

Photochemical Water Splitting

Materials and Applications

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Photochemical Water Splitting

Materials and Applications

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Preface

On January 26, 2011, during his State of the Union address, U.S. President Barack Obama stated: “We’re issuing a challenge. We’re telling America’s scientists and engineers that if they assemble teams of the best minds in their fields and focus on the hardest problems in clean energy, we’ll fund the Apollo projects of our time.... At the California Institute of Technology, they’re developing a way to turn sunlight and water into fuel for our cars.... We need to get behind this innovation.” This reflects the importance and relevancy of solar water splitting in fuel generation. We like to underline the word fuel that is to be a sustainable and renewable fuel, which can produce energy/power without releasing any additional carbon dioxide to the atmosphere, is the biggest challenge for the mankind. As the current convention fuels are gradually running out, sooner or later they will be completely exhausted. We have to be prepared for this situation with a better fuel substitute, otherwise a big energy mess will be created that will end life due to scarcity of food, water, and energy. Therefore, it’s high time to think and act in the direction of ultimate energy sources. There is an extreme need to line up the industrialists, socialists, intellectuals, and political leaders to meet the current energy challenges, while taking great care of our environment. Hydrogen, as a product of water splitting, is a clean and green solution to the aforementioned problem. Nature provides us a clean and renewable source of hydrogen in the form of water. Unfortunately, cleavage of the water to its constituents, that is, hydrogen and oxygen, at an industrial scale represents one of the “Holy Grails” of materials sciences. To facilitate this reaction, the combination of catalytic material and solar energy has been recognized as a feasible approach to break water. Although renewable energy sources such as sunlight and water are available almost free of cost, developing stable, efficient, and cost-effective photocatalytic materials to split water is a big challenge. As devoted efforts to develop effective materials have continued over the last few decades, various materials with size and structures from nano to giant have been explored. Plentiful materials such as metal oxides, metal chalcogenides, carbides, nitrides, and phosphides of various composition like heterogeneous, homogeneous, plasmonic, mesomorphic, metamaterial, and new graphene-based materials have been tested. There have been critical discussions on the merits and demerits of the studied systems. However, some real technological breakthroughs in material development are definitely necessary for practical applications and commercialization of the technology. To accelerate the research and development activities in the area of water splitting, this book may act as a catalyst. Moreover, this book gives a comprehensive overview and description on both fundamentals and applications of photocatalytic water splitting focused on the recent advances in materials. It also highlights the need for common parameters for studying solar water-splitting phenomena. In addition, it provides insight into the various current and past practices and available databases by emphasizing the pros and cons of

the existing and future technologies that are and will be used in water splitting. The book as a whole is our humble effort to give a panoramic view of the developments made in photocatalytic water splitting since the process was discovered.

Neelu Chouhan

University of Kota

Ru-Shi Liu

National Taiwan University

Jiujun Zhang

National Research Council of Canada

Introduction

This book comprises seven chapters. Chapter 1 introduces hydrogen as a green and efficient fuel to satisfy the energy needs of future generations. Relevant issues such as hydrogen fuel efficiency, production, application, safety, the hydrogen economy, environmental effects, and so on are covered in this chapter. Chapter 2 discusses the basic concepts of photochemical water splitting in order to equip readers with basic terminology and fundamental concepts such as electrochemistry of the water splitting phenomena, selection criteria of photocatalytic material, excitation binding energy, overpotential, diffusion length, carrier mobility and penetration in a photocatalyst, electrode overpotential, band gap and band edge position, band edge bending, efficiency, and so on. Chapter 3 discusses the different practical methods of hydrogen generation from water splitting using techniques such as electrolysis, thermochemical water splitting, biocatalytic water splitting, mechanochemical water splitting, plasmolysis, electrolysis, magnetolysis, radiolysis, and photocatalytic and photoelectrocatalytic water splitting. This chapter gives a better understanding of how photochemical methods work and their benefits compared to other methods in water splitting. Chapter 4 describes different aspects of photoelectrochemical (PEC) water splitting, including factors affecting efficiency of PEC; semiconducting photoelectrode materials (electron transfer phenomenon, material and energetic requirements); models of the water splitting process; reactor design and operation, gradient/bias-based reactors; and reactors based on suspension and electrode type. The chapter emphasizes the electrochemistry involved in the water splitting process and various electron transfer reactions at different interfaces of electrodes/cocatalysts, electrode/electrolyte, electrode/sensitizers in the presence of the sacrificial electrolyte at active sites. This is a very important chapter that provides information about the materials involved in different stages of the photocatalytic processes, which is valuable for rational design and optimization of the PEC reactor's efficiency. It also focuses on the challenges and future perspectives of the field. Chapter 5 deals with oxide semiconductors such as ZnO, TiO₂, Fe₂O₃, and WO₃, as well as graphene oxide, which are used as photocatalytic materials for water splitting. This chapter includes the innovative ways to improve the efficiency of the devices such as band gap engineering of the metal oxide, doping, making a solid solution, and addition of quantum dots (QDs)/dyes or plasmonic materials for visible light sensitization, as well as incorporating a Z-scheme to the system. Moreover, a photocatalyst designed at nanoscale can be synthesized and unique aspects of the nanotechnology are discussed in detail. A special attention is given to some metal ion-doped metal oxide photocatalysts. Chapter 6 concentrates explaining the mechanism of the photocatalytic cleavage of water in the presence of scavenger electrolytes (electron scavenger and hole scavenger), photocorrosion, methods for photocorrosion prevention, the mechanism of heterogeneous electrocatalysis, and the mechanism of homogeneous molecular catalysis. The techniques to bridge the gap between heterogeneous electrocatalysis and homogeneous molecular catalysis are also illustrated with suitable examples. This chapter also describes the role of metallic/metallic hydroxide cocatalyst in

the hydrogen evolution reaction (HER)/oxygen evolution reaction (OER) and the nature/role of the active sites on catalyst's surface. Some conceptual advancements of the active materials for hydrogen generation through water splitting are explained in brief. Chapter 7 is devoted to describing the most significant technological advances and vivid aspects of the nanostructured semiconducting materials that are used for water splitting, including their structural properties, energetic transport dynamics, and the material design and strategies to enhance the photoresponse of nanomolecular devices. Different nanoforms of the materials like nanocrystalline, thin films, mesoporous, plasmon resonant, metamaterials are discussed with advancement schemes. Current state-of-the-art key challenges with future approaches in the development of efficient PEC cells for water splitting are also discussed in this chapter.

Authors



Neelu Chouhan, PhD, is an associate professor and the head of the Department of Pure and Applied Chemistry at the University of Kota in India. She earned her BSc in 1989 from MDS University, Ajmer, India, a MSc in 1991, a MPhil in 1993, and a BEd in 1996. She earned her PhD on *Organic Conducting Materials* from Monanlal Sukhadia University, Udaipur, India, in 2006. Dr. Chouhan worked as a lecturer in chemistry at SRD Modi College, Kota (1996–1998), and at Govt. PG College, Bundi (1998–2012). She carried out her 2 years of postdoctoral research fellowship from 2008 to 2009 at the Department of Chemistry, National Taiwan University, Taiwan, and worked on photocatalytic nanomaterials for water splitting. Her research interests are organic superconductors, functional materials, nanomolecular devices, and the photochemistry of water splitting. She is the author or coauthor of more than 30 publications in international scientific journals of high impact factor with a good number of citations, contributed to seven chapters and three books of national/international publications, and has also been granted one international patent.



Ru-Shi Liu, PhD, is currently a professor at the Department of Chemistry, National Taiwan University, Taipei, Taiwan. He earned his BSc in chemistry from Soochow University, Taiwan, in 1981 and the MSc in nuclear science from National Tsing Hua University, Taiwan in 1983. From 1983 to 1985, he worked at the Materials Research Laboratories, the Industrial Technology Research Institute, Taiwan. He earned two PhDs in chemistry—one from National Tsing Hua University in 1990 and the other from the University of Cambridge in 1992. Dr. Liu was an associate professor at the Department of Chemistry in National Taiwan University from 1995 to 1999 before he was promoted to a full professor in 1999. He has also served as an adjunct Pearl Chair professor at the National Taipei University of Technology, Taiwan, since August 2014. His research is focused on the field of materials chemistry. He is the author or coauthor of more than 550 publications in international scientific journals. He has also been granted more than 100 patents.



JiuJun Zhang, PhD, earned his BSc and MSc from Peking University in 1982 and 1985, respectively, and his PhD in electrochemistry from Wuhan University in 1988. Dr. Zhang is now a principal research officer and core competency leader at Energy, Mining, and Environment Portfolio (NRC-EME) of the National Research Council of Canada, Montreal, Canada. Zhang holds several adjunct professorships, including one at the University of Waterloo and the other at the University of British

Columbia. He is the author or coauthor of more than 400 publications with more than 20,000 citations (h-index: 62; i10-index: 142), including 230 peer-reviewed journal papers, 18 books, and 41 book chapters, and has been granted 16 U.S./European/Canada patents. His research is mainly based on electrochemical energy storage and conversion. He has been elected as a fellow of the Electrochemical Society of Electrochemistry (FISE), fellow of the Royal Society of Chemistry (FRSC), fellow of the Engineering Institute of Canada (FEIC), and fellow of the Canadian Academy of Engineering (FCAE).