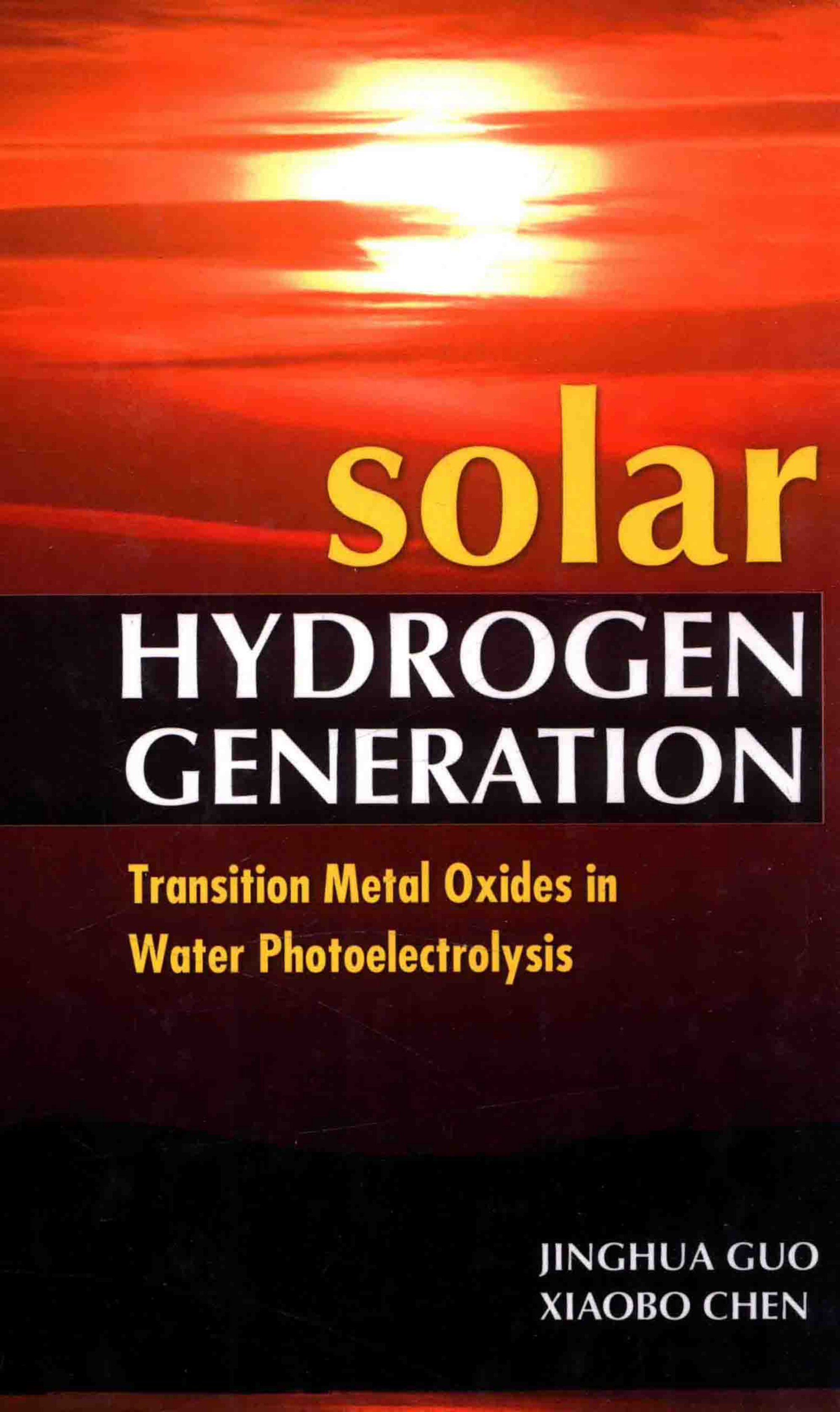

solar HYDROGEN GENERATION

Transition Metal Oxides in Water Photoelectrolysis

JINGHUA GUO
XIAOBO CHEN

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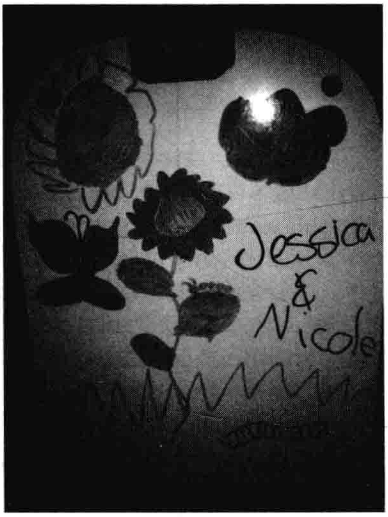

While sitting in the traffic jam again to get through the Caldecott Tunnel on the way to San Francisco and watching aimlessly the ongoing Fourth Bore construction project, Jessica, my daughter, asked if it would be possible to have a flying car and what would be a clean fuel to use. While I wondered if it might take thirty years to see hydrogen-fueled flying cars and hydrogen harvested from sunlight-assistant water splitting, she jumped to her next question—why does the sun shine and for how long? Well, it burns hydrogen too, in a somewhat different way, and will continue to do so for probably another five billions years!

About the Authors

Jinghua Guo, Ph.D., is a staff scientist of Advanced Light Source at Lawrence Berkeley National Laboratory. He was previously a faculty member at Uppsala University, Sweden. Dr. Guo is the author of more than 200 peer-reviewed scientific publications, an editor of the *International Journal of Nanotechnology,* guest editor for the *Journal of Electron Spectroscopy and Related Phenomena,* and a reviewer for scientific journals, including *Physical Review Letters, Nature Chemistry, Nano Letters,* and *Journal of the American Chemical Society.*

Xiaobo Chen, Ph.D., is an assistant professor in the Department of Chemistry at the University of Missouri–Kansas City. He was previously a research scientist at Lawrence Berkeley National Laboratory and University of California–Berkeley. Dr. Chen has published 40 peer-reviewed scientific articles with more than 6,000 citations, holds three U.S. and international patents, is the chair for Materials Research Society Spring Meeting: Titanium Dioxide Nanomaterials in 2011 and 2012, and is a reviewer for many scientific journals, including *Science, Journal of the American Chemical Society,* and *Advanced Materials.*

Preface

This book is intended for researchers and graduate students of materials science and physical chemistry as an extended review in renewable energy science research. In addition, it provides some counts of the state-of-art research in hydrogen generation from photosynthesis.

The search for new ways to efficiently produce clean energy has been rapidly becoming one of the most pressing technological challenges that we are facing. At the same time, enormous progress has been made in developing new materials that are tailored by nanostructuring, supra-molecular assembly, and many other new synthesis methods. Such novel materials might be the key to producing renewable energy through efficient solar energy conversion.

Growing energy consumption worldwide, combined with global warming due to burning of fossil fuels, necessitates the discovery of new materials for novel highly efficient solar energy conversion and storage. This is also an opportunity for condensed matter physics/chemistry and bioscience in fundamental science and applied technology. It becomes increasingly important to understand the fundamental scientific problems with discovering new efficient materials for solar energy conversion and storage applications.

Solar energy conversion requires materials that simultaneously fulfill several requirements regarding their electronic structure and chemical properties in order to ensure stability and efficient utilization of the solar spectrum. No efficient material has been established today that would fulfill all of the requirements; hence, there is an urgent need to understand and tailor materials that will meet the desired requirements. The existing photocatalytic materials, for example, currently do not make use of the entire solar spectrum, but the current class of candidate materials that promise a better spectral utilization have other fundamental shortcomings that limit their overall achievable efficiency. Tandem cells could be a solution, but none of the low-cost materials and preparation processes have produced highly efficient candidates. It is clear that many materials breakthroughs are required to diversify the energy portfolio of the world.

The inherent complexity associated with the materials needed for energy technologies remains a challenge both for experimentalists and theorists, and it becomes a central mission in the first half of twenty-first century. How can the required science and technology breakthroughs be achieved? It is increasingly accepted that the design and optimization of novel materials are strongly enhanced by a cycle. Such a cycle begins with an increased and detailed fundamental knowledge of the status quo materials, an insight-based establishment of a set of desirable parameters, the skills of material scientists to produce such materials, and finally the availability of experimental characterization and theoretical interpretation tools that allow an atomistic comparison between the parameters of the materials produced and the originally envisioned set of parameters defined as desirable. These results and discovered materials then serve as the status quo, and the cycle begins anew.

The ever-increasing demand to diversify the energy portfolio, in particular to minimize environmental impact while supplying the increasing global energy needs, has intensified the urgency to develop alternative energy sources and carriers. Significant research efforts are under way in a broad range of fundamental sciences and applied technologies that have evolved to develop a consensus. Areas of fundamental research to be addressed include the following:

1. Photovoltaics for converting sunlight to electricity
2. Artificial photosynthesis for converting sunlight to fuel
3. Energy efficiency with designed catalysts
4. Carbon capture and carbon chemistry
5. Energy storage and batteries

These are profound challenges, and scientists need to develop advanced theoretical methods and sharper experimental tools that are capable of providing in-depth understanding and ultimate control of these processes to achieve ultimate goals. This book touches on only one of these scientific research areas: photosynthesis for water splitting.

How does one learn about the electronic properties of novel materials for water splitting to determine the efficient catalyst activity and selectivity? About the electron-hole pair formation at the interface of water and catalyst surface upon absorption of sunlight? About bandgaps, band levels, and the band structure of semiconducting catalysts that are of crucial importance in photoelectrochemical and photocatalytic applications? About generation of chemical fuel from direct photooxidation of water under sunlight without external bias? These are profound challenges that have been with us for decades, but are more important than ever today. The intellectual merit of the scientific research will allow scientists to address these questions through the use of theoretical modeling and various experimental tools, including synchrotron radiation based x-ray spectroscopic and microscopic tools fully optimized for the research of renewable energy science and technology.

So far, most of the developments in renewable energy materials have been achieved by the well-tested, Edisonian method of trial and error. However, progress has been slow when compared to the rapid advances in other electronic devices, exemplified by Moore's law for device density in silicon microchips or the increase in magnetic data storage density. This situation calls for a new strategy, where slow evolution of traditional concepts is accelerated by feedback from spectroscopy. A close feedback loop between synthesis, characterization, and theoretical prediction enables a more rational design of new materials than does trial and error. For example, by tailoring the electronic energy levels of the absorber molecules or semiconductors, the donor/acceptor for electron-hole separation, and the eventual transport to a conducting electrode, one can minimize the energy loss in a solar cell. These energy levels can be determined by incisive, element-specific spectroscopic techniques based on synchrotron radiation x-ray spectroscopic and microscopic tools.

This book has been organized in the following way. Chapter 1 describes the basic processes of electrochemistry and photocatalysis for hydrogen production. In an electrochemical reaction, water can be decomposed into hydrogen (H_2) and oxygen (O_2) gases when an electric current is passed through the water. Conversely, photocatalysis splits water directly into H_2 and O_2 by utilizing the sunlight energy only. Chapter 2 focuses on the basics in photocatalytic reactions, and briefly discusses the potential catalysts, including semiconductor catalysts, biomimetic catalysts, and nanostructured catalysts. There are a number of basic points to be considered for efficient photocatalytic water splitting reactions, including stoichiometry of H_2 and O_2 evolution, turnover number (TON), quantum yield, time course, and photoresponse. Over the last three decades the scientific and engineering interest in the application of semiconductor photocatalysis has grown exponentially. Chapter 3 shows semiconductor photocatalysts,, with a primary focus on transition metal oxides, as a durable photocatalyst has been applied to a variety of problems of environmental interest in addition to water and air purification. Chapters 4 and 5 illustrate the corresponding crystal structure versus electronic structure and optical properties versus light absorption of transition metal oxides, respectively. Chapter 6 details the impurity and doped photocatalysts, and the integrated organic and inorganic systems. Chapter 7 briefly discusses surface and interface chemistry, and nanostructure and morphology in photocatalysis applications. In Chapter 8, we introduce the basics of soft x-ray absorption (XAS) and soft x-ray emission spectroscopy (XES), and resonant inelastic soft x-ray scattering (RIXS) followed by descriptions of instrumentation, including beamline, endstation, and spectrometer. Chemical cells are designed for in situ study of the electronic structure of samples in a gas or liquid environment. The application of XAS, XES, and RIXS on TiO_2 crystals of rutile and anatase phases has yielded characteristic fingerprints that provide information on geometric structure, bandgap, and doping effects. A number of in situ electronic structure studies are also presented by way of example.

I would like to express my gratitude to the many colleagues who collaborated over the years on the topics referred to in this book and who helped me in the various stages, to name a few: August Augustsson, Sergei Butorin, Chinglin Chang, Jen-Lung Chen, Jau-Wen Chiou, Xingyi Deng, Frank de Groot, Chungli Dong, Laurent Duda, Heinz Frei, Per-Anders Glans, Xiao Cheng, Peng Jiang, Feng Jiao, Stepan Kashtanov, Yi-Sheng Liu, Yi Luo, Cormac McGuinness, Joseph Nordgren, Miquel Salmeron, Vittal Yachandra, Junko Yano, Kevin Smith, Lionel Vayssieres, Gunnar

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JINGHUA GUO

Berkeley, California

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Contents

CHAPTER 1

Hydrogen Generation: Electrochemistry and Photoelectrolysis