biomedical, defense, chemical, tooling, construction industries, and many more as well. The purpose of this book is to give the reader some generalized concepts on the modification and characterization, as well as some insight on the recent applications of the surfaces. Other than a few old books there is no complete book that describes the whole picture. In addition, we want to get the attention of a broad range of readership including those of undergrad students, technicians, and even individuals that are interested in this topic. The language of the book is clear and concise and provides many excellent illustrations to make their point. The book covers the most basic concepts without complicated analyses so that an individual who is not familiar with the subject can also benefit. We have used as many visuals as possible to show the importance of surface treatments on many applications, including surfaces that are naturally engineered. The first three chapters of the book include basic parts: (1) surfaces in nature, (2) surface modification techniques, and (3) surface characterization techniques. The remaining chapters deal with some emerging chemical and physical applications: (4) surface modification of polymeric membranes for various separation processes, (5) Langmuir–Blodgett films: sensor and biomedical applications and comparisons with the layer-by-layer (LbL) method, (6) surface modification of biopolymer-based nanoforms and their biological applications, (7) enzyme-based biosensors in food industry via surface modifications, and (8) heterogeneous catalysis.

The most remarkable examples of surface engineering are abundant in nature. Since the beginning of the life, all kinds of living organisms from one-celled creatures to plants and animals have adapted to their environments for survival. By long trial and error processes, nature itself has generated a great number of outstanding living creatures with tested and proven sustainable biological functions. There have been numerous studies in materials science, based on

mimicking natural materials. In Chapter 1, examples of biomimetic materials especially the related surfaces are given.

Following the increasing demand for high performance materials from the past century, the field of materials surface modification by various synthetic strategies has undergone enormous expansion. Significant numbers of studies have been carried out to develop efficient techniques for adding new functionalities to a materials surface as well as to understand the fundamental aspects of the various techniques. In Chapter 2, the basics of most significant surface modification processes are given. Although both dry- and wet-coating techniques are involved, emphasis is given to vapor deposition techniques.

The chemical, physical, and morphological features of surfaces including wettability, optical, adhesive, mechanical, and so on play a very crucial role in material properties. Therefore, characterization of a surface is very important for materials science. The properties of natural and fabricated material surfaces can be determined using various characterization techniques. In Chapter 3, some of the most common characterization methods are given.

Starting from Chapter 4, emerging applications of surface science are given. Membranes are industrially important materials that are used extensively in fluid separation processes. The membrane separation process is mainly governed by the characteristics of the membrane top layer. Thus, modifications of membrane surface properties is the practical and effective approach to achieve desired separation efficiency. In general, membrane surface modification can be performed by techniques such as interfacial polymerization (for thin film composite membranes), organic–inorganic blending (for mixed matrix membranes), LbL assembly, photo-initiated polymerization, and conventional spray coating. Chapter 4 aims to overview the surface modification methods available for polymeric membranes development and discusses the importance of surface-modified membranes for various applications, covering aqueous, solvent, and gas phases.

Chapter 5 focuses on Langmuir–Blodgett films that has been an active area of research for more than a century. Many of the methods for the production of thin organic films have been adopted by nanotechnology for the production of hybrid organic–inorganic films, containing molecular layers, nanoparticles, sheet-like inorganic materials, and biopolymers. The chapter focuses mainly on Langmuir–Blodgett films and compares them to LbL films.

Chapter 6 addresses chemical surface modifications of biopolymers-based nanoforms namely nanocellulose, including bacterial cellulose, and nanochitin, for biological applications. These biopolymers provide sustainable solutions to the need for new (bio)materials in biological applications due to their unique biological properties like low toxicity, biocompatibility, biodegradability, and bioactivity. Nonetheless, further chemical functionalization has been advanced in order to optimize their intrinsic properties and/or generate novel functions to develop new materials, in particular functional bionanocomposites.

Biotechnological applications of enzyme-based biosensors have become an important tool for the detection of chemical and biological components for food monitoring due to their exceptional performance capabilities toward food materials, which include high specificity and sensitivity, rapid response, low

cost, relatively compact size, and user-friendly operations. In Chapter 7, detailed information is shared about surface modifications of enzymes, immobilization of enzymes, main characteristics of enzyme based biosensors, and their usage in food analysis.

In Chapter 8, the importance of heterogeneous catalysis is discussed in terms of solid surface science. Considering this purpose, general information about heterogeneous catalysis and surface science including their industrial and economic importance, reaction mechanisms and kinetics in heterogeneous catalysis systems, and preparation and characterization methods for heterogeneous catalysts are given.

Finally, we wish to express sincerely our gratitude to all authors and co-authors of the book, because of their great effort during the preparation of this book.

22 September 2016  
Konya, Turkey

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## 1

## Surfaces in Nature

Mehmet Gürsoy and Mustafa Karaman

*“Natura nihil frustra facit” (Nature does nothing in vain).*

Aristotle (384–322 BC)

### 1.1 Introduction

Human beings have used nature in order to meet their needs. Early inhabitants took advantage of natural resources and materials just for their fundamental needs such as food, shelter, and clothing. Over the past several centuries, science and technology have developed exponentially in the world. Conventional materials and methods such as self-cleaning surfaces, new generation optical devices, biomaterials, and so on are not enough to meet the requirements of high-technology applications.

Thanks to improvements in surface analysis techniques, scientists can look deep into nature. In this way, the relationships between the structure and functions of living organisms can be investigated.

Since the beginning of life, all kinds of living organisms from one-celled creatures to plants and animals have adapted to their environments for survival. By extensive trial and error processes, nature itself has created a great number of outstanding living creatures with tested and proven sustainable biological functions. As a result of the long adaptation process (spanning millions of years), organisms have developed impressive features that have equipped them better to compete for limited resources, defend themselves against their predators, and live longer. Therefore, it can be easily said that nature is the best materials scientist ever. Because of this, copying or mimicking of biological systems is an effective way to produce desired high-technology materials. This approach is called as *biomimicry*.

The word biomimicry is a combination of two Ancient Greek words, “bios” meaning “life,” and “mimesis” meaning “to imitate.” Biomimicry can be defined as that branch of science that seeks to imitate processes or structures existing in nature. The main philosophy behind biomimicry is “If Nature can do it, so can we.” With this approach, nature is used as a guide to tackle problems using biomimetic materials and processes.

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Biomimetic innovation is based on the observation and mimicking of nature. Indeed, observation and learning from nature began in the initial days of mankind. That is why, biomimicry has been accepted as an ancient discipline. Throughout history, nature has inspired us to invent many tools.

During the Renaissance Period, numerous impressive bio-inspired designs were produced by Leonardo Da Vinci. For instance, he designed a flying machine by investigating bird anatomy. His words on nature show why he applied bio-inspired idea on his designs: “Although human genius through various inventions, makes instruments corresponding the same ends, it will never discover an invention more beautiful, nor more ready, nor more economical than does nature, because in her inventions nothing is lacking and nothing is superfluous [1].”

In 1969, the term *biomimetics* was first used by bioengineer Otto Herbert Schmitt in his paper at the Third International Biophysics Congress in Boston [2]. However, biomimicry was popularized by Janine Benyus in her book *Biomimicry: Innovation Inspired by Nature* (1997) [3]. Subsequently, biomimetic approaches have become more and more popular and important during the past decades in almost all research fields.

There have been a lot of studies in materials science, based on mimicking natural materials. In this chapter, examples of biomimetic materials, especially the related surfaces, are given.

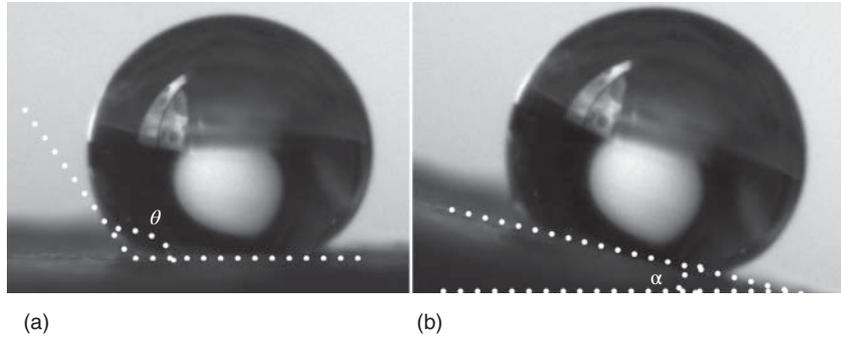
## 1.2 Inspiring Natural Surface Structures

### 1.2.1 Self-Cleaning Surfaces

Self-cleaning surfaces are in great demand for fundamental research and various industrial applications. These types of surfaces must have two important criteria: very high contact angle and low contact angle hysteresis.

Contact angle can be defined as a measure of the wettability of a solid surface by a liquid drop (Figure 1.1a). Theoretically, the contact angle values must be between  $0^\circ$  and  $180^\circ$ . If the contact angle is less than  $90^\circ$ , these surfaces are classed as hydrophilic. If the wetting angle is higher than  $90^\circ$ , these kind of surfaces can be accepted as water repellent. When a contact angle approaches  $180^\circ$ , the surface is considered superhydrophobic. Adhesion of droplets on the surface can be determined by dynamic contact angle measurements. Dynamic contact angle is referred as *advancing contact angle* (the maximum value of the contact angle) and *receding contact angle* (the minimum value of the contact angle). Contact angle hysteresis is the difference between them. There is a strong relation between sliding angle and contact angle hysteresis. Sliding angle is the required minimum angle to move the droplet on surfaces (Figure 1.1b). As the contact angle hysteresis decreases the drops can easily roll off from the surfaces.

In nature, self-cleaning properties have been observed in various plant leaves. On a rainy day, the raindrops do not spread on the plant leaf and these drops completely roll off the leaf. And thus, undesirable particles on the leaves are easily removed by rolling water drops. It is also known that pathogenic microorganisms



**Figure 1.1** (a)  $\theta$  is the water contact angle and (b)  $\alpha$  is defined as the inclination angle at which a water drop rolls off the surface.

cannot germinate and infect leaves without water. For this reason, self-cleaning helps prevent the occurrence of plant diseases [4].

Among the plants that are self-cleaning, lotus is one of the most popular examples due to its very high contact angle and very low hysteresis. These values are  $164^\circ$  and  $3^\circ$ , respectively [5]. That is why, the term *Lotus Effect* is also used in place of “Self-Cleaning Effect” in the literature [6]. The lotus grows in an aquatic environment such as lakes, and shallow and muddy water. It always achieves to remain clean even in dirty waters [7, 8]. For this reason, the lotus is considered as a symbol of purity.

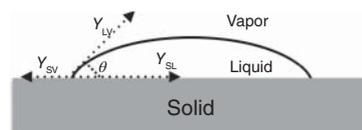
The plants are covered by a cuticular surface except for their roots. The cuticle layer is a natural composite that is the interface between plants and their environment [9]. This composite consists mostly of two parts, soluble lipids and bio-polyesters [10, 11]. Because of the chemical structures of these components, the cuticle layers usually exhibit hydrophobic properties. Lotus leaf surface is also covered by low surface energy cuticular surface, which contains mainly  $-\text{CH}_2-$  groups [12]. The relation between the contact angle and surface energy was formulated in Young’s Eq. (1.1) describing wetting phenomena in terms of thermodynamic equilibrium [13] (Figure 1.2).

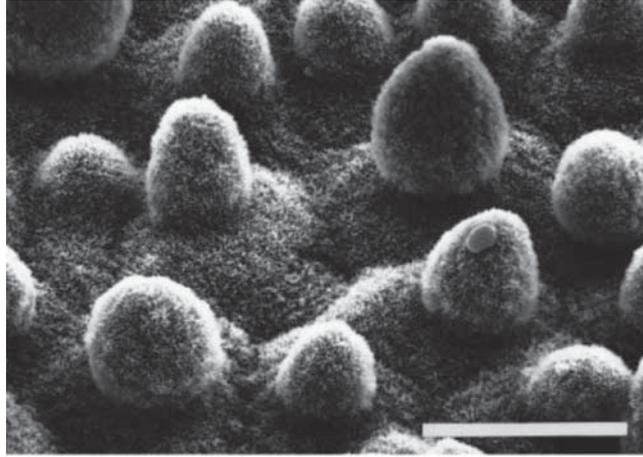
$$\cos \theta = \frac{\gamma_{\text{SV}} - \gamma_{\text{SL}}}{\gamma_{\text{LV}}} \quad (1.1)$$

where  $\theta$  is the contact angle of the liquid,  $\gamma_{\text{SL}}$  is the interfacial surface tensions between the solid and the liquid,  $\gamma_{\text{SV}}$  and  $\gamma_{\text{LV}}$  are the solid and liquid surface free energy, respectively. According to Eq. (1.1), decreasing  $\gamma_{\text{SV}}$  should increase the contact angle value.

However, it is well known that the lower surface energy of  $-\text{CH}_3$  groups or fluorocarbons do not exist in any biological systems [12]. So, the contact angle of

**Figure 1.2** The schematic representation of a liquid drop with the contact angle and tension vectors.





**Figure 1.3** The SEM image of adaxial lotus leaf surface, scale bar = 20  $\mu\text{m}$ . (Barthlott 1997 [9]. Reproduced with permission of Springer.)

a planar cuticular surface can be a maximum of about  $110^\circ$  [14]. Thus, in nature only having low surface energy surface is not enough to be superhydrophobic. By means of scanning electron microscope (SEM), micrometer scale bumps and nanometer scale wax crystals were observed on the lotus leaf surface [9]. The SEM image of adaxial lotus leaf surface structure is given in Figure 1.3.

The effect of surface roughness on the wettability can be explained with the help of the Wenzel model [15, 16]. The Wenzel model describes the following Eq. (1.2).

$$\cos \theta = R_f \cos \theta_0 \quad (1.2)$$

In which,  $\theta$  is the contact angle of a rough surface,  $\theta_0$  is the contact angle of a smooth surface, and  $R_f$  is the surface roughness factor. The roughness factor is defined as the ratio of the actual surface area to the geometric surface area. If the surface is flat,  $R_f = 1$ ; however, this value must be higher than 1 for rough surfaces. For a hydrophilic surface,  $\theta_0$  must be lower than  $90^\circ$ , roughness decreases the contact angle. On the other hand, for hydrophobic surfaces, as in lotus leaf,  $\theta_0$  is greater than  $90^\circ$ . Therefore, according to Wenzel equation, it is expected that increasing the surface roughness increases hydrophobicity [17].

In brief, water repellent surfaces can be produced in two different ways: changing the surface morphology and decreasing the surface free energy. In the former method, the underlying principle is to create micro/nanoscale rough structures on the surfaces. In the latter method, the surfaces are usually coated with hydrophobic functional groups. Only having low surface energy or only having rough surfaces may not be sufficient to be superhydrophobic. Thus, the production of superhydrophobic surfaces mostly requires the combination of two methods.

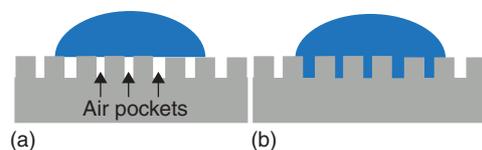
The extraordinary surface morphology of lotus leaf minimizes the contact area between its surface and water drops. The hierarchical micro/nanostructures

provide that air is trapped underneath the water drop. That is why, very high contact angle values are observed on the lotus leaf. The unique structure of the lotus leaf can be directly imitated in order to produce self-cleaning materials.

Roughening fluorinated polymers and silicones directly leads to superhydrophobic surfaces, because of the inherent hydrophobic nature of these kinds of polymers. For example, Barshilia and Gupta [18] treated polytetrafluoroethylene (PTFE/Teflon) surfaces with argon and oxygen plasma to obtain a superhydrophobic surface. The highest average water contact angle and the maximum surface roughness were found for 4 h plasma treatment. During plasma treatment, in spite of changing the surface morphology, functional groups were preserved. The contact angle value increased from  $102^\circ$  to  $158^\circ$ . After 10 months, the contact angle was again measured from the modified surface and almost the same values were found. According to the results, the superhydrophobicity of obtained surface remains unchanged even after a long time. Similarly, Jin *et al.* [19] created a polydimethylsiloxane (PDMS) surface containing micro-, submicro-, and nanostructures using a one-step laser etching method. Etched PDMS surface with these special structures showed high water contact angle ( $162^\circ$ ) and low sliding angle ( $< 5^\circ$ ).

Coating rough or hierarchical surfaces with low surface energy materials is also a common method to produce self-cleaning materials. Ma *et al.* [20], produced superhydrophobic fabrics by a two-step process. In the first step, poly(caprolactone) (PCL) fibers were generated by the electrospinning method. And then, the fiber mat surfaces were coated with perfluoroalkyl ethyl methacrylate (PPFEMA) by Initiated Chemical Vapor Deposition (iCVD). These PPFEMA-coated electrospun fibers exhibited very good self-cleaning properties with contact angle of  $175^\circ$  and sliding angle of lower than  $2.5^\circ$ . These results are attributed to the combination of the inherent roughness of the electrospun mats and the low surface energy of the PPFEMA coating. Liu *et al.* [21] fabricated micro-nanoscale binary structured composite particles of silica/fluoropolymer using an emulsion-mediated sol-gel method to mimic the surface microstructures on the lotus surface. With this method, superhydrophobic surfaces with water contact angle larger than  $150^\circ$  were obtained. Grewal *et al.* [22] investigated the effect of different micro- and nanopatterned surfaces on their wettability and tribological surfaces. The hierarchical patterns were designed, imitating the topography of the adaxial surface of lotus leaf. The advancing and receding contact angle of PTFE-coated hierarchical structure surface was found to be similar to those of the lotus leaf.

The casting method (soft molding) is another simple and effective way to replicate leaf surface structures. Sun *et al.* [23] successfully applied this method for lotus leaf at the first time. They cast PDMS on the lotus leaf, and then the PDMS layer was peeled off. After that, this negative PDMS layer was used to make a positive PDMS layer. According to SEM results, the positive replica and the original lotus leaf showed the same surface structures. The positive template also exhibited similar superhydrophobic properties as the fresh lotus leaf. The contact angle of the positive replica was found as  $160^\circ$  and the water droplets could easily roll off this surface.



**Figure 1.4** (a) Cassie model wetting regime and (b) Cassie impregnating wetting regime.

### 1.2.2 Adhesive Hydrophobic Surfaces

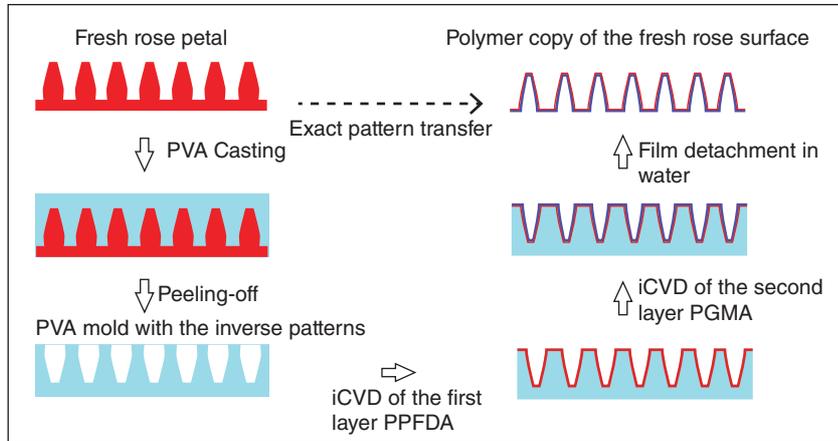
Similarly to lotus leaves, the hierarchical nano- and microstructures on the red rose petal surface provide a high contact angle. However, differently from lotus leaves, water droplets do not slide off the surface of a red rose petal.

Basically, two main hypotheses are used to explain superhydrophobicity on rough surfaces: Wenzel and Cassie wetting regimes. The former regime has been already mentioned in the beginning of this chapter. The Cassie model was developed after the Wenzel's state. According to the Cassie model [24], air is trapped in micro- and nanostructures underneath the water droplets, as seen in Figure 1.4. Because of these air pockets, the liquid cannot wet the surface. It is thus expected that water drops easily roll off this kind of surface, just as in the lotus leaf. The wetting mechanism of lotus leaf is an excellent example for Cassie wetting regime. On the other hand, spherical water droplets usually stick on the red rose petal surfaces. This different behavior can be attributed to difference in the surface topography between the red rose petal and lotus leaf. It is observed that the sizes of the structures on the red rose petal are larger than those of lotus leaves [25]. While water drops cannot enter into the grooves of the lotus surface, they can enter into the grooves of the red rose petal surface.

This phenomenon is known as the *Cassie impregnating wetting regime* as seen in Figure 1.4 [26]. Due to the high adhesion between the water drops and petal surface, the petal surface exhibits a high contact angle. Therefore, water droplets do not fall off even if the petal surface is tilted to  $180^\circ$ . The unique wettability behavior of red rose petal surface was defined as the “petal effect” by Feng *et al.* [27] for the first time in the literature. Recently, there has been a great deal of interest in fabrication of artificial “petal effect” coating and surfaces that mimic the original red rose petal.

Karaman *et al.* produced a thin “petal effect” polymer sheet using a combination of casting and iCVD methods [28]. Firstly, they poured poly vinyl alcohol (PVA) solution on the surface of a fresh red rose petal. The obtained PVA negative mold was placed in an iCVD reactor, then coated by poly(glycidyl methacrylate) (PGMA) and poly(1*H*,1*H*,2*H*,2*H*-perfluorodecyl acrylate) (PPFDA). This schematic duplication process of the red rose petal surface is presented in Figure 1.5. The contact angle of the positive replica was found as  $152 \pm 3^\circ$  and the water did not roll off even when the biomimetic polymer sheet was turned upside down.

Fluorinated polyimide was synthesized by the electrospinning method by Guangming *et al.* [29]. The surface of nanofibers consisted of dented nano- and/or micro bowl-like structures. The air is trapped in bowl-like particles below the water droplets; this situation provides a very high contact angle. Moreover, when the droplet is lifted, the air pocket expands, which creates a negative pressure, and thus the adhesion between water droplet and surface is increased.



**Figure 1.5** The schematic duplication process of the red rose petal surface. (Karaman 2012 [28]. Reproduced with permission of Elsevier.)

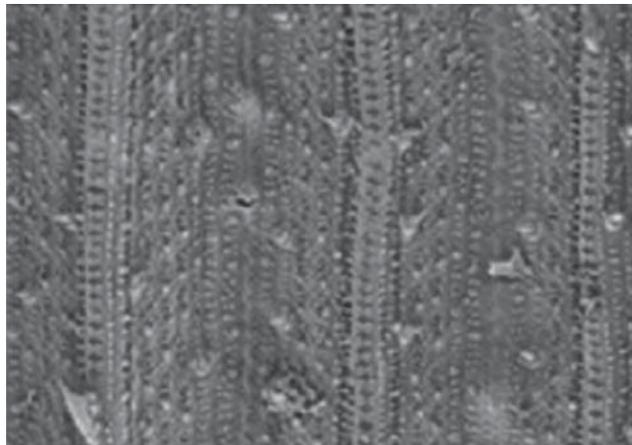
The maximum adhesion force of the petal effect surface was measured as  $127 \mu\text{N}$  and the contact angle was found as  $153^\circ$ .

Recently, the tunable adhesive superhydrophobic surfaces have been produced by controlling the reaction parameters, such as reaction time, particle sizes, surface roughness, and so on. In other words, superhydrophobic surfaces having tunable water adhesion capability allow choosing wetting behaviors, “lotus effect” or “petal effect.” For instance, Liu *et al.* [30] developed a one-step electrodeposition process in that, superhydrophobic surfaces with controlled adhesion can be easily produced by just changing the reaction time. When the reaction time is 10 min, a petal effect surface was obtained and the maximum contact angle was found as  $155.1^\circ$ . When the reaction time increased further up to 30 min, a self-cleaning surface was obtained. Its static contact angle and contact angle hysteresis were found to be  $161.7^\circ$  and  $3^\circ$ , respectively.

Another fabrication of superhydrophobic surfaces with tunable water droplet adhesion was carried out by Xie *et al.* [31]. They used both  $\text{O}_2$  plasma etching and plasma deposition of thin films to create a superhydrophobic wood surface. Firstly, wood substrates were exposed to  $\text{O}_2$  plasma, and then were coated with pentafluoroethane (PFE) films. The obtaining surfaces showed lotus effect properties with high contact angle ( $161.2^\circ \pm 1.5^\circ$ ) and low sliding angle ( $\sim 15^\circ$ ). When wood samples were coated with diamond-like carbon (DLC) after the etching property, these surfaces also exhibited high contact angle ( $153.7^\circ \pm 2.7^\circ$ ). However, differently from PFE-coated wood, DLC-coated samples showed a petal effect.

### 1.2.3 Unidirectionally Superhydrophobic Surfaces

In superhydrophobic structures that show lotus effect property, having low contact angle hysteresis is not enough for some applications, the unidirectional movement of water is also important. The water droplets move in all directions on the lotus leaf surfaces. On the other hand, the water drops on rice leaf surfaces



**Figure 1.6** The SEM image of adaxial rice leaf surface [35]. (Yao <http://link.springer.com/article/10.1007/s11434-012-5220-1>. Used under CC BY 4.0 <https://creativecommons.org/licenses/by/4.0/>.)

roll along just the long-axis direction [32]. The difference between lotus leaf and rice leaf can be attributed to surface topography. Actually, there are similar structures on both these natural surfaces. However, while these microstructures are randomly located on a lotus leaf, they are set on a one-dimensional order (parallel to the leaf edge) on the rice leaf [33]. This observation is consistent with the difference between the parallel and perpendicular direction sliding angles on the rice leaf. These values of parallel direction and perpendicular to the leaf edge were found as  $3\text{--}5^\circ$  and  $9\text{--}15^\circ$ , respectively [34]. Rice leaf surface structure is an excellent example for the fabrication of unidirectionally superhydrophobic surfaces. The hierarchical structures can be seen in Figure 1.6 [35].

Yang *et al.* used the combination of lithography- assisted electrochemical etching, anodic oxidation, and fluoridation methods to fabricate artificial rice leaf structures [36]. They achieved to fabricate a three-level microstructure (macro/micro/nano) of rice leaves on aluminum. This biomimetic structure shows superhydrophobicity and anisotropic sliding behavior.

Zhu *et al.* fabricated the large area surface with ordered binary structure arrays by mimicking the rice leaf surface structure [37]. The underlying pattern on the substrate can be easily modified by changing the polymer solution concentration, which provides the fabrication of various topographies. The obtaining surfaces demonstrate anisotropic wettability similarly to rice leaf.

In another study, Yao *et al.* developed a two-step soft transfer to produce an artificial rice leaf structure [35]. The obtained biomimetic rice surface exhibited superhydrophobicity and anisotropic sliding properties that were similar to those of natural rice. Parallel and perpendicular sliding angles were found as  $25^\circ$  and  $40^\circ$ , respectively.

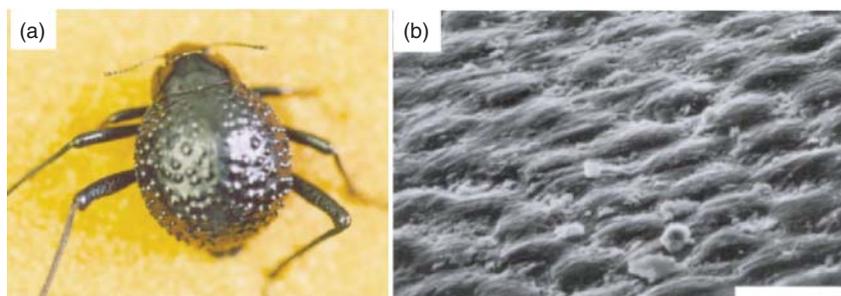
Wu *et al.* used improved laser interference lithography to fabricate micropillar arrays for adjusting two-directional unidirectional wetting structures [38]. They systematically investigated the effect of laser beam intensity ratio and resin

thickness on anisotropic wetting behavior. According to appropriate parameters, micropearl arrays were designed and modifying them with fluoroalkylsilane created biomimetic surfaces exhibiting wettability properties very similar to those of rice leaf.

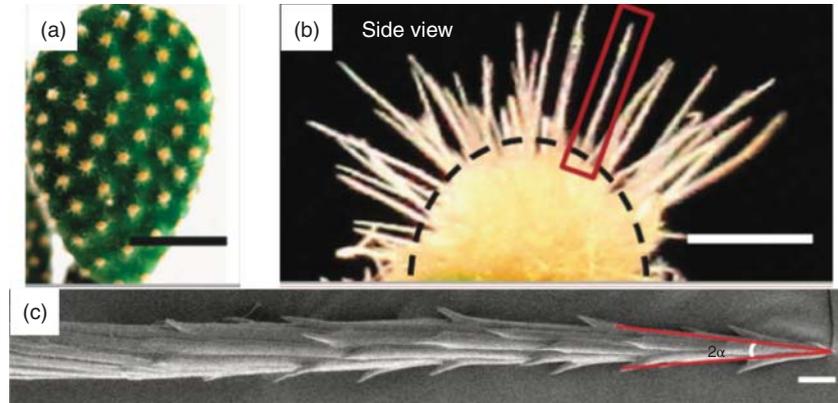
#### 1.2.4 Fog Harvesting Surfaces

Access to safe and sufficient water is of vital importance to people. However, water scarcity is one of the major environmental issues, in today's world. According to World Health Organization (WHO) reports, an estimated 2.5 billion people have no access to improved sanitation and, unfortunately, each year hundreds of thousands children die from water-related diseases such as diarrhea [39–41]. Learning from living creatures that live in arid conditions is an efficient way to obtain clean water. For instance, Namib Desert beetles (*Stenocara*) overcome the lack of water by collecting moisture from air. Actually, collecting fine fog droplets is not easy in the heat and breeze of the desert. The fog collecting mechanism of *Stenocara* was revealed by Parker and Lawrence. They discovered an array of hydrophilic bumps on the beetle backs, which are surrounded by hydrophobic waxy lines [42]. The fine moisture droplets collect on hydrophilic bumps and start to grow. When the collecting droplets reach sufficient weight, they detach and roll down the tilted hydrophobic beetle's back surface to the mouth. The hierarchical structures on the Namib Desert beetle's back can be seen in Figure 1.7 [42].

Zhai *et al.* successfully mimicked the back of the *Stenocara* beetle creating hydrophilic patterns on superhydrophobic surfaces [43]. Garrod *et al.* used a two-step plasma chemical method to produce the hydrophilic–hydrophobic pattern, which is similar to the *Stenocara* beetle's back [44]. Another study that is inspired by the fog harvesting surface structure of the *Stenocara* beetle's back was carried out by Dorrer and R  he [45]. They fabricated various superhydrophobic surfaces patterned with smooth, circular patches of hydrophilic domains. According to the results, it was found that the pinning force for a given pump was constant and independent of the drop volume. Except for the Namib Desert beetle, some other organisms have water collection ability. Cactus is one of these organisms. It can survive in extremely arid conditions because of its efficient fog collection mechanism. A cactus consists of conical spines



**Figure 1.7** (a) The photo of an adult female *Stenocara* sp. and (b) the SEM image of the *Stenocara* sp. dorsal surface, scale bar = 10  $\mu\text{m}$ . (Parker 2001 [42]. Reproduced with permission of Nature Publishing Group.)



**Figure 1.8** (a) The photograph of the cactus *Opuntia microdasys* scale bar = 5 cm, (b) the photograph of a single cluster containing a lot of spines, scale bar = 100 mm, and (c) the SEM image of the spine, scale bar = 20  $\mu\text{m}$ . (Ju 2012 [46]. Reproduced with permission of Nature Publishing Group.)

and hierarchically hydrophilic/hydrophobic structures [46]. The fog collection system of cactus is based on the Laplace pressure gradient and the wettability difference [47–49]. The hierarchical structures of the cactus' spines can be seen in Figure 1.8 [46]. Cao *et al.* produced biomimetic microtip arrays, which are similar to those of cactus, using a modified magnetic particle-assisted molding method [49]. The morphology of the tips is adjusted by changing the weight ratio of PDMS to magnetic particles. The optimal ratio of PDMS to magnetic particles was found to be 2 : 1. Andrews *et al.* reported that the *Cotula fallax* plant can also collect water from moisture due to its unique hierarchical 3D arrangement formed by its leaves and the fine hairs covering them [50].

### 1.2.5 Anti-reflective Surfaces

Anti-reflective coatings are used in many technological applications such as glasses computer screens, solar cells, military hardware, and so on. The purpose of using anti-reflective coating is to maximize the transmission of light through an optical surface [51].

In nature, anti-reflective structures are found in some insects. These structures can be found in their eyes, which make it possible to see objects in even low-light environments. These natural anti-reflective structures can also be found on their body surface that helps in hiding from enemies by reducing reflections [52]. For example, the eyes of the moth consist of hexagonal arrays that reduces optical losses. The dimensions of this structure are smaller than the wavelength of the light, so the reflection of light is effectively suppressed [53]. The hierarchical structure of the moth eye is shown in Figure 1.9 [54].

Moth eyes inspired anti-reflective structures that have been fabricated by various methods. One of these studies was carried out by Raut *et al.* [55]. They produced anti-reflective structures using “sacrificial layer mediated nanoimprinting.” For wavelengths between 400 and 1000, while non-anti-reflective