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Introduction: A Delicate Collection of Advances in Solar-to-Chemical Conversions

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Tremendous efforts have been made by worldwide researchers toward effective solar energy conversion and utilization. Compared with solar panels or solar cells that convert solar energy to electricity, photocatalytic process can store solar energy to chemical energies and then has attracted extensive attention. This book seizes this great timing to delicately collect the fundaments of solar-to-chemical technologies. Researchers, students, and broad readership would use this book to become experts from beginners. The researchers in the fields and the community may also find it useful for further advances to this exciting area.

This book will cover the fundamentals in solar energy conversion to chemicals, either fuels or chemical products. Natural photosynthesis will be firstly presented to give a tutorial introduction while main attention will be focused on artificial processes for solar energy conversion and utilization. The chemical processes of solar energy conversion via homogeneous and/or heterogeneous photocatalysis will be described with the mechanistic insights. Reaction systems afford a variety of applications, for example, water splitting for hydrogen or oxygen evolution, photocatalytic CO_2 reduction to fuels, and light-driven N_2 fixation, etc. Emerging photocatalysis in upgrading or reforming fossil fuels will also be covered. Design and theoretical fundamentals of solar energy conversion to chemicals will be explained in detail based on semiconductor photocatalysis. Enormous research outcomes in the individual field are related to solar-to-chemical conversion, while this might be the first delicate collection detailing the fundamentals of each catalytic process, along with most challenging issues that hinder the processes move to an industrial scale. Therefore, it is believed that this book will be unique and can offer the readers a broad view of solar energy utilization based on chemical processes and their perspectives for future sustainability.

This book includes 16 chapters and the brief information and highlights of each chapter are as follows:

Chapter 1: Introduction: A Delicate Collection of Advances in Solar-to-Chemical Conversions. This chapter briefs the background of this book, introduces the objectives, and provides the main information of each chapter of the book. It is

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expected that the readers would have a general idea of this book and can then directly move to the specific contents for perusing. It is anticipated that this chapter alone can work as the abstract of the book.

Chapter 2: Artificial Photosynthesis and Solar Fuels. This chapter contributes to the conceptual processes in the conversion of solar energy into chemical energies, i.e. solar fuels. The engineered processes mimicking natural photosynthesis mark the term of artificial photosynthesis. The basic principles for converting carbon dioxide and water into value-added solar fuels, which can be hydrogen, oxygen, and hydrocarbons, are outlined. The core of the technology is photocatalysis, typically being facilitated by semiconductor materials. Via the process, a variety of solar fuel products can be produced. They may include (i) hydrocarbons (methane, methanol, formaldehyde, formic acid, and C2), (ii) carbon monoxide, (iii) oxygen, and (iv) hydrogen. This is because of the multi-electron, multi-hole, and multi-proton reactions. The mechanism and selectivity were examined. The strategies for facing the challenges in this exciting area were proposed at the end of the chapter.

Chapter 3: Natural and Artificial Photosynthesis. This chapter provides an overview of the most important process, i.e. natural photosynthesis. Such a process has been literally powered the whole planet with various species and the ecosystem. It introduces the detailed processes, including light harvesting, charge separation and accumulation, water oxidation, and nitrogen fixation. With the insights into them, inspirations are achieved for artificial photosynthesis, which leads to the fantastic explorations on solar-to-chemical conversions.

Chapter 4: Photocatalytic Hydrogen Evolution. This chapter mainly introduces heterogeneous photocatalytic reactions for hydrogen evolution. The basic principles involved in photocatalytic hydrogen evolutions are introduced. Following that, photocatalytic hydrogen evolution reactions under ultraviolet (UV) light, visible light, and near-infrared light irradiations were investigated in detail. Because of the light absorption ability, which is determined by the band gap of a semiconductor, specific semiconductors only work better in a specific condition. As a result, titanium dioxide and its modified counterparts are mainly introduced in UV reactions, carbon nitride and various modified ones are presented in visible-light photocatalysis, and upconversion materials are discussed for near-infrared light reactions. Comprehensive survey on materials for the specific light regions was also available. For providing the insights into the reactions, the roles of sacrificial reagents and reaction pathways were also discussed in this chapter.

Chapter 5: Photoelectrochemical Hydrogen Evolution. The status, opportunities, and challenges in the hydrogen energy are discussed. Other than powdered photocatalysis, this chapter concerns photoelectrochemical (PEC) and photovoltaic-driven water electrocatalysis (PV + EC). The key of these processes is the efficient photoelectrode fabrication, which determines the light harvest, charge separation and transfer, and surface reactions. The configurations of PEC and the strategies for promoting charge transfer through the semiconductor film and providing strong driving force for carriers' separation are reviewed. The catalyst design for achieving such strategies was paid with extra attention.

Chapter 6: Photocatalytic Oxygen Evolution. Water oxidation half-reaction has been regarded to be the primary barrier in solar fuel production, because such a reaction requires multiple protons and electrons to be involved. This chapter identifies the critical challenge of water oxidation to be the design of efficient, low-cost catalysts with excellent stability. The morphology, structure, and photocatalytic water oxidation performances of various earth-abundant materials are reviewed. Both homogeneous and heterogeneous reactions are discussed. Moreover, quantum size effect, localized surface plasmon resonance, active facet exposure defect engineering, and heterojunction construction in low-dimensional materials are discussed in terms of enhanced photocatalytic water oxidation.

Chapter 7: Photoelectrochemical Oxygen Evolution. This chapter reviews the fundamentals of PEC oxygen evolution toward higher efficiencies as compared with powdered or homogeneous photocatalytic oxygen evolution. It discusses the factors affecting the photoanodic current, the relationship between electrode potentials and pH in the electrolyte, the evaluation method of PEC performance of photoanode materials, the relationship between flat band potential and photocurrent onset potential, the selection strategy of photoanode materials, and PEC device for water splitting. The determining parameters, such as nanostructuring, morphology control, donor doping, cocatalyst loading, heterojunction formation, and electron-conductive materials, are discussed for better design of photoanode materials. It concludes that the rational material design and the knowledge of thermodynamics and kinetics are required and the low-cost photoanode materials composed of inexpensive earth-abundant elements control the feasibility of this technology.

Chapter 8: Photocatalytic and Photoelectrochemical Overall Water Splitting. After the discussions of the individual hydrogen or oxygen evolution processes, this chapter focuses on the overall water splitting processes. The fundamental scientific requisites, mechanism aspects, and development horizons for overall water splitting are comprehensively covered. Then the development of photocatalytic technologies and hybrid systems integrating photovoltaic devices and photoelectrodes in photoelectrochemical platforms for overall water splitting are introduced. An extensive library of light-responsive semiconductor-based materials, attractive cocatalysts, and plasmonic nanostructures and assessed synthesis approaches, e.g. the construction of heterojunctions between state-of-the-art semiconductors, is presented. It is expected that the development of practical and adequate materials for solar-driven overall water splitting systems can further advance this exciting system.

Chapter 9: Photocatalytic CO_2 Reduction. After hydrogen/oxygen evolutions, another main topic in solar fuels, i.e. CO_2 reduction, starts in this chapter. Photocatalytic CO_2 reduction has been regarded to be economical, recyclable, and safe, therefore holding a great promise for addressing worldwide energy and environmental problems. In this chapter, the whole process of photocatalytic CO_2 reduction is analyzed in terms of energy and mass flow. Discussions are made to illustrate the effects of the flow of solar energy through concentrator, reactor, reaction solution, and photocatalyst and the mass flow from the adsorption and activation of reactants (such as CO_2) on the surface of the photocatalysts to the formation of CO, CH_4, and other products through photocatalytic reaction. Contributions are also made to present the energy loss and obstacles contained in the transformation processes and the possible strategies to improve the overall reaction efficiency.

Chapter 10: Photoelectrochemical CO_2 Reduction. As inspired by PEC water splitting, PEC reduction of CO_2 can also integrate and optimize both photocatalysis and electrocatalysis toward an improved CO_2 reduction system with a higher efficiency and stability. This chapter first introduces the fundamentals and reaction parameters in the concerned systems; then research advances on the development catalyst materials are surveyed. This includes the semiconductors, cocatalysts, and hybrid semiconductors. Novel reactor systems for PEC CO_2 reduction are introduced. At last, research opportunities and challenges are identified.

Chapter 11: Photocatalytic and Photoelectrochemical Nitrogen Fixation. Using solar energy to convert nitrogen in air to valuable chemicals is a direct mimicking system to natural photosynthesis. Artificial photocatalytic and PEC reduction of N_2 to ammonia emerged as a fantastic venue to this end. This chapter introduces the recent advances in photocatalytic and photoelectrochemical N_2 reduction to NH_3. The fundamental principles on N_2 reduction are presented. Then, the current design strategies, mainly including the defect engineering, structural regulation, interface control, heterojunction construction, cocatalyst engineering, and biomimetic engineering, for the preparation of heterogeneous catalysts are summarized. At last, the remaining challenges as well as future perspectives in this very exciting research field are outlined.

Chapter 12: Photocatalytic Production of Hydrogen Peroxide Using MOF Materials. In theory, oxygen and water can be employed to produce hydrogen peroxide using solar energy, which fortunately was demonstrated to be feasible through photocatalysis. It was reported that synthesis of H_2O_2 from O_2 reduction reaction using metal organic frameworks (MOFs) is attractive and promising. In this chapter, the H_2O_2 production through visible-light-induced O_2 reduction by an MOF, MIL-125-NH_2, coupled with oxidative reaction of benzyl alcohol was achieved in a single-phase system composed of acetonitrile and benzyl alcohol. These works creatively developed the application of MOFs in the field of new energy production.

Chapter 13: Photocatalytic and Photoelectrochemical Reforming of Methane. Solar energy can serve as the input energy for methane activation because of the wide distribution and large reserve. With that, photocatalysis and photoelectrocatalysis are recognized as effective approaches for methane reforming on which more attention has been put in the field of energy preparation. In this chapter, photocatalytic and photoelectrochemical methane reforming are introduced. The differences between these two catalytic processes are investigated in detail. After that, recent research progresses on the methane activation reactions via these two techniques are provided. The related reaction mechanisms are discussed insightfully. At last, promising perspectives on the methane upgrading via solar energy excitation are proposed.

Chapter 14: Photocatalytic and Photoelectrochemical Reforming of Biomass. It is very interesting to combine two renewable resources, e.g. solar energy and biomass, together in one process. Recently photocatalytic and photoelectrochemical reforming of biomass was demonstrated. This chapter discusses the photocatalytic conversion of processed and native lignin, carbohydrates, native lignocellulose, glycerides, and glycerol to hydrogen and value-added chemicals. Also, the photoelectrochemical (PEC) reforming of biomass to electricity, hydrogen, and biomass-derived molecules such as glycerol and alcohols, as well as converting 5-hydroxymethylfurfural to corresponding valuable chemicals, is reviewed.

Chapter 15: Reactors, Fundamentals, and Engineering Aspects for Photocatalytic and Photoelectrochemical Systems. Novel catalyst materials and new reactions have always been the hotspots in the research endeavors. As the places for the ultimate step, the reactors and associated parameters should also be given attention. This chapter provides insightful discussions on the key factors for practical approach of photocatalysis and PEC in solar fuel production. In particular, (i) fundamental rationales and mechanisms, (ii) the design and setup of photoreactors, and (iii) engineering aspects of photocatalytic and PEC systems with potential scalability are provided.

Chapter 16: Prospects of Solar Fuels. By several dream reactions, solar energy can be captured and stored in terms of solar fuels. This chapter first concludes the available processes that have been demonstrated to be feasible, and then attention is paid to explore the feasibility of the processes. Tremendous efforts are required from research, commercialization, and policies to achieve the solar fuel production at a large scale.