Design, Fabrication, Properties and Applications of Smart and Advanced Materials

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CRC Press
Taylor & Francis Group
A SCIENCE PUBLISHERS BOOK

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CRC Press
Taylor & Francis Group
Boca Raton London New York

CRC Press is an imprint of the
Taylor & Francis Group, an **informa** business
A SCIENCE PUBLISHERS BOOK

CRC Press
Taylor & Francis Group
6000 Broken Sound Parkway NW, Suite 300
Boca Raton, FL 33487-2742

Printed on acid-free paper
Version Date: 20160121

International Standard Book Number-13: 978-1-4987-2248-3 (Hardback)

Library of Congress Cataloging-in-Publication Data

Names: Hou, Xu
Title: Design, fabrication, properties, and applications of smart and advanced materials / [edited by] Xu Hou.
Description: Boca Raton : Taylor & Francis, 2016. | "A CRC title." | Includes bibliographical references and index.
Identifiers: LCCN 2015048869 | ISBN 9781498722483 (hardcover : alk. paper)
Subjects: LCSH: Smart materials.
Classification: LCC TA418.9.S62 D46 2016 | DDC 620.1/1--dc23
LC record available at http://lccn.loc.gov/2015048869

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and the CRC Press Web site at
http://www.crcpress.com

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Preface

Advances in the research and technology of materials offers great promise. Materials science forms the foundation for those engaged in materials development because the intramolecular and intermolecular interactions, the interface properties, the mechanical properties, the chemical properties, the electrical properties, the thermal properties, the optical properties, the magnetic properties, the structures, and the components of materials that scientists study and engineers design with are all based on these material properties.

How to select the "BEST" material is usually a challenging task, requiring tradeoffs between properties. Designing smart materials is one of the important and effective ways to develop advanced functional materials that have one or more properties which can be significantly changed in a controlled fashion by external stimuli, such as light, stress, temperature, moisture, pH, electric or magnetic fields, etc. In this book, the authors introduce various smart and advanced materials, the strategies for design and preparation of novel materials from macro to micro/nano or from biological, inorganic, organic to composite materials. Meanwhile, the authors will make systematic introduction in each chapter about their latest research progress and the latest applications in the related fields.

The development of these smart and advanced materials and their potential applications is a burgeoning new area of research, and a number of exciting breakthroughs may be anticipated in the near future from the concepts and results reported in this book. The book can also be used as a textbook for undergraduate and graduate education.

January 2016

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1

Introduction

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ABSTRACT

This book is organized into 14 chapters. The first chapter gives a brief introduction to smart and advanced materials, and then shows an example of the strategy for the design and fabrication of smart and advanced materials. Chapters 2–7 introduce smart materials for DNA, Protein, Controlled Drug Release, Cancer Diagnosis & Treatment, Fluorescence Sensing and Controlled Droplet Motion. Chapters 8 and 9 summarize a comprehensive overview of advanced materials for Thermoelectric and Thermo-Responsive Application. Chapter 10 presents an overview of Self-Healing Polymeric Materials, while Chapter 11 examines advanced materials for Soft Robotics. Finally Chapters 12–14 introduce a comprehensive overview of advanced materials for Biomedical Engineering, Solar Energy Harnessing & Conversion, and Reflective Display Applications. The authors in each chapter will systematically introduce their current research progress and report the latest applications in their related fields.

Materials science is an interdisciplinary field which deals with the discovery and design of novel materials. The material of choice in a given era is often a defining point, such as Stone Age, Bronze Age, Iron Age, Steel Age, Cement Age, and the Silicon Age (Naumann 2010). With further advances in the

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field, our society has entered into a new era in the 21st century. Now we cannot just use a single type material to represent this era, but various and different types of materials, such as nanomaterials, composite materials, and smart materials. This indicates that a completely new substance civilization of human society has started (Kumar 2010, Schwartz 2008).

A material is defined as a substance that is intended to be used for certain applications (Hummel 2004). Materials exhibit a myriad of properties, such as interface properties, mechanical properties, chemical properties, electrical properties, thermal properties, optical properties, and magnetic properties. These properties determine a material's usability and hence its real-world applications. According to the specific application requirements, materials can generally be divided into four classes: inorganic (ceramics, glass, etc.), organic (polymer, biomolecular, etc.), metal (elemental metals and alloys) and composite materials (Pedro and Sanchez 2006).

Selecting the "BEST" material is usually a challenging task, requiring tradeoffs between various material properties. Designing smart and advanced materials (also called "intelligent" or "responsive" materials) is one of the key ways to develop advanced functional materials, those that have one or more properties or functions that can be significantly tunable by external stimuli, such as light, stress, temperature, pH, electric, moisture or magnetic fields. In this book, we introduce various smart and advanced materials, as well as the strategies for design and preparation of novel materials, from macroscopic to nanoscopic, from biological, inorganic, organic or composite materials.

This book is organized into 14 chapters. The first chapter gives a brief introduction to smart and advanced materials, and then shows an example of the strategy for the design and fabrication of smart and advanced materials. Chapters 2–7 introduce smart materials for DNA, Protein, Controlled Drug Release, Cancer Diagnosis & Treatment, Fluorescence Sensing and Controlled Droplet Motion. Chapters 8 and 9 summarize a comprehensive overview of advanced materials for Thermoelectric and Thermo-Responsive Application. Chapter 10 presents an overview of Self-Healing Polymeric Materials, while Chapter 11 examines advanced materials for Soft Robotics. Chapters 12–14 introduce a comprehensive overview of advanced materials for Biomedical Engineering, Solar Energy Harnessing & Conversion, and Reflective Display Applications. The authors in each chapter will make systematically introduce their current research progress and report the latest applications in their related fields.

Various methods and strategies have been proposed to develop smart and advanced materials. This chapter is intended to utilize a specific research example to present one of the design strategies and fabrication processes of bio-inspired nanochannel materials. The strategies and processes may also be extended to other smart and advanced materials.

'Learning from Nature' provides various biological materials with an assortment of smart functions over millions of years of evolution. These serve as a major source of bio-inspiration for smart and advanced materials (Jiang and Feng 2010, Hou et al. 2015)

The bio-inspired study of the design and development of smart and advanced materials has been receiving a great deal of attention. For instance, ion pumps and ion channels are used by cells to transport ions across membranes. Various components of biological channels are not uniform in distribution, and their structures are also asymmetric (Kew and Davies 2010). Based on bio-inspired asymmetric design ideas, the following presents the design and fabrication of smart and advanced nanochannel materials.

Herein, I will suggest three routes for the design and fabrication of assorted smart and advanced nanochannel materials (Fig. 1). The first step is materials selection. According to the specific application requirements, various materials can be selected for building smart and advanced nanochannels, such as biological materials, inorganic materials, organic materials and composite materials (Hou 2013). After materials selection, the second step is to obtain different shapes and structures of nanochannel materials by utilizing various fabrication technologies, such as physical & chemical etching, laser cutting and photolithography. The final step

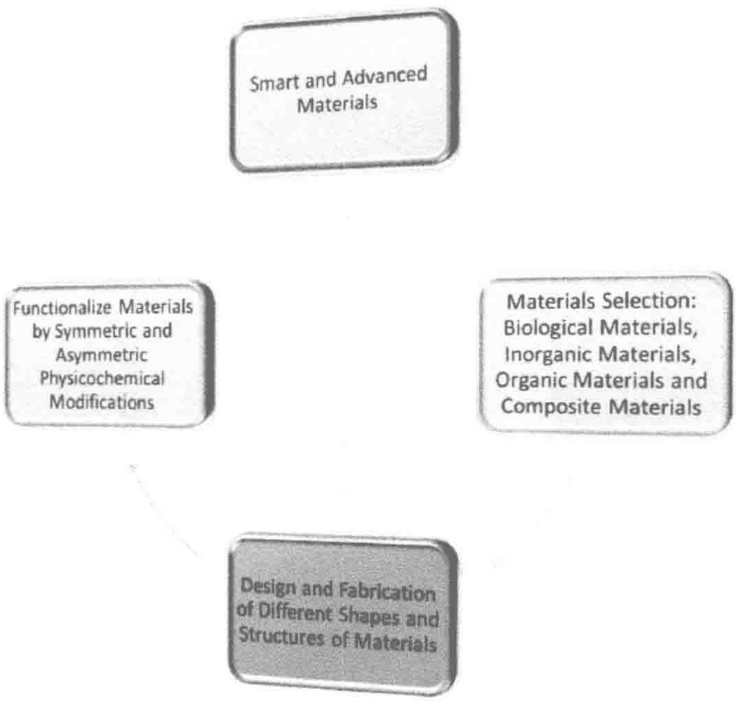

Figure 1. The design and fabrication of smart and advanced materials.

is to functionalize nanochannel materials by symmetric and asymmetric physicochemical modifications. It is worth mentioning that if the selection materials have certain functional properties, the nanochannels prepared by them will have the same characteristic.

By using symmetric & asymmetric shapes/structures and symmetric & asymmetric physicochemical modifications, various smart and advanced nanochannels have been developed (Hou et al. 2011, Hou et al. 2012). Following on from this there are two typical examples that show the key points of the symmetric and asymmetric design approach of smart and advanced nanochannels.

Before introducing these examples, there are two basic concepts: ionic gating and ionic rectification. Ionic gating is defined to evaluate the performance of ion passing through the nanochannel, which is observed the close state as the ionic current value approaches to zero under the same voltage (Fig. 2a) (Yameen et al. 2009). Ionic rectification of nanochannels is observed as an asymmetric current-voltage curve (Fig. 2b) (Yameen et al. 2009). The current recorded for one voltage polarity is higher than the current recorded under the same absolute value of voltage of opposite polarity. Therefore, this asymmetric curve indicates a certain extent of the preferential direction of ionic flow inside the nanochannels.

Azzaroni et al. developed pH gating ionic transport properties inside the single nanochannel by using the chemical modification of the inner surface

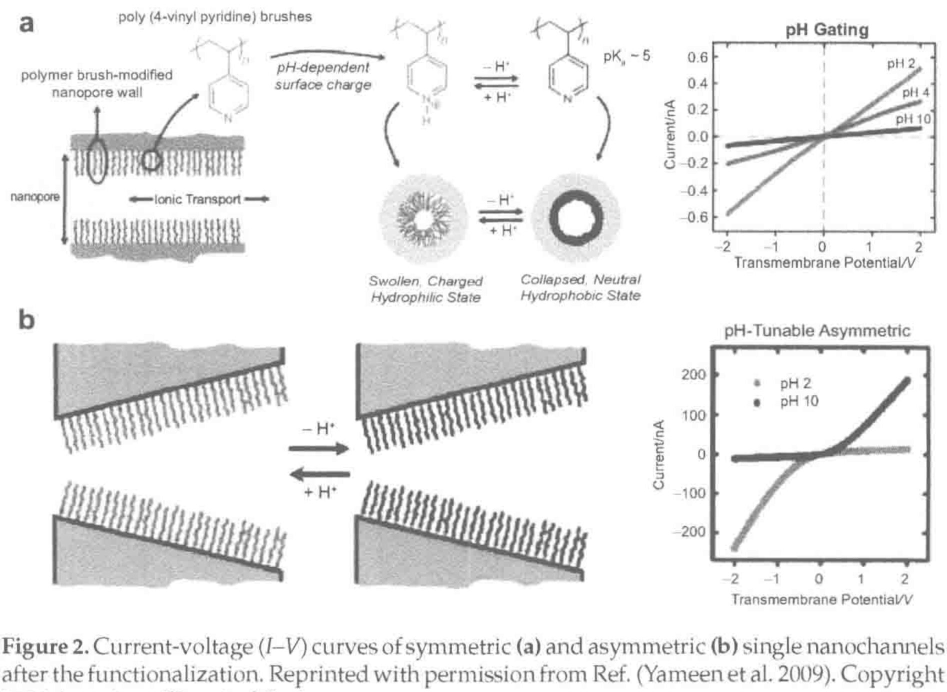

Figure 2. Current-voltage (*I–V*) curves of symmetric **(a)** and asymmetric **(b)** single nanochannels after the functionalization. Reprinted with permission from Ref. (Yameen et al. 2009). Copyright 2009 American Chemical Society.

of the symmetric cylindrical-shaped nanochannel (Fig. 2a). Meanwhile, they also developed pH-tunable asymmetric ionic transport properties inside the single nanochannel by utilizing the chemical modification of the inner surface of the asymmetric conical-shaped nanochannel (Fig. 2b). The above two workings show good examples of how to prepare simple-function pH controllable nanochannel systems.

Inspired by ion channels, in which the components are asymmetrically distributed between the cell membrane surfaces, the pH gating and pH-tunable asymmetric ionic transport properties can also be combined together in the only one system. Figure 3 shows a smart nanochannel, which displays the advanced feature of providing simultaneous control over the pH gating and pH-tunable asymmetric ionic transport properties (Hou et al. 2010). Its gating property inside the channel is caused by the pH response of the functional molecule, and the pH-tunable asymmetric ion transport property is caused by the symmetrically shaped nanochannel with the asymmetric chemical modification. Here the design idea is to prepare symmetrically shaped nanochannels for asymmetric chemical modification approaches to functionalize diverse specific local areas precisely with functional molecules. Based on this design, the nanochannels with a gradual structural transformation from asymmetric to symmetric shapes can obtain a gradual change in pH responsivity, which has the advantage of providing continuous ionic transport control, including asymmetric

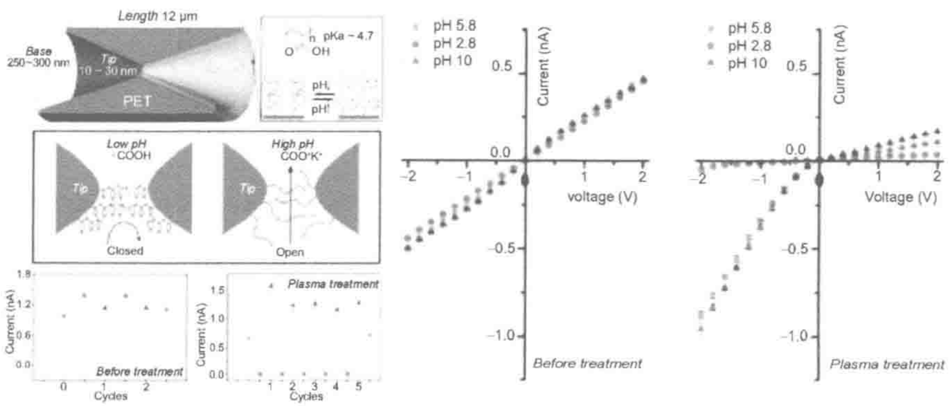

Figure 3. Scheme of the single hour-glass shaped nanochannel after plasma-induced graft polymerization, and hypothetical conformations of hydrogen bonding between the copolymers and water which reveal two kinds: the intramolecular hydrogen bond among the carboxylic acid groups in the polymer chains when the pH is below p*Ka*, and the intermolecular hydrogen bonds between PAA chains and water molecules when the pH is above p*Ka*. Explanation of pH-dependant water permeation through the single hourglass shaped nanochannel. Reversible variation of the ionic current transport of the single nanochannels before (left bottom) and after (right bottom) plasma treatment at 2 V. *I–V* properties of the single nanochannel under different pH conditions (pH 5.8, ■; pH 2.8, ●; pH 10, ▲). Reproduced from Ref. (Hou et al. 2010) by permission of John Wiley & Sons Ltd.

shape and asymmetric ionic transport; asymmetric shape but symmetric ionic transport; and symmetric shape and symmetric ionic transport under certain pH conditions (Fig. 4) (Zhang et al. 2015). Moreover, by using the asymmetric chemical modification approaches to achieve symmetric pH gating behaviors inside the asymmetric nanochannels, the foundation is laid to build diverse, stimuli-gated artificial asymmetric shaped nanochannels with symmetric ionic gating features (Fig. 5) (Zhang et al. 2015).

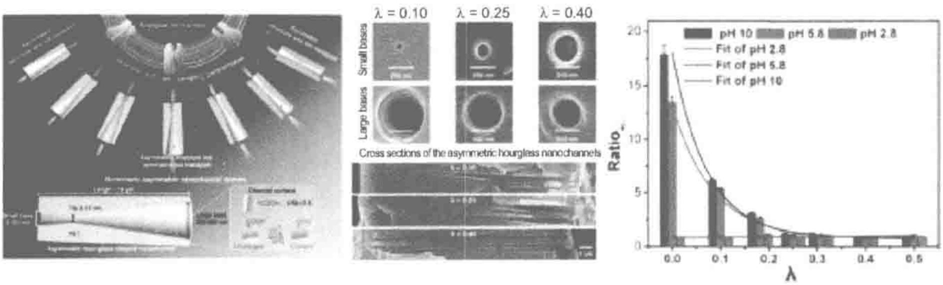

Figure 4. Bio-inspired single asymmetric hourglass nanochannel system demonstrating continuous shape and ionic transport transformation. Asymmetric hourglass biological ion channels give a hint to the process of creating the artificial nanochannel with evolving structure. Precise control of the tip position along the longitudinal axis of the channel allows us to transform the nanochannel structure from an asymmetric cone to a totally symmetric hourglass. (left) Geometry and pH responsive surface properties of a specific asymmetric hourglass nanochannel. (center) Ionic rectification degrees (ratio$_{+/-}$) of the sequential asymmetric nanochannels under pH 2.8, pH 5.8, and pH 10 conditions. Ratio$_{+/-}$ = I_{+2V}/ | I_{-2V} |. (right) Reproduced from Ref. (Zhang et al. 2015) by permission of John Wiley & Sons Ltd.

The inner surface chemical properties and shapes of the nanochannels are two key factors to control ionic transport properties inside the channels. There are two strategies for designing multiple responsive nanochannel materials (Hou 2013).

According to above two factors, I suggest two strategies for designing multiple responsive nanochannel materials. The first strategy focuses on the design and synthesis of functional molecules with multiple responsive properties on the inner surfaces of the nanochannel materials. For example, the light and pH cooperative nanochannel system was been developed by modifying the inner surface of the asymmetric nanochannel with light responsive molecules (Fig. 6) (Zhang et al. 2012). When light was on, the nanochannel could be either cation selective or anion selective according to the pH. However, when light was off, the channel was non-selective, due to the neutral molecules on the inner surface of the channel. At the same time, the asymmetric shape of the nanochannel allowed the system to exhibit ionic rectification as well. Therefore, this nanochannel material can be used as a nanofluidic diode that displays both light-gated and pH-tunable transport properties.

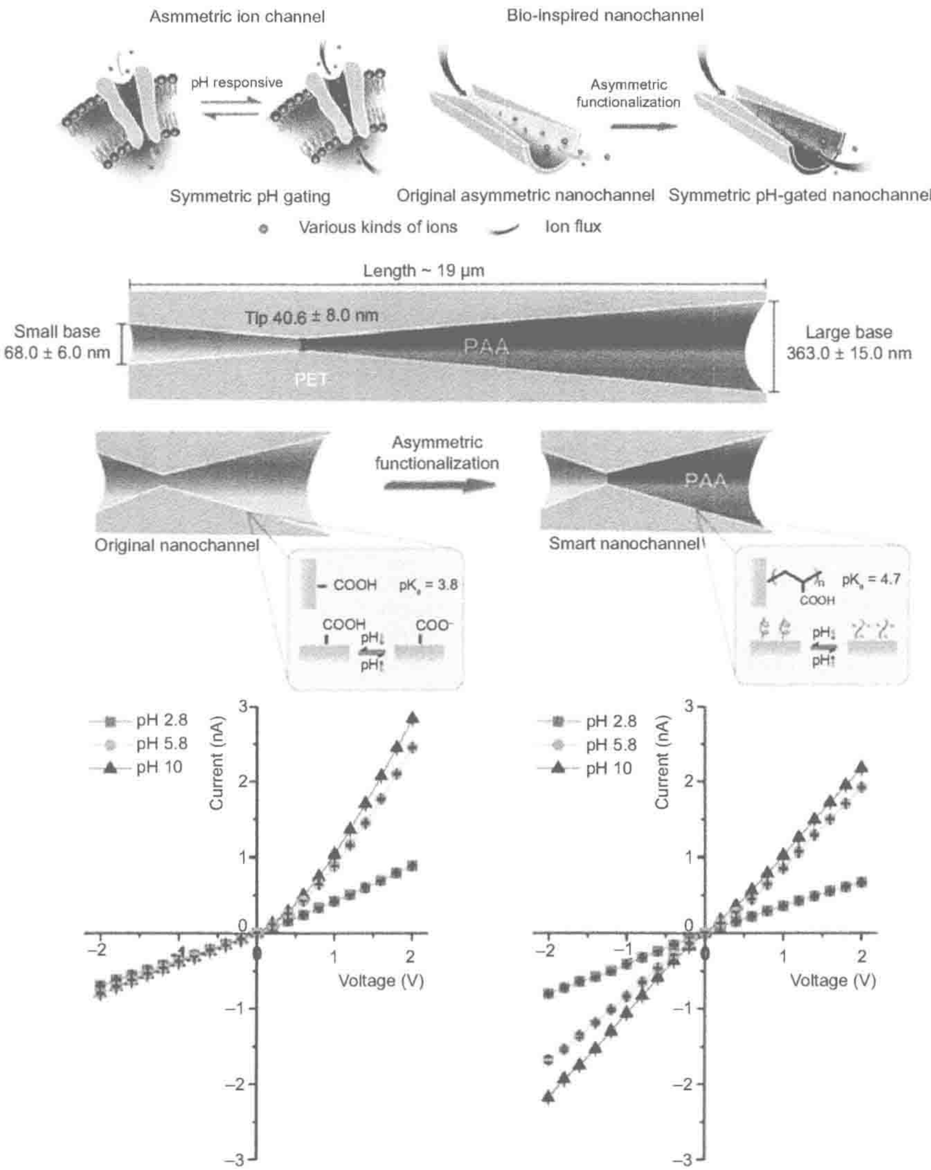

Figure 5. Drawing shows a biological asymmetric hourglass-shaped ion channel with symmetric pH-gating ionic transport property. The bio-inspired smart single asymmetric hourglass-shaped nanochannel illustrates symmetric pH responsive ionic transport property after asymmetric functionalization of the large base side of the channel. Schematic representation of the cross section of the asymmetric nanochannel asymmetrically modified with PAA. *I–V* properties of the asymmetric nanochannel before (bottom left) and after (bottom right) modification under different pH conditions (pH 2.8, ■; pH 5.8, •; pH 10, ▲). Reproduced from Ref. (Zhang et al. 2015) by permission of John Wiley & Sons Ltd.

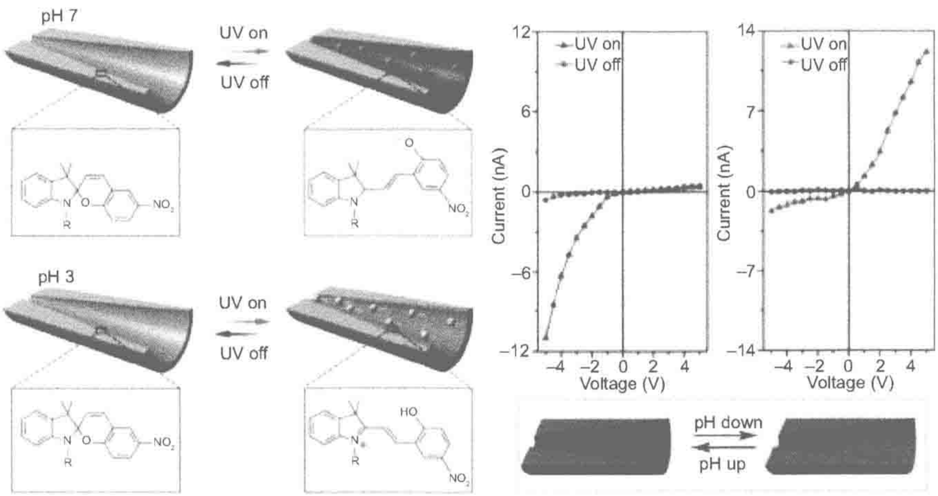

Figure 6. Scheme of the light-gated nanofluidic diode system at different pH values. The nanochannel is initially in the closed state due to the neutral and hydrophobic spiropyran; At pH 7, under UV light irradiation, the nanochannel turns into the open state due to the spiropyran being hydrophilic and negatively charged. Therefore, cations are the majority carriers and prefer to flow from the tip to the base. At pH 3, under UV light irradiation, the nanochannel is positively charged. Therefore, anions are the majority carriers and prefer to flow from the base to the tip. *I–V* curves of the spiropyran-modified nanochannels when UV light is off and under UV light irradiation. At pH 7, the nanochannel was in the closed state when UV light is off. Under UV light, the nanochannel was negatively charged and cations were the majority carries. The cations preferred to flow from the tip to the base to maintain the lower resistance, leading to current flowing in the same direction. At pH 3, the nanochannel was in the closed state when UV light is off. Under UV light, the nanochannel was positively charged and anions were the majority carriers. The anions preferred to flow from the tip to the base to maintain the lower resistance, leading to current flowing in the opposite direction. Explanation of the pH-tunable nanofluidic diode induced by the different polarities of the excessive surface charge. Reproduced from Ref. (Zhang et al. 2012) by permission of John Wiley & Sons Ltd.

The second strategy is to prepare various symmetric and asymmetric shaped nanochannels for different chemical modification approaches, to functionalize diverse specific local areas precisely with different functional molecules. Based on above two factors, once the channels are prepared, it is difficult to change them within a wide range of shapes. Therefore, the chemical modification of the inner surface of the channels with functional molecules is more flexible in the advancement of smart nanochannels, due to the fact that physicochemical modification of the channels can change both the sizes and physicochemical properties of the channels. For instance, an asymmetric responsive symmetric hourglass-shaped nanochannel system was developed, which displayed the advanced feature of simultaneous control over both pH and temperature tunable asymmetric ionic transport properties (Fig. 7) (Hou et al. 2010).