

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*

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*Department of Chemistry and Chemical Engineering  
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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.

## Acknowledgments

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# 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

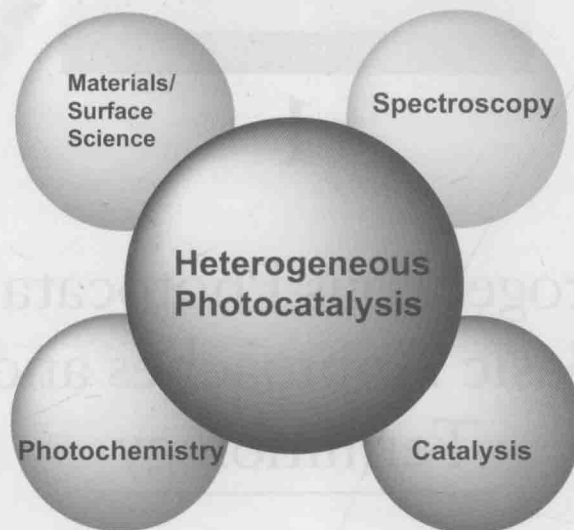


FIGURE 1.1 The four pillars that have had a great impact in the development of heterogeneous photocatalysis.

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



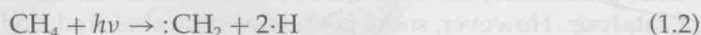
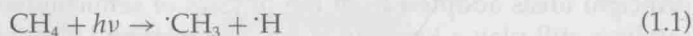
actively studied [11–13] and analyzed within the confines of the electronic theory of catalysis [14–16] based on major approaches and concepts of the physics of semiconductors. The principal ideas adopted from the physics of semiconductors and the electronic theory of catalysis still play a key role in fundamental and applied studies pertaining to heterogeneous photocatalysis. In fact, many researchers still consider photocatalysis only as a part of catalysis. However, some postulates typical of traditional catalysis sound rather contentious in photocatalysis. For instance, by analogy with catalysis, one of the postulates would suggest that a photocatalytic process should favor only thermodynamically allowed chemical reactions. From this point of view, the light should cause the decrease of the potential energy barrier relative to the dark catalytic reaction and thereby cause the acceleration in establishing the chemical equilibrium between reagent and product in the heterogeneous system. Those photoreactions taking place in heterogeneous systems that were thermodynamically unfavorable, such as water photolysis, were classified as being not photocatalytic but photosynthetic, in spite of the similarity in all major steps of the photoprocesses and that the sole reason for both types of photoreactions is the free energy of the actinic light. In fact, the action of the free energy of light turns the system into a thermodynamically open system so that, by definition, the concept of thermodynamic equilibrium is not applicable.

Another major pillar of heterogeneous photocatalysis is molecular spectroscopy of adsorbed molecules. Pioneering studies in this area were focused on the understanding of changes in the molecular structure induced by adsorption of the molecule onto the solid surfaces [17–19]. However, light cannot only be used as the probe but is also an active factor in the transformation of adsorbed molecules. As a result, the effects of photodissociation and photodesorption of adsorbed molecules were established together with the photostimulated adsorption (photoadsorption) of simple molecules on the surface of dispersed semiconductors and insulators [19,20].

The photochemistry of heterogeneous systems also became an important pillar of heterogeneous photocatalysis. By definition, photochemistry considers thermodynamically open systems. Thus, heterogeneous photocatalysis can also induce those reactions that lead to light energy conversion and storage by formation of higher energy products, as occurs in natural photosynthesis [21,22]. The concepts taken from photochemistry suggest that the photocatalytic process occurs through electronically excited states of the photocatalyst induced by light absorption. Quite often, photocatalyzed reactions cannot be distinguished from photosensitized reactions examined in photochemistry [23].

Historically, many photoreactions that presently are called photocatalytic were earlier considered as photosensitized reactions so that the term used to describe that particular substance was referred to as a photosensitizer rather than a photocatalyst. Indeed, two major characteristics of photosensitized reactions are also typical of photocatalytic processes: (i) the red shift of the spectral limit of the photoreaction and (ii) alteration of the reaction pathway compared to that of the photochemical reaction. For example, the photochemical decomposition of methane (Reaction (1.1)) occurs under irradiation with photon energy corresponding to the absorption band edge of methane ( $\lambda \approx 160$  nm). However, the methane decomposition reaction can be photosensitized by mercury vapor through formation of the unstable species  $\{\text{HgCH}_4\}^*$  formed by interaction of photoexcited (at  $\lambda = 254$  nm) Hg atoms with methane molecules to produce two  $\cdot\text{CH}_3$  radicals [24]. Direct photochemical

formation of  $\cdot\text{CH}_2$  radicals from methane occurs only at shorter wavelengths ( $\lambda < 130\text{ nm}$ ; Reaction (1.2)) [25]



The red shift of the spectral limit of a photoprocess and alteration of the reaction pathway are distinguishable fingerprints of heterogeneous photocatalytic reactions. Enhancing the ability of photocatalysts to sensitize photochemical reactions, especially toward visible light, is currently one of the major challenges and areas of interests in applied heterogeneous photocatalysis.

Photoelectrochemical studies have played a partial role in the development of fundamental and applied heterogeneous photocatalysis. One school espouses the notion that the beginnings of modern applied photocatalysis are due to a short note that appeared in the journal *Nature* in 1972 on the electrochemical photolysis of water over a  $\text{TiO}_2$  photoanode [26]. However, the role that connected photoelectrochemistry and heterogeneous photocatalysis with particulate systems was only clarified several years later (1979) in a study [27] that described the principles and applications of semiconductor electrodes in photoelectrochemical (PEC) cells (liquid junction photovoltaic, photoelectrosynthetic, photocatalytic). And most importantly, the study described in some details the factors important to the design of *practical systems* and the *extension of the principles of PEC cells to particulate systems* for carrying out heterogeneous photocatalysis and photosynthesis. The close interconnection between a photoelectrochemical cell and a photocatalytic nanoparticulate system made by Bard [27] and most recently re-emphasized by Lianos [28] is illustrated in Figure 1.2.

Photocatalytic processes occurring in heterogeneous systems are complex and multifarious starting, as it were, from the absorption of photons by the solid photocatalyst and ending with

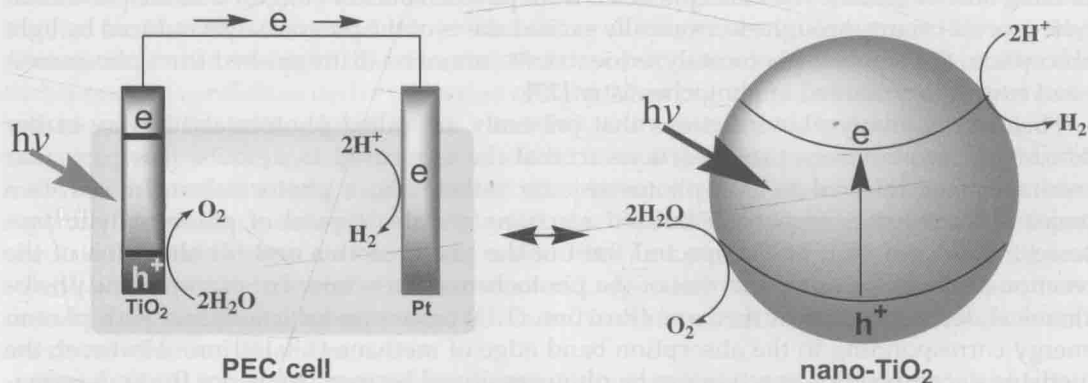


FIGURE 1.2 Schematic illustration of the interconnection between a photoelectrochemical cell and a photocatalytic nano-TiO<sub>2</sub> particulate system in converting light energy into a solar fuel ( $\text{H}_2$ ) from the water splitting process.