

SOLAR FUEL GENERATION



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Edited by

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I dedicate this book

To my inspirational parents who guided me to where I am, and for their endless support and encouragement. I am honored to have them as my parents.

And my loving little Angels: Anvika and Anushka, who bring a smile to my face even when I am down.

And my wife!

And I hope they will live in a cleaner world powered by green energy!



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Preface

Driven by the ever-growing demand for energy and the rising atmospheric CO₂ level, there is a thriving interest to tap renewable energy sources. The Sun supplies about 7,000 times more energy than the total energy demand on the Earth. Only a very small fraction of abundantly available solar energy is consumed by biological photosynthetic processes to be stored as biomass (carbohydrates and oils) that can be used as fuels. The development of technologies that can capture solar energy and convert and store it in usable form on a massive scale (greater than what is available with existing technologies) is highly desired for a long-term solution to meet the ever-increasing energy demand. Biological photosynthesis provides a blueprint to translate solar energy into energy-rich molecules (such as H₂ and carbohydrates), commonly known as *solar fuels*. These solar fuels have enormous potential to store a high density of energy in the form of chemical bonds that are transportable. There are two direct pathways to generate solar fuels. One is solar H₂ generation and the other is CO₂ photo-reduction to fuels.

This book provides a comprehensive insight into the current scenario, perspectives, and promising state-of-the-art approaches (photocatalytic and photoelectrochemical H₂ generation, PV-water electrolysis, solar-assisted thermochemical H₂ generation, microbial H₂ generation, and photocatalytic CO₂ reduction) being developed to produce solar fuels. It discusses the fundamental concepts that are crucial to design such solar fuel generating devices.

One of the promising approaches to solar H₂ generation is the splitting of water. One way to split water using solar energy is photoelectrochemical (PEC) water splitting. It relies on the semiconductor photoelectrodes that upon harvesting solar radiation drive the water splitting, which produces H₂ on the cathode and O₂ on the anode. Another way is photocatalytic water splitting, in which the photocatalysts are suspended in an aqueous solution. Upon solar irradiation, charge carriers generated in the photocatalyst facilitate water splitting redox reactions at the catalytic sites on its surface. This approach obviates the need of wiring and has a simple and low-cost photocatalytic reactor design. The third approach is PV-electrolysis, which utilizes the electricity generated through a solar photovoltaic (PV) cell to split water in an electrolyzer. Chapter 2 presents the assessment of these three approaches in terms of economic and technological feasibility. These approaches still face the challenge of finding the right materials that surpass the problems of recombination of photogenerated charge carriers, stability, cost, and, of course, the overall efficiency. Chapters 3 and 4 discuss these challenges and possible strategies to overcome these issues to some extent.

Water splitting can also be driven by high-temperature heat to generate H₂- thermochemical H₂ generation. It consumes only water that generates H₂ and O₂, and the reactants used in this process are reused within each cycle, enabling a closed loop. The high-temperature heat can be provided by solar concentrators. Chapter 5 presents the details of this process.

There are microbes that use solar energy to generate H₂ as a result of their metabolic process. However, the low rate of H₂ production and/or sensitivity to O₂ are causes of concern. Various strategies are being explored for their feasible exploitation to produce H₂. Chapter 6 provides an overview on solar bio-hydrogen generation, including various microbial and enzymatic hydrogen-producing processes, their associated processes and mechanism, and, most importantly, the technological advancements made in this area so far *vis-à-vis* the challenges.

Finding easier and more economical ways to convert CO₂ to energy-rich fuels has been the mainstay of researchers over the past decade. One way to achieve this conversion is photocatalytic reduction of CO₂ to energy-rich fuels such as methanol or methane. It is similar to the photocatalytic solar H₂ generation, except for the fact that CO₂ replaces water as the substrate for photocatalysis. The existing set-up that is already efficient in transportation of natural gas and liquid fuels, in particular, makes those CO₂ reduction products even more attractive. Two major challenges, selectivity and energetics, are preventing this domain of research from developing from its infancy. These vital issues are addressed along with the state-of-the-art process in Chapter 7.

This book will be useful for graduate students and researchers (chemists, physicists, and material scientists) who are engaged in energy research to provide an overview and state-of-the-art approaches to produce solar fuels that appear promising to meet long-term energy requirements of our planet.

This project would not have been possible without the collective contribution of many people. First and foremost, I express my sincere thanks to all the authors. I also thank Prof. B. K. Mishra for his support and encouragement, and my students Biswajit, Kamala, Asim, Aditya, and Smruti for assisting me while editing this book. I also thank the team of Taylor & Francis for their support throughout this project: Iris Fahrner, Alex Edwards, B. Sundaramoorthy, Shikha Garg, and especially Aastha Sharma.

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Dr. Yatendra S. Chaudhary is a senior scientist at CSIR-Institute of Minerals and Materials Technology, Bhubaneswar, India, and a faculty member at the Academy of Scientific and Innovative Research (AcSIR), New Delhi, India. Dr. Chaudhary earned his PhD for his research on nanostructured photocatalysts for solar-driven water splitting in 2004. Subsequently, he moved to Tata Institute of Fundamental Research (TIFR), Mumbai, India, where he carried out research in materials chemistry. He designed enzyme–semiconductor based photocata-

lysts for visible light driven CO_2 reduction and H_2 production while working at University of Oxford, United Kingdom. His research accomplishments in the area of nanomaterial and solar fuel research have earned him recognitions such as Green Talent-2011 Award from the Federal Ministry of Education and Research (BMBF), Germany, CSIR-Young Scientist Award-2013 in Chemical Sciences section from the Council of Scientific and Industrial Research, India, and the prestigious Marie Curie Fellowship by the European Union. Dr. Chaudhary has been leading various projects funded by Ministry of New and Renewable Energy, Council of Scientific and Industrial Research, and Science and Engineering Research Board, New Delhi, mainly focusing on the design of artificial photosynthesis devices to produce fuel using solar radiation. He is also a reviewer for many Royal Society of Chemistry and American Chemical Society journals and is a member of the editorial boards of the *Journal of Nanoscience* and *International Journal of Photoenergy*.

His research activities are focused on various facets of colloids and materials chemistry for solar fuel generation. The major focus is on designing the heterostructured photocatalysts with desired morphologies and size to exploit the advantages associated with nanomaterials (such as quantum confinement effects and surface area), hetero-interface with appropriate energetics, and layered structure of semiconductors for efficient solar H_2 generation and CO_2 reduction to fuels.



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