Steven L. Suib
Editor

New and Future Developments in Catalysis

Solar Photocatalysis

NEW AND FUTURE DEVELOPMENTS IN CATALYSIS

SOLAR PHOTOCATALYSIS

Edited by

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NEW AND FUTURE DEVELOPMENTS IN CATALYSIS

Introduction

This book focuses on solar photocatalysis and catalysts used in such processes. Photo-assisted catalysis using UV and/or visible light has been the focus of numerous labs for a very long time. The term photo-assisted catalysis or photo-assisted catalyst means that light is required to form an excited state species and that is the active phase. Without light no such species exists. There has been a renewed interest in this area as the cost of fuels has skyrocketed. Various approaches have been proposed including development of solar ponds, reactors to carry out solar photocatalysis, and the types of catalysts and catalytic reactions to be studied. Steady progress has been made in the design of such systems which are now quite complicated due to the multicomponent nature of these materials.

One of the key reactions being studied is the solar photocatalytic decomposition of water. This reaction is very complicated and requires two separate active sites, one for reduction of hydrogen and the other for generation of oxygen. Various materials including zeolites, polymers, transition metal complexes, phosphorous containing catalysts, and others have been used as catalysts in these systems. Another reaction being studied includes the decontamination and disinfection of water.

Several excellent chapters in this book cover the fundamental design and current strategies that researchers are using in order to make such devices function. Some researchers have focused on single site systems and others on composite materials. Another difficult reaction is the reduction of carbon dioxide and there are many recent studies in this area. Use of solar photocatalysis for environmental remediation is another very active area of research right now.

The use of solar photocatalysis in order to disinfect bacteria is the subject of one chapter. Composite materials of titania nano-size particles embedded in membranes is another unique approach. Composites are often necessary because two or more reactions are required such as the reduction of hydrogen and oxidation of oxide ions in the splitting of water. Development of analytical methods to study such complicated systems is discussed in a separate chapter. Studies of the mechanisms of such reactions are well underway and in certain cases well-developed theories exist and desirable materials and approaches have been determined. Various methods of deposition of active components including microwave radiation, photochemical, thermal, and electrochemical methods are summarized.

The area of solar photocatalysis is an exciting area of research that will be under investigation for quite some time. There are inherent problems regarding absorption of radiation, minimizing back reactions, and efficiently transporting electrons through these complicated systems that need continual improvement. The Chapters in this book provide detailed understanding of the challenges ahead and necessary improvement in photo-assisted catalysts, the different steps of photo-assisted catalytic processes, and the development of working composite systems.

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Contents

6. Solar Photocatalysis for Environment Remediation

ANA PRIMO AND HERMENEGILDO GARCÍA

7. Self-Cleaning Materials Based on Solar Photocatalysis

PIERRE PICHAT

8. Photocatalysts for Solar Hydrogen Conversion

JASON M. THORNTON AND DANIEL RAFTERY

9. Innovative Photocatalysts for Solar Fuel Generation by CO_2 Reduction

KEVIN D. DUBOIS AND GONGHU LI

10. Solar Photocatalytic Disinfection of Bacteria

C. KARUNAKARAN

11. Surface-Modified Anisotropic TiO_2 Nanocrystals Immobilized in Membranes: A Biologically Inspired Solar Fuel Catalyst

JAMES D. HOEFELMEYER

12. Current Development of Photocatalysts for Solar Energy Conversion

W. DAVID WEI, JOSEPH S. DUCHENE, BRENDAN C. SWEENY, JINYONG WANG, AND WENXIN NIU

13. Role of Advanced Analytical Techniques in the Design and Characterization of Improved Catalysts for Water Oxidation

SHERY L.Y. CHANG, MONIKA FEKETE, ROSALIE K. HOCKING, ALEX IZGORODINA, ARCHANA SINGH, FENGLING ZHOU, DOUGLAS R. MACFARLANE, AND LEONE SPICCIA

14. Z-Scheme Type Water Splitting into H_2 and O_2 Under Visible Light Through Two-Step Photoexcitation Between Two Different Photocatalysts

RYU ABE

15. Solar Photocatalytic Processes: Water Decontamination and Disinfection

S. MALATO, P. FERNÁNDEZ-IBÁÑEZ, M.I. MALDONADO, AND I. OLLER

16. The Application of Semiconductor Photocatalysis for the Removal of Cyanotoxins from Water and Design Concepts for Solar Photocatalytic Reactors for Large Scale Water Treatment

DETLEF W. BAHNEMANN, LINDA A. LAWTON, AND PETER K.J. ROBERTSON

17. Nanocrystal Assembly of Hierarchical Porous Architecture for Photocatalysis

JIE LI, LEI LIU, AND ZHONG-YONG YUAN

18. Mesoporous Materials Catalysts for Photodegradation of Water Pollutants: From Chemical Templates to Biotemplates

MEIQING MAO, JIAQIANG WANG, JIAO HE, AND ZHIYING YAN

CHAPTER

1

Heterogeneous Photocatalysis: Basic Approaches and Terminology

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1.1 INTRODUCTION

Heterogeneous photocatalysis is the interdisciplinary field of science that originated from the intersection of several areas of Chemistry and Physics, and to some extent Photobiology (natural photosynthesis). From a historical point of view, heterogeneous photocatalysis rests on four basic pillars: (i) heterogeneous catalysis, (ii) photochemistry, (iii) molecular spectroscopy of adsorbed molecules and solid-state spectroscopy, together with (iv) materials science and surface science of semiconductors and insulators (Figure 1.1). As such, most of the basic approaches and terminology used in heterogeneous photocatalysis originated from these four areas.

The aim of this chapter is to describe some of the basic approaches and terminology used in heterogeneous photocatalysis; the latter was recently the object of an extensive examination of various terms that are summarized in the Glossary of Terms Used in Photocatalysis and Radiation Catalysis (IUPAC recommendations 2011) [1].

To the best of our best knowledge, the terms "photocatalysis" and "photocatalyst" (*photokatalyse* and *photokatalytisch*) were introduced for the very first time by Plotnikow in a 1910

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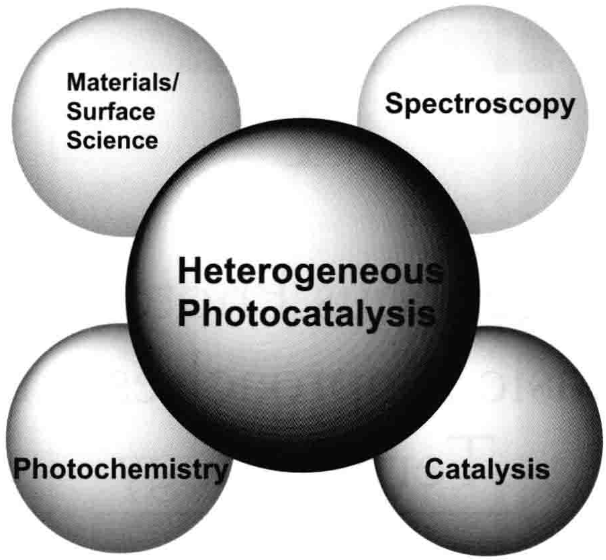

FIGURE 1.1 The four pillars that have had a great impact in the development of heterogeneous photocatalysis.

textbook on photochemistry [2]. The word *photocatalyst* was later introduced in France in 1913 by Landau [3,4]. Presently [1], the term "photocatalysis" is described as a change in the rate of a chemical reaction or its initiation under the action of ultraviolet, visible, or infrared radiation in the presence of a substance—the *photocatalyst*—that absorbs light and is involved in the chemical transformation of the reaction partners, while a "photocatalyst" is the substance able to produce, by absorption of ultraviolet, visible, or infrared radiation, chemical transformations of the reaction partners, repeatedly coming into intermediate chemical interactions with them and regenerating its chemical composition after each cycle of such interactions.

Several pioneering studies have had a significant impact on heterogeneous photocatalysis, studies that dealt with the photostability of dyes in heterogeneous systems and of pigments (similar studies later concerned the photostability of thermo-control coatings [5]) and that demonstrated that the optical characteristics of the compositions are strongly affected by the environmental conditions under the action of light. Most pigments and thermo-control coatings contained the white pigments ZnO and TiO_2 and various dyes including organic dyes (see, e.g., Ref. [6]). TiO_2 in its pristine or modified form is the most popular photocatalyst and is the basic source of several modern composite photoactive materials [7]. At the same time, experimental studies conducted in the physics of semiconductors demonstrated a significant effect of the environment on the photoconductivity and photo-EMF (see, e.g., Ref. [8] and other textbooks on the physics of semiconductors), especially with respect to the surface manifestation of phenomena that have been attributed to surface photostimulated adsorption and interfacial chemical reactions.

Shwab [9,10] irradiated metal-oxide semiconductor catalysts to modify their electronic properties without serious changes in the material structure (compared to doping) in order to verify the role played by electronic factors in heterogeneous catalysis. Such role was