ADVANCED TOPICS IN SCIENCE AND TECHNOLOGY IN CHINA

Liang-Yin Chu

Smart Membrane Materials and Systems

From Flat Membranes to Microcapsule Membranes

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Preface

As emerging artificial biomimetic membranes, smart or intelligent membranes that are able to respond to environmental stimuli are attracting ever-increasing interest from various fields. Their surface characteristics and/or permeation properties including hydraulic permeability (pressure-driven convective flow of solvents) and diffusional permeability (concentration-driven molecular diffusion of solutes) can be dramatically controlled or adjusted self-regulatively in response to small chemical and/or physical stimuli in their environments, such as temperature, pH, ionic strength, electrical field, photo irradiation, glucose concentration, oxidoreduction and/or chemical or biological species. Such environmental stimuli-responsive smart membranes could find myriad applications in numerous fields ranging from controlled drug delivery, to chemical separation, to water treatment, to bioseparation, to chemical sensors, to chemical valves, to tissue engineering, etc. The development of these smart or intelligent membranes is of both scientific and technological interest.

The author has been devoted to the development of smart membrane materials and systems since 1999, when he was a research fellow in Prof. Shin-ichi Nakao's group at the Department of Chemical System Engineering at the University of Tokyo. He is currently a professor at Sichuan University where he leads the Membrane Science and Functional Materials Group (http://teacher.scu.edu.cn/ftp_teacher0/cly/) with a diverse and interdisciplinary focus on the development of new membranes for separation and systems for controlled release, especially smart membrane materials and systems. Since 1999, he has successfully developed various environmental stimuli-responsive smart membranes, including thermo-responsive, pH-responsive, glucose-responsive, molecular-recognizable and dual-/multi-stimuli-responsive ones, for different applications from controlled release, to chemical valves, affinity separation, chiral resolution, chemical sensors, etc.

This book is the first one that comprehensively and systematically introduces smart or intelligent membranes with environmental stimuli-responsive functions. The contents range from flat membranes to microcapsule membranes with various response properties, such as thermo-response, pH-response, glucose-response, molecular-recognition and dual-/multi-stimuli-response, and so on. Each chapter is independent, in which the design concept, fabrication strategy and methods, microstructures and performance of smart membranes are clearly described. Lively schematic illustrations and pictures throughout the text help make the theory and technologies more accessible to readers. The author sincerely hopes that this book will be a valuable reference work for designing and fabricating artificial biomimetic smart membranes for various application purposes and for grasping the current status of smart membrane materials and systems.

The book is composed of 12 chapters. In Chapter 1, a brief introduction of smart or intelligent membranes as emerging artificial biomimetic membranes will be outlined. In Chapter 2, the emphasis is focused on the design, microstructures and performance of thermo-responsive gating membranes, because in many cases the environmental temperature fluctuations can occur naturally and the temperature stimuli can be easily designed and artificially controlled. The contents of this chapter on thermo-responsive gating membranes are also valuable for designing and fabricating other stimuli-responsive gating membranes. In Chapters 3 and 4, smart microcapsules with thermo-responsive gating membranes and with thermo-responsive hydrogel membranes are introduced respectively, which are designed for the purpose of controlled release. In Chapters 5 and 6, the contents are focused on developments of thermo-responsive membranes for chiral resolution and for affinity separation, respectively. In Chapter 7, pH-responsive gating membrane systems with pumping effects for improved controlled release performance are introduced. In Chapter 8, smart microcapsules with pH-responsive hydrogel membranes, which are promising for pH-responsive controlled release, are introduced. In Chapters 9 and 10, the contents are focused on glucose-responsive and molecular-recognizable smart membranes, which have high potential in applications in glucose-responsive self-regulated insulin delivery for diabetes therapy and in specific site-targeted drug delivery and/or chemical sensors. In Chapter 11, dual-/multi-stimuli-responsive smart membranes, which are preferable for more comprehensive systems, are introduced. Finally, perspectives on the development of smart membrane materials and systems are given in Chapter 12.

Most of the contents in this book are the fresh achievements of the author's group on smart membranes since the beginning of this new century. The author gratefully acknowledges financial support for the continuous study of smart membranes from the National Natural Science Foundation of China for Distinguished Young Scholars (Grant No. 20825622), the National Basic Research Program of China (Grant No. 2009CB623407), the National Natural Science Foundation of China (Grant No. 20206019, 50373029, 20674054, 20990220, 21076127), the NSFC-KOSEF Scientific Cooperation Program (Grant Nos. 20511140501), the "Chang Jiang Scholars Program" of the Ministry of Education of China for Distinguished Professors, Sichuan Youth Science and Technology Foundation for Distinguished Young Scholars (Grant Nos. 03ZQ026-41, 08ZQ026-042), the Key Project of the Ministry of Education of China (Grant Nos. 106131), the Specialized Research Fund for the Doctoral Program of Higher Education of the Ministry of Education of China (Grant Nos. 20040610042, 200806100038), the Fok Ying Tung Education Foundation (Grant No. 91070), the Scientific and Technological Creation and Innovation Foundation of Sichuan

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The author is very grateful to Profs. Shin-ichi Nakao and Takeo Yamaguchi at the University of Tokyo in Japan, Profs. Wenmei Chen and Jiahua Zhu at Sichuan University in China and Prof. David A. Weitz at Harvard University in USA, who helped the author carry out investigations in the field of smart membranes. The author would like to thank all his former and current students who contributed to the study on smart membranes, especially Dr. Rui Xie, Dr. Xiaojie Ju, Dr. Yan Li, Dr. Mei Yang, Dr. Pengfei Li, Dr. Tao Meng, Dr. Jianbo Qu, Dr. Haidong Wang, Dr. Changjing Cheng, Wei Wang, Li Liu, Yongchao Chen, Lin Hu, Yijian Liang, Wenchuan Yang, Jianping Yang, Shibo Zhang, Jiyun Wang, Yao Jin, Shuowei Pi, Yalan Yu, Chuanlin Mu, Zhuang Liu, Nannan Deng, Lili Yue, and Jie Wei, for their hard work and creative research on developing smart membrane materials and systems.

Finally, the author is deeply indebted to his family members, especially his wife, Jianjun Qin and his son, Dikai Chu, for their love, encouragement and support.

Liang-Yin Chu
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Zhejiang University is one of the leading universities in China. In Advanced Topics in Science and Technology in China, Zhejiang University Press and Springer jointly publish monographs by Chinese scholars and professors, as well as invited authors and editors from abroad who are outstanding experts and scholars in their fields. This series will be of interest to researchers, lecturers, and graduate students alike.

Advanced Topics in Science and Technology in China aims to present the latest and most cutting-edge theories, techniques, and methodologies in various research areas in China. It covers all disciplines in the fields of natural science and technology, including but not limited to, computer science, materials science, life sciences, engineering, environmental sciences, mathematics, and physics.

Contents

1

Introduction

In this chapter, membranes and their development progress are introduced briefly at the beginning, from which the readers can see that the development of environmental stimuli-responsive smart materials is essential and important. Then, the environmental stimuli-responsive gating model of biomembranes in the natural world and some typical artificial environmental stimuli-responsive smart materials, including thermo-responsive, pH-responsive, glucose-responsive and molecular-recognizable ones, are introduced, to show the original natural model and possible material candidates for designing and fabricating artificial smart membranes. Next, several bio-inspired design concepts are described for artificial biomimetic environmental stimuli-responsive smart membranes. Finally, some potential applications of smart membrane materials and systems are discussed.

1.1 A Glance at Membranes and Their Development

We are living in a membrane world. Our life depends upon membrane technology so much nowadays. In the past several decades, membrane scientists have successfully developed membranes for microfiltration, ultrafiltration, nanofiltration, reverse osmosis, dialysis, electrodialysis, pervaporation, gas separation, controlled release, etc., and membrane technologists have successfully applied the membranes in numerous fields from chemical engineering to biomedical engineering, petrochemical engineering, environmental engineering, mechanical manufacture, food engineering, pharmaceutical engineering, biochemical engineering, the electronics industry, the textile industry, spaceflight, gas separation, water treatment, drug delivery, etc. Membrane technology is playing a more and more important role in modern life and global sustainable development.

Although the achievements in the membrane fields have been very significant up to now, commercialized membranes are still single-function membranes. For example, membrane separation is only achieved by either size difference, or solution-diffusion difference, or electrostatic charge difference, except for some charged ultrafiltration and nanofiltration processes carried out by both size and electrostatic charge differences. The permeability of existing commercial membranes cannot be self-regulatively adjusted by the change in environmental conditions. That means the permeation performances of membranes are not able to respond to environmental stimuli. However, the biomembranes in nature have environmental stimuli-responsive channels across the membranes,[1-3] that means the permeability of biomembranes has environmental stimuli-responsive characteristics.

Bionic technology is endlessly bringing us new ideas, new principles, new approaches and new theories from the natural world for developing the novel high-tech world. Unexceptionally, biomembranes provide original inspiration for membrane scientists and technologists to develop mimetic functional membranes, which are highly attractive for achieving more advanced and comprehensive membrane systems, *e.g.*, composite-function membranes with not only a selectivity factor but also an environmental stimuli-response factor and a gate factor. Since the middle of the 1980s, membrane scientists and technologists have been much devoted to the development of bio-inspired environmental stimuli-responsive smart membranes. Because they have great potential for applications in myriad fields from controlled drug delivery to chemical separation, water treatment, bioseparation, chemical sensors, chemical valves and tissue engineering, such environmental stimuli-responsive smart membranes are attracting ever-increasing attention from various fields.

1.2 Environmental Stimuli-Responsive Gating Model of Biomembranes

Nature gives us endless examples of sophisticated environmental stimuli-responsive smart systems. Ion channels are pore-forming proteins that help establish and control the small voltage gradient across the cell membrane of all living cells, by allowing the flow of ions down their electrochemical gradient.[4] In some ion channels of the cell membrane, passage through the pore is governed by a "gate", which may be opened or closed by chemical or electrical signals, temperature or mechanical force, depending on the variety of channels. For example, activated by a membrane voltage or a signaling molecule, a potassium ion channel can switch from a closed to an open state and the process is reversible. Therefore potassium ions can be selectively allowed to cross the membrane (**Fig.1.1**). Such an environmental stimuli-responsive gating function of biomembranes provides an exciting model for membrane scientists and technologists to develop artificial smart membranes.

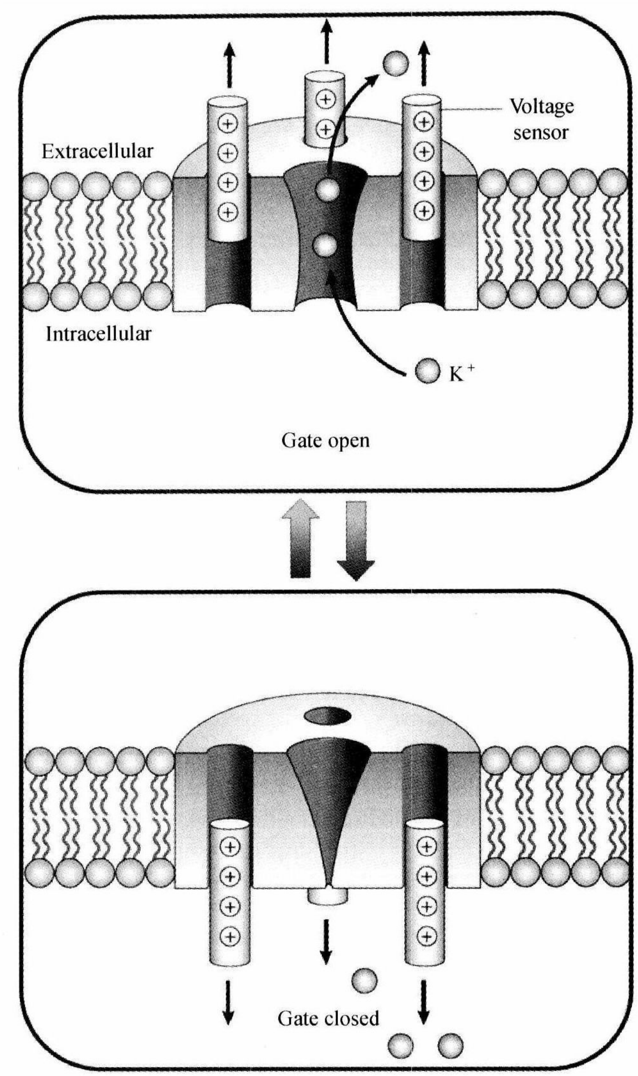

Fig.1.1. Stimulus-responsive ion channel gating model of the cell membrane (Modified with permission from Ref. [3]). Copyright (2004), Nature Publishing Group

1.3 Environmental Stimuli-Responsive Smart Materials

Environmental stimuli-responsive smart materials, or intelligent materials, are the kind of marvelous materials that have the capability to sense their environment signals, process these data and respond. They have one or more properties that can be significantly changed in a controlled fashion by external stimuli, such as