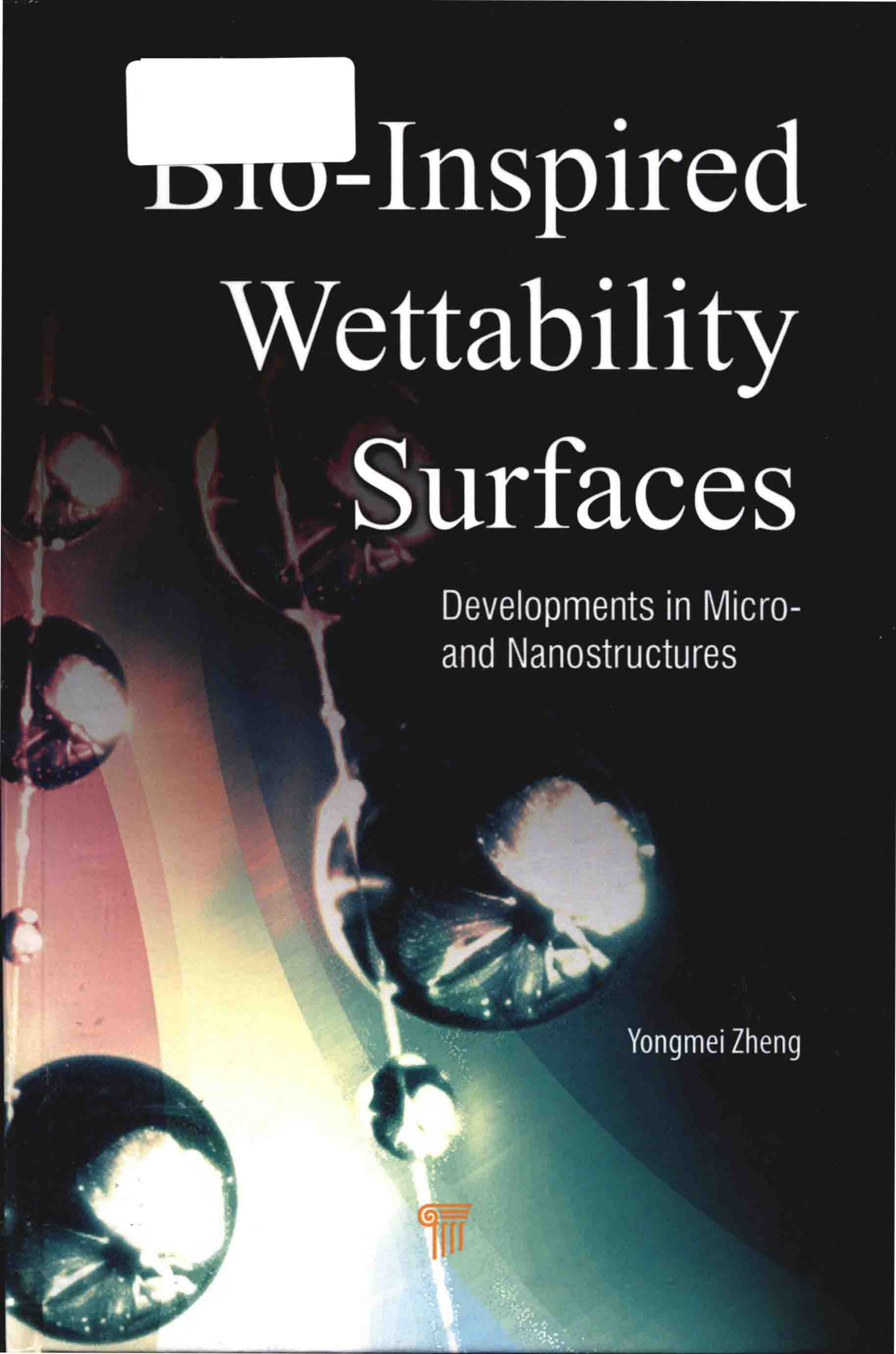
Bio-Inspired Wettability Surfaces

Developments in Micro- and Nanostructures

Yongmei Zheng



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PAN STANFORD PUBLISHING

Published by

Pan Stanford Publishing Pte. Ltd.
Penthouse Level, Suntec Tower 3
8 Temasek Boulevard
Singapore 038988

Email: editorial@panstanford.com
Web: www.panstanford.com

British Library Cataloguing-in-Publication Data
A catalogue record for this book is available from the British Library.

Bio-Inspired Wettability Surfaces: Developments in Micro- and Nanostructures

ISBN 978-981-4463-60-7 (Hardcover)
ISBN 978-981-4463-61-4 (eBook)

Printed in the USA

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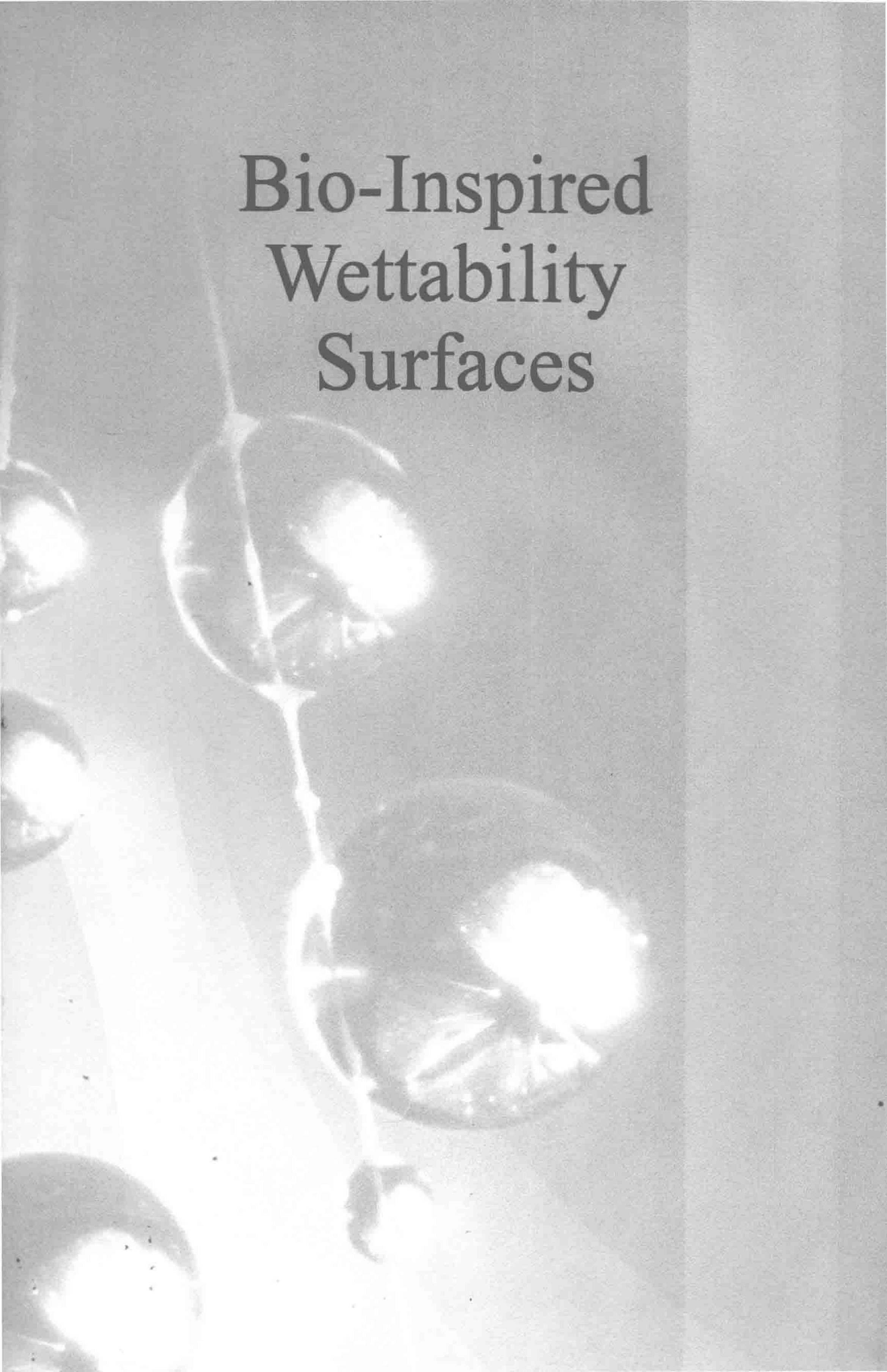
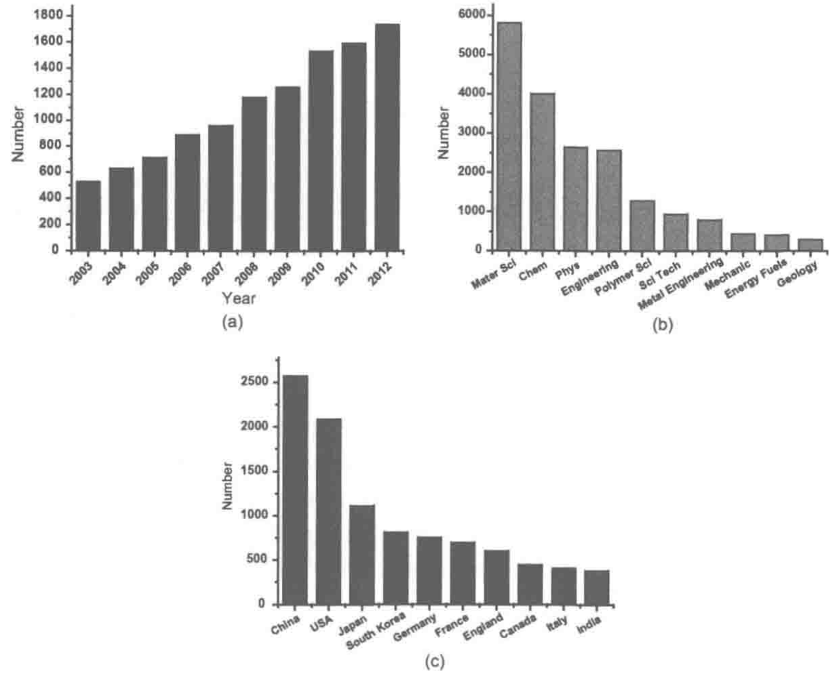


Preface

There has been an exciting confluence of research areas, such as physics, chemistry, biology and materials science, in recent years. A kernel consists in organic materials with high/low surface energy, has various-style micro- and nanostructures, such as regular/irregular, ordered/disordered, rough/smooth that can be endlessly arranged and combined, and is greatly provided with adaptability to perfectly display the biological functions that developed during the thousands of years evolution in nature. Interestingly, the biological surfaces develop the micro-/nanostructure with gradient features to smartly achieve the wetting controls. For example, the ultra-hydrophobic water repellency on lotus leaf; directional water collection on wetted spider silk; direction adhesion of super-hydrophobic butterfly wing, and fog-collecting hydrophobic/hydrophilic pattern on beetle back. Biological surfaces provide endless inspiration for the design and fabrication of functional interface materials with unique wettability, generating promising applications such as micro-fluidic devices, functional textiles, corrosion resistance, liquid transportation, and anti-fogging and water-collecting devices.

Researches on wettability, water repellency, bioinspiration, and biomimetics have shown an increasing trend, and has includeed realms of materials science, chemistry, physics, engineering, polymer science, science technology, metal engineering, mechanics, energy fuels, geology, and so on. On the global front, China has published the largest number of results in recent years of the researches conducted and products developed.

The book introduces the recent researches on wettability of biological and bio-inspired surfaces through its four chapters. The first chapter focuses on the wettability features and effect in a lotus leaf. It discusses the basic concept of wettability and suggests methods for fabrication bio-inspired surfaces and achieving functional surfaces. In the second chapter, wettability features and effect in a butterfly wing are described. It specifically stresses on the anisotropic wettability resulting from anisotropically structured surfaces. Anisotropy ranges from one dimension to two dimensions



Number of researches on wettability, water repellency, and bio-inspired and biomimetic materials (a) in recent years, (b) in different areas, and (c) in various countries.

on a surface for droplet movement. Many fabricating methods of bio-inspired surfaces can be developed further to obtain fluid-controlling functional surfaces. In the third chapter, the wettability features and effect of spider silk are introduced and novel mechanisms of water collection resulting from gradient multi-structures have been described. Some methods to fabricate bio-inspired materials that were developed by our team have also been introduced. Finally, the fourth chapter presents the wettability features and effect of beetle back for fog collection and discusses about the methods for fabricating hydrophobic/hydrophilic patterns.

The book offers the mechanisms of smart wetting control, such as water collection and repellency, on biological micro-/nanostructure gradient interfaces that were developed by the us in recent years. It also suggests ideas to mimic biological features to realize bio-inspired functional surfaces with unique wettability. The book will help researchers to develop innovatory designs from novel materials for future scientific works.

The book is a result of the collective and creative research efforts of our team. I would like to thank Drs. Qunfeng Cheng, Yongping Hou, and Yuan Chen for their efforts and support in helping me write Chapters 1, 2, and 3 and 4, respectively. I especially thank Stanford Chong for offering me the opportunity to publish my favorite book.

I would also like to acknowledge the support given by the National Key Basic Research Program of China (2013CB933001), the National Natural Science Foundation of China (21234001, 21473007), and the Doctoral Fund of Ministry of Education of China (20121102110035) to bring out this book.

Summer 2015

Contents

Chapter 1

Lotus Leaf Effect: Micro- and Nanostructures

1.1 Janus Feature of Lotus Leaf

Inspired by the ancient Roman god Janus with two opposing faces, the Janus particles are firstly fabricated.[1] Then, the Janus fabrics,[2] Janus nanoparticles,[3] and nanosheets[4] are also demonstrated. In fact, this kind of Janus feature can be found in nature. Recently, we discovered that the lotus leaf shows the Janus feature: the surface of the back-side of a superhydrophobic lotus leaf can be easily completely wetted with water in the air and repels oil droplets in water, as shown in Fig. 1.1.[5] Three water droplets form spheres on the upper side of lotus leaf floating on the water surface, and three oil (*n*-hexane) droplets stay as perfect spheres under water on its back-side.

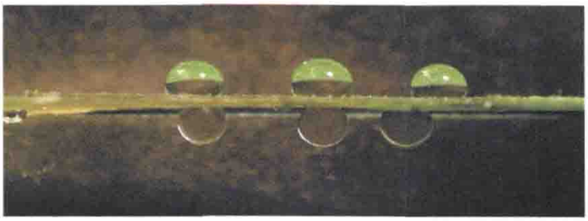


Figure 1.1 Digital photograph shows the Janus feature of lotus leaf flowing on the water surface: three water droplets form spheres on its upper side in the air, and three oil (*n*-hexane) droplets stay as perfect spheres under water on its back-side.

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It is well known that the lotus leaf has attracted immense scientific interest due to its superior self-cleaning property (Fig. 1.2), exhibiting a high water contact angle (CA) above 160° and a small sliding angle (SA) ~2°.[6] Barthlott and Nienhuis first revealed that the large CA is attributed to the epicuticula wax and the micrometer-scale papillae structure of the lotus leaf surface.[7] Jiang et al. later found that there are the micro-/nanoscale hierarchical structures on the lotus leaf.[8] After considering the contribution of the nanostructures, the theoretical model calculation indicates the CA can be over 160°, which is well consistent with the observed experimental results. It is obvious that the upper side of lotus leaf with a typical micro-/nanoscale hierarchical papillae and the epicuticular wax makes raindrops easily roll across the upper side of lotus leaf carrying away dirt and debris. On the other hand, we found that there are many microfolds around the margin of lotus leaf in the form of ring-bands, introducing high-energy barrier against water to block the water underneath preventing overflow onto its upper surface.[9] Thus, the upper side of lotus leaf can keep itself clean from the dirt particles that are brought away when the water droplets roll off. This self-cleaning effect is usually called "lotus effect," which shows great importance in fundamental research and potential in industrial applications.

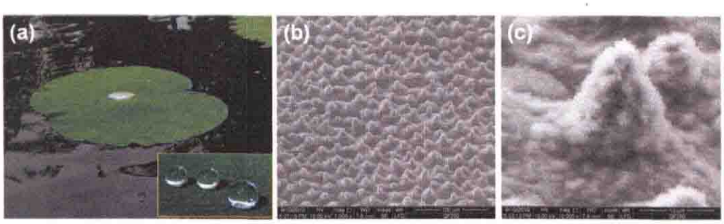


Figure 1.2 (a) Digital photograph of the floating lotus leaf on the water and water droplet on the superhydrophobic upper side of lotus leaf. (b) Low magnification SEM image of the surface morphology of the upper side of lotus leaf. (c) High-resolution SEM (HRSEM) image of a single papilla with branch-like nanostructures.

Inspired by micro-/nanoscale hierarchical structure of the upper side of lotus leaf, many methods are developed to construct the superhydrophobic self-cleaning surfaced, such as phase separation,[10,11] oxygen plasma treatment,[12] sol–gel foam,[13] electrospinning,[14] self-assembly technique,[15] and so on. Because there are many reviews that have reported these methods,[6,16–18] in this chapter, we will focus on the lower side of lotus leaf.

In fact, the lotus leaf comes out of the mud soiled and remains undefiled spite of general corruption, depends not only on the upper side but also the lower side of lotus leaf. Usually, the property of lower side of lotus leaf is often neglected. In this chapter, the surface morphology and wetting properties of lower side will be focused on. The environment scanning electron microscope (ESEM) images show that its lower side is made of many cells (Fig. 1.3a), and every cell consists of numerous tabular and slightly convex papillae with 30–50 μm in length and 10–30 μm in width (Fig. 1.3b). The single papilla is further tested by atomic force microscope (AFM). Every single papilla is covered with nanogrooves structure with a size of 200–500 nm and the height of single papilla is around 4 μm (Fig. 1.3c). Moreover, the epidermal glands of its lower side may secrete some hydrophilic compounds, such as the ferns.[19]

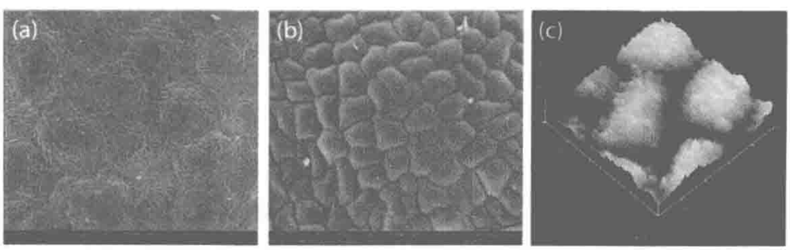
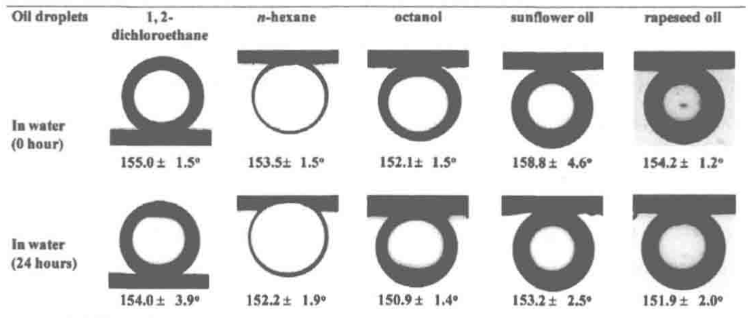


Figure 1.3 Environment SEM (ESEM) images (a & b) show its lower side is made of many cells, and every cell consists of numerous tabular and slightly convex papillae with 30–50 μm in length and 10–30 μm in width. (c) Atomic force microscope (AFM) image further shows the tabular papillae are covered with nanogrooves structure with a size of 200–500 nm and the height of single papilla is around 4 μm.

The lower side of lotus leaf can be completely wetted with water in the air due to absence of three-dimensional wax crystals on its lower side, similar to other species grown completely in water or partially floated on the water surface. However, under water the lower side of lotus leaf shows superoleophobic properties for apolar and amphiphilic oils, including 1,2-dichloroethane, *n*-hexane, octanol, sunflower oil, and rapeseed oil; and the stability of superoleophicity is very well after keeping it underwater for 24 h. All the oil contact angles (OCA) are over 150° as listed in Table 1.1.

Table 1.1. The oil contact angles (OCAs) of apolar and amphiphilic oils, such as 1,2-dichloroethane, *n*-hexane, octanol, sunflower oil, and rapeseed oil on lower side of lotus leaf is over than 150°, with keeping 24 h under water, showing the stability of superoleophobicity of its lower side is very well



Oil droplets	1, 2-dichloroethane	*n*-hexane	octanol	sunflower oil	rapeseed oil
In water (0 hour)	155.0 ± 1.5°	153.5 ± 1.5°	152.1 ± 1.5°	158.8 ± 4.6°	154.2 ± 1.2°
In water (24 hours)	154.0 ± 3.9°	152.2 ± 1.9°	150.9 ± 1.4°	153.2 ± 2.5°	151.9 ± 2.0°

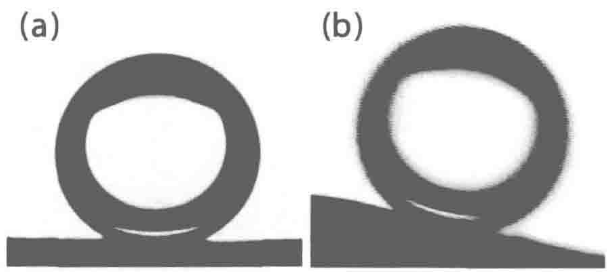


Figure 1.4 (a) Lower side of lotus leaf shows superoleophobicity with oil contact angle (OCA) of 155.0 ± 1.5° for 1, 2-dichloroethane. (b) When the tilt angle reaches about 12.1 ± 2.4°, the oil droplet easily rolls off from its lower side.

On the other hand, we also studied the sliding property of oil droplet on its lower side, take 1,2-dichloroethane as an example. The tilt angle with oil is about 12.1 ± 2.4°, with the OCA of 155.0 ± 1.5°, as shown in Fig. 1.4. The oil droplets can easily roll off on its lower side when the lotus leaf swings with external wind, and this means that its lower side is very difficult to be contaminated by the oil droplets under water and keeps itself clean in the mud.

1.1.1 Mechanism of Underwater Superoleophobicity

The wettability of solid surface is commonly evaluated by the Young's equation, which was originally applied in air. For superoleophobic