

Steven L. Suib  
Editor



# New and Future Developments in Catalysis

Solar Photocatalysis

# NEW AND FUTURE DEVELOPMENTS IN CATALYSIS

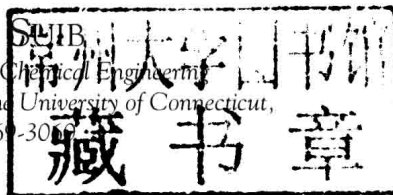
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## SOLAR PHOTOCATALYSIS

*Edited by*

STEVEN L. SUIB

*Department of Chemistry and Chemical Engineering  
and Institute of Materials Science, The University of Connecticut,  
Storrs, CT 06269-3009*



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# NEW AND FUTURE DEVELOPMENTS IN CATALYSIS

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# Introduction

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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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# Contributors

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- Ryu Abe** Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 615-8510, Japan
- Detlef W. Bahnemann** Institut fuer Technische Chemie, Gottfried Wilhelm Leibniz Universitaet Hannover, Callinstrasse 3, D-30167 Hannover, Germany
- Subhrakanti Chakraborty** Department of Chemistry, The Ohio State University, Columbus, OH 43210, USA
- Shery L.Y. Chang** School of Chemistry, Monash University, Victoria 3800, Australia  
Monash Centre for Electron Microscopy, Monash University, Victoria 3800, Australia
- Anna Cybula** Department of Chemical Technology, Gdansk University of Technology, 80-233 Gdansk, Poland
- Kevin D. Dubois** Department of Chemistry and Materials Science Program, University of New Hampshire, Durham NH 03824, USA
- Joseph S. DuChene** Department of Chemistry and Center for Nanostructured Electronic Materials, University of Florida, Gainesville, FL 32611, USA
- Prabir K. Dutta** Department of Chemistry, The Ohio State University, Columbus, OH 43210, USA
- A.V. Emeline** Department of Photonics, V.A. Fock Institute of Physics, Saint-Petersburg State University, Ulianovskia Str. 1, Petrodvoretz, Saint-Petersburg, 198504, Russia
- Monika Fekete** School of Chemistry, Monash University, Victoria 3800, Australia
- ARC Centre of Excellence for Electromaterials Science, ACES, Monash University, Victoria 3800, Australia
- P. Fernández-Ibáñez** Plataforma Solar de Almería (CIEMAT), Carretera Senés, km 4, 04200 Tabernas (Almería), Spain
- Hermenegildo García** Instituto Universitario de Tecnología Química CSIC-UPV, Universidad Politécnica de Valencia, 46022 Valencia, Spain
- Jiao He** Department of Applied Chemistry, The Universities' Centre for Photocatalytic Treatment of Pollutants in Yunnan Province, Key Laboratory of Medicinal Chemistry for Natural Resource, Ministry of Education, Yunnan University, Kunming, PR China
- Rosalie K. Hocking** School of Chemistry, Monash University, Victoria 3800, Australia  
ARC Centre of Excellence for Electromaterials Science, ACES, Monash University, Victoria 3800, Australia
- James D. Hoefelmeyer** Department of Chemistry, University of South Dakota, Vermillion, SD 57069, USA
- Alex Izgorodina** ARC Centre of Excellence for Electromaterials Science, ACES, Monash University, Victoria 3800, Australia
- Takashi Kamegawa** Division of Materials and Manufacturing Science, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan
- C. Karunakaran** Department of Chemistry, Annamalai University, Annamalaiagar 608002, Tamil Nadu, India
- V.N. Kuznetsov** Department of Photonics, V.A. Fock Institute of Physics, Saint-Petersburg State University, Ulianovskia Str. 1, Petrodvoretz, Saint-Petersburg, 198504, Russia



- Linda A. Lawton** The Robert Gordon University, Schoolhill, Aberdeen, AB10 1FR, United Kingdom
- Gonghu Li** Department of Chemistry and Materials Science Program, University of New Hampshire, Durham NH 03824, USA
- Jie Li** Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), College of Chemistry, Nankai University, Tianjin 300071, China
- Lei Liu** Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), College of Chemistry, Nankai University, Tianjin 300071, China
- Douglas R. MacFarlane** School of Chemistry, Monash University, Victoria 3800, Australia  
ARC Centre of Excellence for Electromaterials Science, ACES, Monash University, Victoria 3800, Australia
- S. Malato** Plataforma Solar de Almería (CIEMAT), Carretera Senés, km 4, 04200 Tabernas (Almería), Spain
- M.I. Maldonado** Plataforma Solar de Almería (CIEMAT), Carretera Senés, km 4, 04200 Tabernas (Almería), Spain
- Meiqing Mao** Department of Applied Chemistry, The Universities' Centre for Photocatalytic Treatment of Pollutants in Yunnan Province, Key Laboratory of Medicinal Chemistry for Natural Resource, Ministry of Education, Yunnan University, Kunming, PR China
- Michał Nischk** Department of Chemical Technology, Gdansk University of Technology, 80-233 Gdansk, Poland
- Wenxin Niu** Department of Chemistry and Center for Nanostructured Electronic Materials, University of Florida, Gainesville, FL 32611, USA
- B. Ohtani** Catalysis Research Center, Hokkaido University, Sapporo 001-0021, Japan
- I. Oller** Plataforma Solar de Almería (CIEMAT), Carretera Senés, km 4, 04200 Tabernas (Almería), Spain
- Pierre Pichat** Photocatalyse et Environnement, CNRS/Ecole Centrale de Lyon (STMS), 69134 Ecully CEDEX, France
- Ana Primo** Instituto Universitario de Tecnología Química CSIC-UPV, Universidad Politécnica de Valencia, 46022 Valencia, Spain
- Daniel Raftery** Department of Chemistry, Purdue University, 560 Oval Drive, West Lafayette, IN 47907, USA
- Peter K.J. Robertson** The Robert Gordon University, Schoolhill, Aberdeen, AB10 1FR, United Kingdom
- V.K. Ryabchuk** Department of Photonics, V.A. Fock Institute of Physics, Saint-Petersburg State University, Ulianovskia Str. 1, Petrodvorets, Saint-Petersburg, 198504, Russia
- N. Serpone** Dipartimento di Chimica, Università di Pavia, via Taramelli 10, Pavia 27100, Italy
- Archana Singh** School of Chemistry, Monash University, Victoria 3800, Australia  
ARC Centre of Excellence for Electromaterials Science, ACES, Monash University, Victoria 3800, Australia
- Leone Spiccia** School of Chemistry, Monash University, Victoria 3800, Australia  
ARC Centre of Excellence for Electromaterials Science, ACES, Monash University, Victoria 3800, Australia
- Brendan C. Sweeny** Department of Chemistry and Center for Nanostructured Electronic Materials University of Florida, Gainesville, FL 32611, USA
- Jason M. Thornton** Department of Chemistry, Purdue University, 560 Oval Drive, West Lafayette, IN 47907, USA
- Jiaqiang Wang** Department of Applied Chemistry, The Universities' Centre for Photocatalytic Treatment of Pollutants in Yunnan Province, Key Laboratory of Medicinal Chemistry for Natural Resource, Ministry of Education, Yunnan University, Kunming, PR China
- Jinyong Wang** Department of Chemistry and Center for Nanostructured Electronic Materials, University of Florida, Gainesville, FL 32611, USA
- W. David Wei** Department of Chemistry and Center for Nanostructured Electronic Materials, University of Florida, Gainesville, FL 32611, USA

**Hiromi Yamashita** Division of Materials and Manufacturing Science, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan

**Zhiying Yan** Department of Applied Chemistry, The Universities' Centre for Photocatalytic Treatment of Pollutants in Yunnan Province, Key Laboratory of Medicinal Chemistry for Natural Resource, Ministry of Education, Yunnan University, Kunming, PR China

**Zhong-Yong Yuan** Key Laboratory of Advanced Energy Materials Chemistry (Ministry of

Education), College of Chemistry, Nankai University, Tianjin 300071, China

**Adriana Zaleska** Department of Chemical Technology, Gdansk University of Technology, 80-233 Gdansk, Poland

Chair of Environmental Engineering, University of Gdansk, 80-952, Poland

**Fengling Zhou** School of Chemistry, Monash University, Victoria 3800, Australia

ARC Centre of Excellence for Electromaterials Science, ACES, Monash University, Victoria 3800, Australia



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# Heterogeneous Photocatalysis: Basic Approaches and Terminology

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A.V. Emeline<sup>a</sup>, V.N. Kuznetsov<sup>a</sup>,  
V.K. Ryabchuk<sup>a</sup>, and N. Serpone<sup>b</sup>

<sup>a</sup>Department of Photonics, V.A. Fock Institute of Physics,  
Saint-Petersburg State University, Uljanovskia Str. 1, Petrodvoretz,  
Saint-Petersburg, 198504, Russia

<sup>b</sup>Dipartimento di Chimica, Università di Pavia, via Taramelli 10,  
Pavia 27100, Italy

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## 1.1 INTRODUCTION

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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



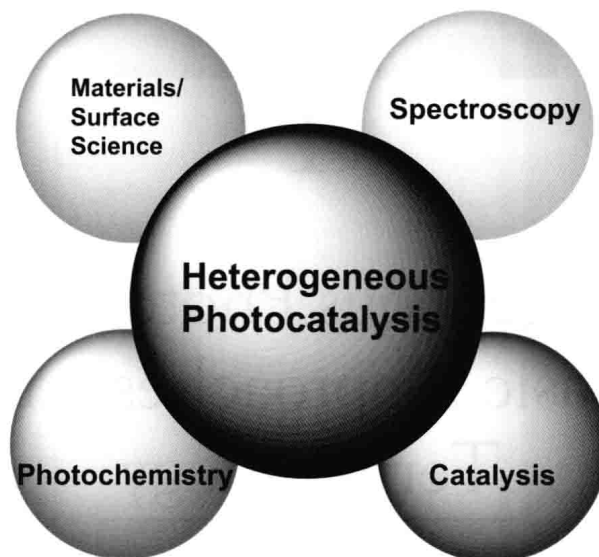


FIGURE 1.1 The four pillars that have had a great impact in the development of heterogeneous photocatalysis.

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<sub>2</sub> and various dyes including organic dyes (see, e.g., Ref. [6]). TiO<sub>2</sub> 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