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Introduction

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1.1 Challenges and Objectives in the Use of Solar Energy

The increase in the world population and rampant unregulated economic growth have all led to accelerated energy consumption and the unabated release of nonbiodegradable materials such as toxic agents, plastics, and industrial wastes such as solvents and by-products into the air and sea and various waterways. This has, in turn, led to pollution-related diseases and abnormal climate changes such as global warming. Thus, humanity is now facing the serious and urgent issues of the lack of natural energy resources and fossil-fuel-driven environmental destruction and pollution on a global scale. While our industries are constantly providing a variety of new products and materials based on innovative new technologies, it is now imperative to focus on recycling those materials, reducing waste, and raising awareness of the great impact that our consumerism has on our environment.

The greatest challenge for researchers is to develop environmentally harmonious, ecologically clean and safe, sustainable, and energy-efficient chemical technologies. Photocatalysis, which utilizes the inexhaustible energy of the sun, can be harnessed and converted into clean chemical or electrical energy for nontoxic, economically viable technologies. In this book, we will present not only the fundamentals of photocatalysis but also the advances in research such as the photocatalytic splitting of water to produce clean H_2, the photocatalytic reduction of CO_2 to form hydrocarbons, the photocatalytic fixation of N_2, photo-induced super hydrophilicity to design useful materials, and promising applications of photocatalytic systems for the purification of polluted water.

UV-Visible Photocatalysis for Clean Energy Production and Pollution Remediation: Materials, Reaction Mechanisms, and Applications, First Edition. Edited by Xinchen Wang, Masakazu Anpo, and Xianzhi Fu.

1.2 Brief History of the Progress in Photocatalysts and Photocatalytic Reactions

Metal oxide-semiconducting photocatalysts such as TiO_2 materials have been the focus of much attention for their ability to induce efficient and effective reactions at room temperature under sunlight irradiation. In fact, as shown in Figure 1.1, in the past half-century, many scientists have studied the effect of UV light irradiation on semiconductors [1, 2]. In 1972, Honda and Fujishima reported the photosensitization effect of a TiO_2 electrode in the electrochemical photolysis of water at the TiO_2 electrode with a Pt counter electrode under UV light irradiation [3]. Schrauzer and Guth reported the photolysis of water and the photoreduction of nitrogen on TiO_2 photocatalyst in 1977 [4]. Since then, many researchers have investigated the development of inorganic semiconducting materials for the photocatalytic decomposition of water to produce hydrogen [5–7].

As a photocatalytic material, TiO_2 is cost-efficient, nontoxic, and has relatively high activity and stability even in aqueous solutions. Thus, as shown in Figure 1.1, it was first applied to the photocatalytic decomposition of water to produce hydrogen under relatively strong UV light irradiation [1, 5, 6]. In relation to these reactions, the idea of a dye-sensitized solar cell was reported by Gratzel in 1991 [8]. There is also a report on the photocatalytic degradation or mineralization of organic pollutants on inorganic semiconducting materials under relatively weak UV light irradiation [9]. Since then, various visible-light-responsive photocatalysts have been reported, and the separate evolution of H_2 and O_2 from water using a visible-light-responsive TiO_2 thin film photocatalyst was successfully carried out in 2004 [10]. Moreover, the highly efficient photocatalytic splitting of water to produce an H_2 and O_2 mixture using particulate oxynitrides and oxychalcogenides as semiconducting powdered materials under visible-light irradiation was reported by Kudo and Domen [11].

In 2009, Wang et al. reported the highly efficient production of H_2 and O_2 from water using a visible-light-responsive polymeric graphic carbon nitride (g-C_3N_4) photocatalyst [12]. Since then, as one of the most promising photocatalytic materials over metal oxides and sulfides, graphic carbon nitride (g-C_3N_4) nanomaterials have been investigated by many researchers with a focus on their design, construction, and optimization to establish the high conversion of light energy into chemical energy [7, 13]. For this material, chemical engineering technologies such as element doping have been applied. Various heterojunctions have also been reported to enhance the efficiency of the photocatalytic splitting of water to produce hydrogen [14]. Significantly, almost 100% quantum yield for the photocatalytic splitting of water using Al-doped $SrTiO_3$ with metal cocatalysts as well as the large-scale photocatalytic production of H_2 from water under sunlight irradiation has been reported by Domen and coworkers [15]. Such remarkable progress in the photocatalytic splitting of water has spurred further research into such practical applications that will lead to clean renewable energy technologies and the purification of the environment.

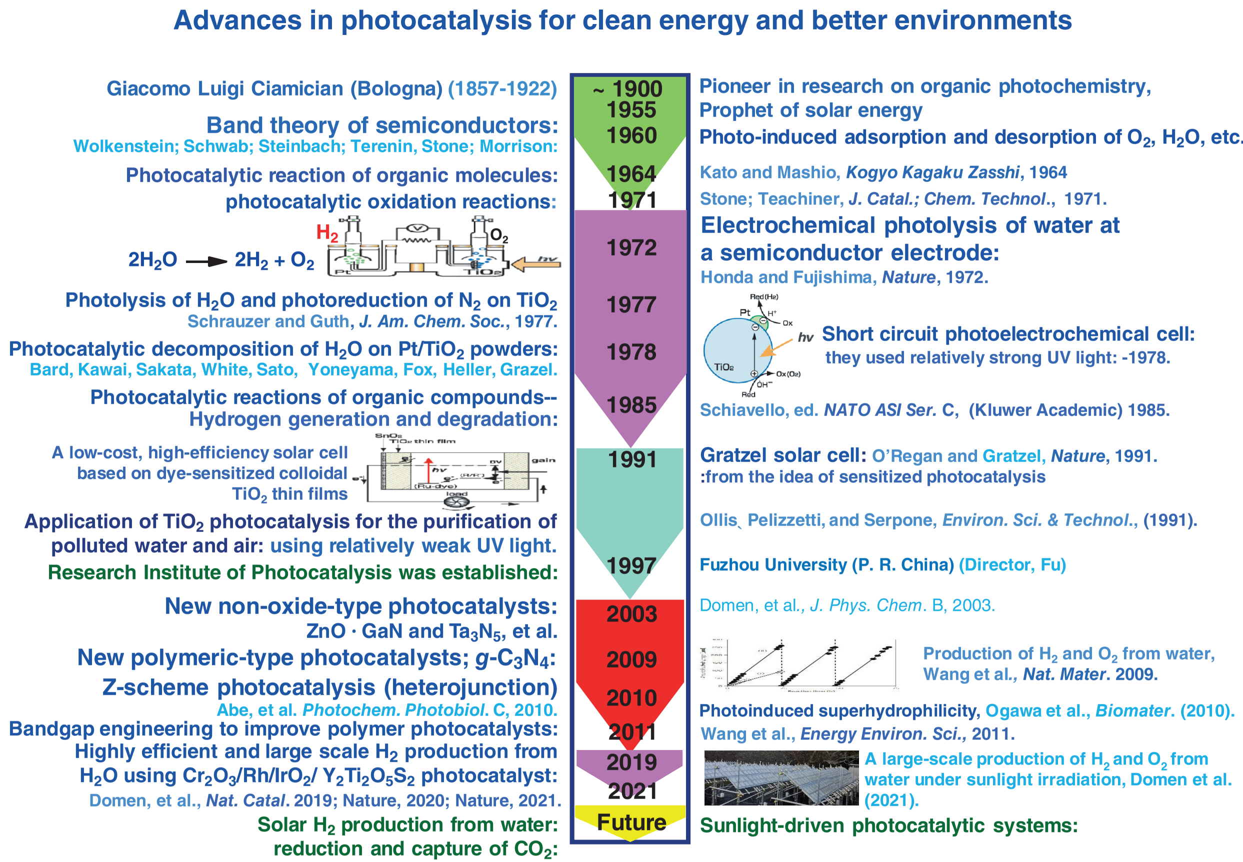

Figure 1.1 Progress in research on photocatalysts and their practical applications (past, present, and future).

1.3 Brief Introduction of the Chapters

This book consists of four categories of the fundamentals of photocatalysis which are detailed in four chapters, the photocatalytic splitting of water to produce hydrogen in seven chapters, the photocatalytic reduction of CO_2 and fixation of N_2 in six chapters, and the application of photocatalysis in four chapters.

Chapter 2 introduces dual-functioning photocatalysis to produce hydrogen from the treatment of wastewater as a promising approach to address both global environmental issues and energy problems. The fundamentals of dual-functional photocatalytic reactions via heterojunction formation and cocatalysts are also explained. **Chapter 3** summarizes the reaction mechanism of the photocatalytic oxidation of alcohol with O_2 using a carbon nitride photocatalyst. Special attention is given to strategies that improve selectivity toward carbonyl compounds and dehydrogenation employing a hydrogen-evolving cocatalyst. **Chapter 4** introduces an S-scheme heterojunction as a new concept in photocatalysis. S-scheme heterojunctions lead to an enhancement in photocatalytic reactions, including hydrogen evolution from water, the reduction of CO_2, the degradation of organic pollutants, and the production of H_2O_2. **Chapter 5** summarizes the effect of defects on the electronic and optical properties of the ZnO photocatalyst. Special attention is given to the role of the defects in the regulation of the Fermi level to enrich photogenerated carriers as well as working as adsorption sites, resulting in an enhancement of the photocatalytic performance.

Chapter 6 summarizes the recent advances in the study of visible-light-responsive water-splitting photocatalysts. Special attention is focused on recent strategies for their development, including controlling defects, dual-cocatalyst loading, and surface nanolayer coating. This chapter also introduces the future approaches to the design of active long-wavelength-responsive photocatalytic systems. **Chapter 7** summarizes the essential design principles and emerging configurations of dual redox cocatalysts, showing their synergistic operations and discussing the selection process of a pair of redox cocatalysts for a special photocatalytic redox reaction. Special attention is given to investigations into the photocatalytic splitting of water to produce hydrogen. **Chapter 8** explains that nonmetal-based carbon nitride is an inexpensive, conjugated polymeric semiconductor with high chemical stability and excellent physicochemical properties for sustainable hydrogen production from water. Special attention is focused on various preparation methods to improve its photocatalytic performance, i.e. by its coupling with other semiconductors, the use of cocatalysts, doping with metals, or the induction of defects. **Chapter 9** summarizes the significant advances in the design and photocatalytic splitting of water using perylene diimide and porphyrin-based supramolecular materials. Special attention is focused on the ongoing challenges and opportunities for the future development of supramolecular photocatalysts in high-quality nanodevices. **Chapter 10** summarizes the development of the visible-light-responsive TiO_2 thin film photocatalyst on a Ti foil substrate by an radiofrequency-magnetron sputtering (RF-MS) deposition method for the separate evolution of hydrogen and oxygen from water. The integration of this photocatalytic reaction system and an artificial light-type plant factory to realize the production of pure hydrogen and fresh vegetables using sunlight efficiently and effectively is introduced. **Chapter 11** summarizes the features of the photocatalytic evolution of hydrogen on CdS semiconductors. Special attention is focused on the merit and/or demerits of the CdS photocatalytic material as well as several improvements for enhancing the hydrogen production performance of CdS. **Chapter 12** explains the theoretical approach for the efficient photocatalytic splitting of water to produce hydrogen. Special attention is focused on band structure engineering and carrier separation of three-dimensional and two-dimensional photocatalytic materials to improve the yield of hydrogen evolution.

Chapter 13 gives an overview of the progress in the development of cocatalysts for the photocatalytic conversion of CO_2 by H_2O as an electron donor. Special attention is focused on the effects of various cocatalysts on the reduction of CO_2. **Chapter 14** summarizes the photocatalytic activity of the single-site Ti-oxo species prepared within silica or silicate for the reduction of CO_2 with H_2O. Special attention is focused on the preparation and characterization of the single-site species in nano spaces of silica and silicate materials. **Chapter 15** summarizes the potential strategy to create an efficient catalyst for the directional conversion of CO_2 through regulating the coordination modes of CO_2 on two-dimensional oxide nanosheets. **Chapter 16** summarizes the progress on layered double hydroxides (LDHs)-based nanomaterials for solar energy conversion through the reduction of CO_2 by fine-tuning the composition, coordination environment, hybrid structure, and topological transformation of LDHs. **Chapter 17** introduces the background and reaction mechanism of the photocatalytic fixation of N_2, explaining the influencing factors such as types of materials, and also provides a brief overview of its current challenges and future prospects. **Chapter 18** provides a general overview of the investigations on the photocatalytic fixation of N_2 and introduces the research highlights in these research fields.

Chapter 19 discusses the contributions of photocatalysts to the remediation of polluted environments and their reaction conditions. Detailed analytical methods of the reactants, products, and intermediates are provided. The reaction mechanisms of a few case studies using model reactions are reported. **Chapter 20** summarizes the development of photocatalytic reactors in the treatment of wastewater using biotemplated photocatalysts with structural specialty, complexity, and related unique properties. Special attention is focused on the design, assembly, and manufacturing of skid-mounted photocatalytic reactors. **Chapter 21** introduces the high surface wettability of TiO_2 thin films and TiO_2-based binary oxide thin films under UV light irradiation, and its dependence on their surface morphology, surface area, and crystal phase. **Chapter 22** introduces the advances in surfaces with super wettability and photocatalytic activity in terms of their formation and applications. Special attention is focused on the challenges and opportunities for the further development of surfaces with both super wettability and photocatalytic activity.

These chapters provide useful information on the various advances in the development of photocatalysis and photocatalytic materials, significantly, for the photocatalytic production of clean hydrogen from water as well as the photocatalytic purification of polluted water under sunlight irradiation.

1.4 Conclusion and Perspectives

Most traditional inorganic metal oxide and sulfide photocatalysts function only under UV light, which makes up less than 3–4% of the sunlight reaching the earth. Thus, visible-light-responsive inorganic photocatalysts which effectively and efficiently utilize sunlight by more than 30–35% have been intensely studied. Polymeric metal-free graphitic carbon nitride (g-C_3N_4) nanomaterials have also been developed as efficient photocatalysts operating even under visible-light irradiation. Various sciences and technologies to control the morphology of photocatalysts and the formation of a heterojunction to enhance photocatalytic activity and stability have also been developed. These investigations continue the research of Ciamician (1857–1922), the father of organic photochemistry, who conducted the first systematic studies on the behavior of organic substances toward light. Further research into the development of highly efficient and photocatalytic reaction systems will be vital in establishing artificial photosynthetic systems to convert solar energy effectively and efficiently into useful chemical or electrical energy, thus ensuring a stable energy source as well as a cleaner and more sustainable environment for future generations.

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