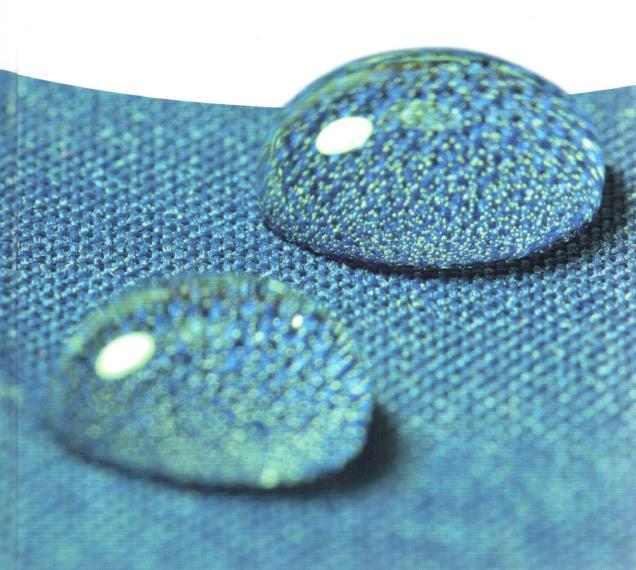
Zhiguang Guo and Fuchao Yang

Surfaces and Interfaces of Biomimetic Super-hydrophobic Materials



Surfaces and Interfaces of Biomimetic Superhydrophobic Materials

Zhiguang Guo Fuchao Yang

Authors

Professor Zhiguang Guo

Lanzhou Institute of Chemical Physics State Key Laboratory of Solid Lubrication 730000 Lanzhou

China

and

China

Hubei Collaborative Innovation Centre for Advanced Organic Chemical Materials Hubei University 430062 Wuhan

Dr. Fuchao Yana

Hubei Collaborative Innovation Centre for Advanced Organic Chemical Materials Hubei University 430062 Wuhan China

and

Lanzhou Institute of Chemical Physics State Key Laboratory of Solid Lubrication 730000 Lanzhou China

Cover fotolia_@MG

All books published by Wiley-VCH are carefully produced. Nevertheless, authors, editors, and publisher do not warrant the information contained in these books, including this book, to be free of errors. Readers are advised to keep in mind that statements, data, illustrations, procedural details or other items may inadvertently be inaccurate.

Library of Congress Card No.: applied for

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

Bibliographic information published by the Deutsche Nationalbibliothek The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available on the Internet at http://dnb.d-nb.de.

© 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Boschstr. 12, 69469 Weinheim, Germany

All rights reserved (including those of translation into other languages). No part of this book may be reproduced in any form - by photoprinting, microfilm, or any other means - nor transmitted or translated into a machine language without written permission from the publishers. Registered names, trademarks, etc. used in this book, even when not specifically marked as such, are not to be considered unprotected by law.

Print ISBN: 978-3-527-34264-8 ePDF ISBN: 978-3-527-80671-3 ePub ISBN: 978-3-527-80670-6 Mobi ISBN: 978-3-527-80669-0 oBook ISBN: 978-3-527-80672-0

Cover Design Adam-Design, Weinheim, Germany Typesetting SPi Global Private Limited. Chennai, India Printing and Binding CPI Group (UK) Ltd, Croydon, CR0 4YY

Printed on acid-free paper

Contents

Preface xi

1	Introduction for Biomimetic Superhydrophobic Materials 1
1.1	Water Harvesting 2
1.2	Self-Cleaning 6
1.3	Corrosion Resistance 9
1.4	Photochromism 13
1.5	Robust and Durable Superhydrophobic Materials 15
1.6	Transparent and Conductive Superhydrophobic Film 16
1.7	Anti-fingerprint Superhydrophobic Film 18
1.8	Anti-icing Ability 18
1.9	Summary 20
	References 22
2	Superhydrophobic Surfaces from Nature and Beyond Nature 25
2.1	Superhydrophobic Plant Surfaces in Nature 26
2.1.1	Lotus Leaf 26
2.1.2	Salvinia 27
2.1.3	Petal 29
2.2	Superhydrophobic Surfaces of Animals in Nature 31
2.2.1	Springtail 31
2.2.2	Fish Scale 31
2.2.3	Shark Skin 33
2.2.4	Snail Shell 33
2.2.5	Mosquito Eyes 33
2.2.6	Clam's Shell 33
2.3	Chemical Composition of Plant and Animal Surfaces 34
2.4	Inspired and Beyond Superhydrophobicity: from Natural
	to Biomimetic Structures 38
2.4.1	Inspired by Natural Superhydrophobic Surfaces 38
2.4.2	Biomimetic Superhydrophobic Materials 40
2.4.2.1	Lotus-Leaf-Like Surface with Superhydrophobicity
	and Self-Cleaning 40
2.4.2.2	Salvinia-Like Surface with Superhydrophobicity and Air Retention 42
2.4.2.3	Petal-Like Surface with Superhydrophobicity and Special Adhesion 43

vi	Content	S
	2.5	Summary 46 References 47
	3	Advances in the Theory of Superhydrophobic Surfaces and Interfaces 59
	3.1	
	3.2	Basic Theories: Contact Angle and Young's Equation 60
	3.3	Wenzel Model: Adaptability and Limitations 62
	3.4	Cassie-Baxter Model: Adaptability and Limitations 64 Improved Models 66
	3.4.1	11.
	3.4.2	Fractal Structure 66 Fractal Structure 68
	3.4.3	Contact Angle Hysteresis 69
	3.4.4	Generalized Models of W. 1 1 G
	3.5	Cassie—Wenzel and Wenzel Cassie—Baxter 72
	0,0	Cassie-Wenzel and Wenzel-Cassie Transitions on Superhydrophobic Surfaces 74
	3.5.1	The Lefters in The Colonia
	3.5.2	Cassie–Wenzel Transition 75
	3.5.3	Wenzel-Cassie Transition 76
	3.5.4	Analyzing Transitions from Thermodynamic and Kinetic Points
		of View 76
	3.6	Summary 77
		References 77
	4	Fabrications of Noncoated Superhydrophobic Surfaces
		and Interfaces 85
	4.1	Etching Method 87
	4.2	Lithography 89
	4.3	Anodization 92
	4.4	Laser Processing 93
	4.5	Sol-Gel Process 95
	4.6	Electrodeposition 97
	4.7	Hydrothermal Method 101
	4.8	Direct Reproduction 103
	4.9	Other Fabrication Methods 104
4	4.10	Summary 105
		References 106
5		Diaminostic Complete Lands and the Complete L
-	,	Biomimetic Superhydrophobic Nanocoatings: From Materials
	5.1	to Fabrications and to Applications 117
	5.1.1	Materials for Nanocoatings 118 Inorganic Materials 118
	5.1.2	
	5.1.3	Inorgania O II I : 13 f
	5.2	Fabrications of Superhydrophobic Nanagarting 123
	5.2.1	Fabrications of Superhydrophobic Nanocoatings 123 Sol–Gel Processes 123
	.2.2	Chemical Vapor Deposition 124
	.2.3	Spray Process 125

5.2.4 5.2.5	Electrospinning Process 126 Electrodeposition 126
5.2.6	Solution Immersion Process 127
5.2.7	Others Techniques 128
5.3	Biomimetic Transparent and Superhydrophobic Coating 128
5.3.1	The Two Competitive Characters: Transparency and Superhydrophobicity 129
5.3.2	Various Materials for Transparent and Superhydrophobic
0.0.2	Surfaces 130
5.3.2.1	Inorganic Materials 130
5.3.2.2	Organic Material Polymers 138
5.3.2.3	Hybrid Materials 143
5.3.3	Potential Applications 144
5.4	Summary 146
	References 148
6	Adhesion Behaviors on Superhydrophobic Surfaces and Interfaces 161
6.1	Liquid–Solid Adhesion of Superhydrophobic Surfaces 162
6.1.1	Surfaces with Special Adhesion in Nature 162
6.1.2	Artificial Superhydrophobic Surfaces with Special Adhesion 164
6.1.3	Switchable Liquid–Solid Adhesions on Superhydrophobic Surfaces 167
6.1.3.1	By Controlling the Chemical Composition and Rough Structures 167
6.1.3.2	By Controlling the External Stimuli 168
6.2	The Adhesion Conversion from Liquid–Solid to Solid–Solid States 173
6.2.1	Mechanism of Ice Crystallization 174
6.2.2	Anti-adhesion Icing Properties of Superhydrophobic Surfaces 176
6.3	Solid–Solid Adhesion of Superhydrophobic Surfaces 179
6.3.1	Protein Adsorption on Superhydrophobic Surfaces 179
6.3.2	Cell Adhesion on Superhydrophobic Surfaces 181
6.3.3	Bacterial Adhesions on Superhydrophobic Surfaces 181
6.4	Summary 183
	References 184
7	Smart Biomimetic Superhydrophobic Materials with Switchable
	Wettability 191
7.1	Single-Response Smart Responsive Surfaces 192
7.1.1	pH-Responsive Wettable Materials 192
7.1.2	Photo-Induced Self-Cleaning Properties 194
7.1.3	Temperature-Responsive Wettable Materials 201
7.1.4	Ion-Responsive Wettable Materials 206
7.1.5	Other External Stimuli 207
7.2	Dual-Responsive and Multiple-Responsive Surfaces 214
7.3	Summary 217 References 219
	References 217

viii	Contents
,	

8	Biomimetic Superhydrophobic Materials Applied for Oil/Water Separation (I) 229
8.1	Mr. III M. I. D. I
8.2	Metallic Mesh-Based Materials 230 Fabric-Based Materials 234
8.3	
8.4	Sponge and Foam-Based Materials 236
8.5	Particles and Powdered Materials 240 Other Bulk Materials 241
8.6	
8.7	Theories Underlying Oil/Water Separation Behavior 242
0.7	Summary 243 References 243
	References 243
9	Biomimetic Superhydrophobic Materials Applied for Oil/Water
	Separation (II) 249
9.1	The Formation of Oil/Water Emulsions 249
9.2	Modified Ceramic Separation Membranes 251
9.3	Polymer-Based Separation Membranes 253
9.3.1	In Situ Polymerization 253
9.3.2	Mussel-Inspired Deposition 254
9.3.3	Electrospinning Deposition 255
9.3.4	Phase-Inversion Process 255
9.4	Inorganic Carbon-Based Membranes 259
9.4.1	Carbon Nanotube- or Graphene-Based Membranes 259
9.4.2	Cellulose-Based Membranes 259
9.5	Non-Two-Dimensional Separating Methods 266
9.6	Summary 267
	References 268
10	Biomimetic Superhydrophobic Materials Applied for Anti-icing/ Frosting 273
10.1	
10.2	Introduction of Anti-icing/Frosting 273 Ice and Frost Formation Mechanism 275
10.2.1	Ice Formation Mechanism 277
	Classical Ice Nucleation Theories 277
10.2.1.2	Modified Iso New Isotto Till to the State of
10.2.2	Frost Formation Mechanism 282
10.3	Noticeal Company of the Line of the Company of the
10.3.1	Natural Superhydrophobic Examples 284 Natural Superhydrophobic Examples 284
	Mosquito's Eyes 284
10.3.1.2	Butterfly's Wings 296
10.3.2	Natural Icephobic Examples 298
	Pitcher Plant 298
	Skunk Cabbage 298
10.4	Anti-icing Performances of SHPSs under Various Situations 299
10.4.1	SHPSs Versus Deposited Water Droplets 299
10.4.1.1	Timely Droplet Rolling 299
10.4.1.2	Sessile Droplet Freezing Delay 303
10.4.2	SHPSs Versus Impact Water Droplets 307
	1

10.4.2.1	Impact Resistance Improvement 307
10.4.2.2	Anti-icing SHPSs upon Impact Droplets 309
10.4.2.3	Contact Time Minimization 312
10.4.2.4	Oblique Impact Dynamics on Inclined SHPSs 313
10.4.3	SHPSs Versus Condensed Water Droplets 316
10.4.3.1	Wetting Transition of Condensed Microdroplets 316
10.4.3.2	Coalescence-Induced Jumping and Charging 317
	Inter-droplet Ice Bridging and Edge-Initiation Effect 321
10.5	Design and Icing-Delay Performances of SLIPSs 324
10.5.1	SLIPSs Design 324
10.5.2	Droplet Impact and Condensation on SLIPSs 326
10.5.3	Anti-frosting Performance of SLIPSs 329
10.6	Icephobic Performances of SHPSs 331
10.7	Icephobic Performances of Advanced Surfaces and Techniques 336
10.7.1	Slippery Lubricant-Infused Porous Surfaces 336
10.7.2	Self-Lubricating Liquid Water Layers 337
10.7.3	Other Icephobic Strategies 340
10.8	Theories behind Anti-icing Research 343
10.8.1	Surface Wettability Theories and Models 343
10.8.2	Water and Ice Adhesion to Solid Surface 345
10.8.3	Droplet Impacting and Bouncing 346
10.8.4	Spontaneous Jumping Departure of Condensed Droplets 348
10.9	Summary 350
	References 352

11 Conclusions and Outlook 373

Index 377

Preface

The field of surface wettability has had an extraordinary period of development in the last decade due to its potential applications. When a new field appears, its growth is judged by the number of publications, presentations, and patents. In the past decade year, more than 10 000 papers have been published on surface wettability. It is well known that the surface wettability of a solid surface depends mainly on its surface structure and surface composition. Discovering the relationship between surface structure and surface properties is very important for scientists working in the field of surface chemistry.

The idea for this book titled *Surfaces and Interfaces of Biomimetic Super-hydrophobic Materials* (*SIBSM*) came about in 2011 when I came back from Belgium to China and constituted my own research group in the Chinese Academy Sciences (CAS). More scientists paid attention to this field when more papers, preprints, talks, and words of mouth became available.

I am pleased to edit this book with Dr Fuchao Yang, who is now a lecturer in Hubei University, China, and who also was my PhD student in CAS during 2013–2016. *SIBSM* contains the recent progress, thoughts, and work of my group and many of the world's foremost scientists who work in the field of biomimetic superhydrophobic materials. We discuss the theory, fundamentals, fabrication, properties, applications, and uses of these very special materials inspired by Nature.

SIBSM contains 10 aspects of the superhydrophobic story, covered in the following chapters: (1) Nature is a huge gallery of art involving nearly perfect structures and forms evolved over the millions of years development. Inspired by Nature, scientists have recently fabricated many biomimetic surfaces through various smart and easy routes. Many plants and animals in nature, showing waterrepellent properties with fine microstructures, such as the lotus leaf, the water skipper, and wings of the butterfly, are discussed. Some creatures with typical structures are also referred to, for instance, the rice leaf, desert beetle, rose petals, mosquito eyes, springtail, fish scale, shark skin, snail shell, lower surface of the lotus leaf, and clam's shell. (2) We start the theory from the classical wetting models to the most recent theoretical advances of superhydrophobic surfaces (SHPSs) with regard to the wetting process, and some promising breakthroughs in the advancement of the theory are proposed. (3) Further study on the relationship between structures and properties will be conducive to better transferring the micro- and nanostructures to engineering materials so as to obtain the desired superhydrophobic performances and a wide range of applications. The methods

to fabricate SHPSs with micro- and nanostructures are varied and generally divided into two. One comprise top-down methods including etching, lithography, anodization, and laser processing. And the other is bottom-up methods containing electrodeposition, hydrothermal method, sol-gel process and electrospinning.. (4) Oil spills and industrial organic pollutants have induced severe water pollution, and special wettability materials have been developed over the past decade to separate oil/water mixtures. On this topic, we mainly focus on the development of materials with either superhydrophobic or superhydrophilic properties in oil/water separation applications. (5) The purification of oily water, especially oil/water emulsions, is one of the important topics of environmental protection. Traditional filter membranes, to some extent, are useful for the separation of oil/water mixtures, but they have many limitations and there is no effective way to achieve emulsified oil/water separation. Superwetting materials, based on bionics, have opened a brand-new door to membrane separation techniques. (6) The adhesion behavior of SHPSs has become an emerging topic to researchers in various fields as a vital step in understanding the interaction between materials and organisms. Controlling the chemical compositions and topological structures via various methods or technologies is essential to fabricate and modulate different adhesion properties, such as low adhesion, high adhesion, and anisotropic adhesion on SHPSs. We summarize the recent developments in both natural and artificial SHPSs with various adhesive properties and pay attention to SHPSs switching between low and high adhesion. (7) Superhydrophobic nanocoatings, a combination of nanotechnology and SHPSs, have received extraordinary attention recently, focusing both on novel preparation strategies and investigations of their unique properties. In this part we summarize the contributions to this field reported in recent literature, mainly including materials, fabrication, and applications. (8 and 9) Recently, particular attention has been paid to smart surfaces that can show switchable and reversible water wettability under external stimuli such as pH, temperature, light, solvents, and electric field. In this section, several kinds of smart SHPSs (pH-responsive wettable surfaces, photo-induced self-cleaning surfaces, solvent-responsive wettable surfaces, and magnetically controllable behavior of superhydrophobic microspheres) based on our and other groups' published works are systematically summarized. (10) We primarily investigate the ice and frost formation mechanism for the rational design of anti-icing/antifrosting surfaces. Significantly, the complex dynamics and thermodynamics of water droplets on the SHPSs under various freezing conditions that might be encountered in natural atmosphere (e.g., raindrops, condensation frosting) are comprehensively discussed. Critically, we explain why SHPSs play a fairly limited role in reducing ice adhesion strength. Furthermore, a family of novel superwetting materials termed icephobic surfaces (IPSs) for effortless ice detachment is introduced. Finally, future challenges and possible breakthroughs in this field are pointed out. It is believed that under the unremitting efforts of scientists, the second generation of anti-icing/de-icing techniques based on superwetting interfaces will be put to practical applications in the near future.

The book is aimed at the following readers:

Advanced students and instructors in the fields of science and engineering.

 Professional scientists and engineers, who may be trained in more traditional disciplines but who need to learn about this emerging area.

· Policymakers and management experts looking for an understanding of the scientific challenges, prospective uses, and emerging markets for surface wettability.

The overall goal is to capture the multidisciplinary and multifunctional flavor of surfaces and interfaces of biomimetic SHPSs while providing in-depth discussions on select areas.

Importantly, I should show my appreciation to the contributors for their effort and dedication in preparing the chapters, to Hubei University, and to my PhD students, Mr Liwei Chen, Mr Yifan Si, Mr Gang Wen, Mr Lieshuang Zhong, Mr Pan Tian, Mr Zelinlan Wang, and Miss Xiaoyu Gao, for their continuous assistance and hard work in drawing the figures and putting the chapters together. I also thank Mr Hai Zhu and Miss Ting Jiang for correcting the proof. I also thank Dr Lifen Yang of Wiley, who gave me the idea of starting a book in the beginning this year, and her publication team for their continuous help and support. Finally, I am indebted to my wife, Yan Xin, and my two daughters, Zhehan and Zheyuan, for their kind and endless enthusiasm and support.

I also wish to acknowledge the financial support by the National Natural Science Foundation of China (No 51522510 and 51675513).

November 2016 Wuhan, China

Prof. Zhiguang Guo

WILEY-VCH

A comprehensive and systematic treatment that focuses on surfaces and interfaces phenomena inhabited in biomimetic superhydrophobic materials, offering new fundamentals and novel insights.

As such, this new book covers the natural surfaces, fundamentals, fabrication methods and exciting applications of superhydrophobic materials, with particular attention paid to the smart surfaces that can show switchable and reversible water wettability under external stimuli, such as pH, temperature, light, solvents, and electric fields. It also includes recent theoretical advances of superhydrophobic surfaces with regard to the wetting process, and some promising breakthroughs to promote this theory.

As a result, materials scientists, physicists, physical chemists, chemical engineers, and biochemists will benefit greatly from a deeper understanding of this topic.



Professor Zhiguang Guo received his PhD degree from Lanzhou Institute of Chemical Physics (LICP), Chinese Academy of Sciences (CAS) in 2007. After that, he joined Hubei University. From October 2007 to August 2008, he worked in University of Namur (FUNDP), Belgium, as a post-doctoral research fellow. From September 2008 to March 2011, he worked in the Funds of National Research Science (FNRS), Belgium, as a 'Charge de Researcher'. During February 2009 to February 2010, he worked in the Department of Physics, University of Oxford, UK, as a visiting scholar. Currently, he is a full Professor in LICP financed by the 'One Hundred Talented People' program of CAS and the 'Excellent Youth Foundation' of National Natural Science Foundation of China (NSFC). In 2014, he obtained the award of SHIZHU WEN in Tribology, and in 2015 he obtained the National Natural Science Prize of China (Second Class) and in 2016. he obtained the 'Outstanding Youth Award' of International Society of Bionic Engineering. Now, he is an associate editor of RSC Adv, and the editorial broad member of Journal of Bionic Engineering and Chemistry Letters. To date, he has published more than 140 papers focusing on the surfaces and interfaces of superhydrophobic materials with more than 3000 times citations and H index 31.



Dr Fuchao Yang received his Master degree from College of Physics and Electronic Engineering at Northwest Normal University in 2013. Since then he joined Prof. Zhiguang Guo's group at LICP to pursue his PhD degree. From July 2016, he is a lecture in Hubei University after graduated from LICP in phD, China. His research interest is focused on the wetting behavior of superhydrophobic surfaces and fabricating surfaces with micro- and nano-structures applied for functional nanomaterials.

ISBN 978-3-527-34264-8

