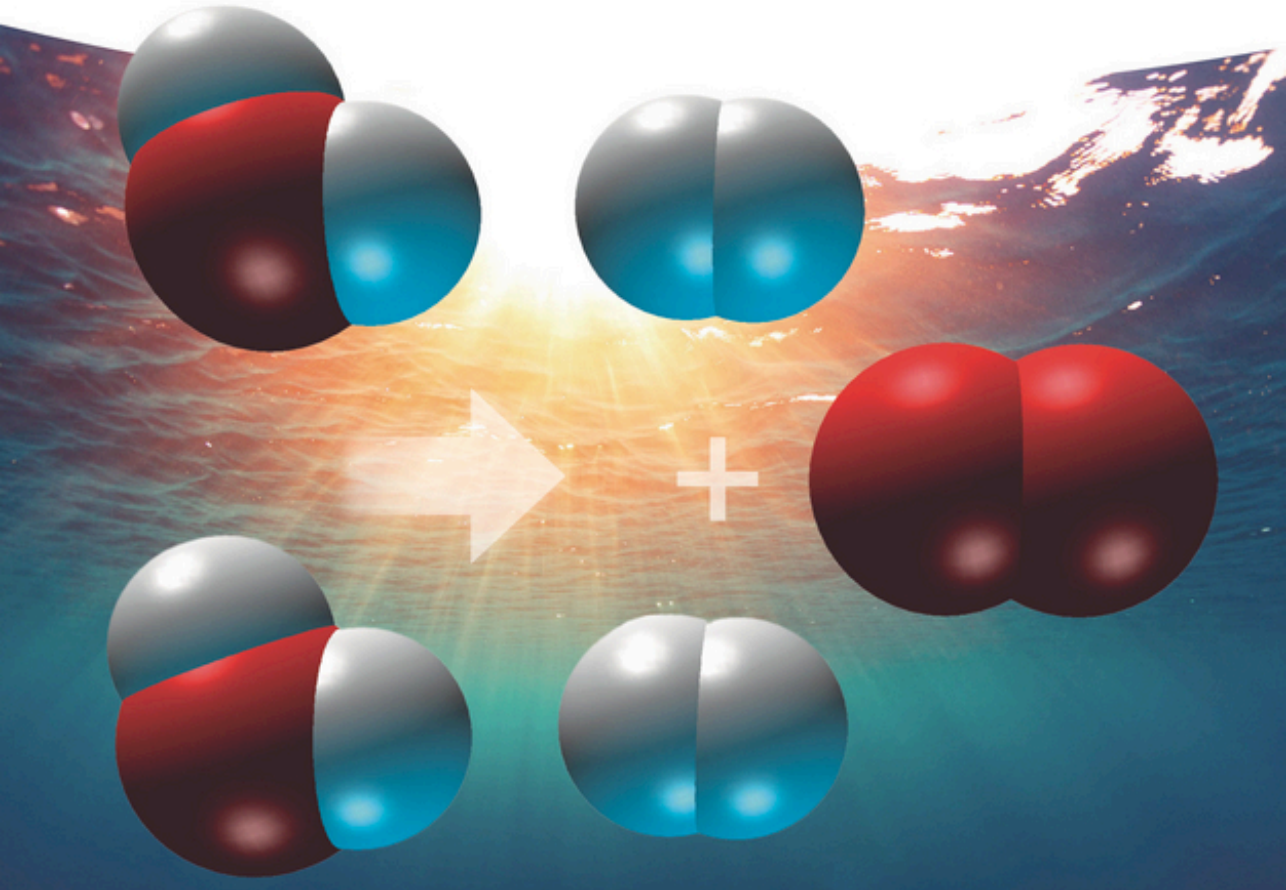
WILEY-VCH

Edited by Srabanti Ghosh

Visible-Light-Active Photocatalysis

Nanostructured Catalyst Design, Mechanisms, and Applications



Visible-Light-Active Photocatalysis: Nanostructured Catalyst Design, Mechanisms, and Applications

Visible-Light-Active Photocatalysis: Nanostructured Catalyst Design, Mechanisms, and Applications

Edited by Srabanti Ghosh

WILEY-VCH

Editor

Dr. Srabanti Ghosh
CSIR - Central Glass and Ceramic
Research Institute
Fuel Cell & Battery Division
196, Raja S. C. Mullick Road
700 032 Kolkata
India

Cover
Background image Fotolia:
Dudarev Mikhail

Library of Congress Card No.: applied for

British Library Cataloguing-in-Publication Data
A catalogue record for this book is available from the British Library.

Bibliographic information published by the Deutsche Nationalbibliothek
The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available on the Internet at <http://dnb.d-nb.de>.

Print ISBN: 978-3-527-34293-8
ePDF ISBN: 978-3-527-80814-4
ePub ISBN: 978-3-527-80815-1
Mobi ISBN: 978-3-527-80816-8
oBook ISBN: 978-3-527-80817-5

Cover Design Schulz Grafik-Design, Fußgönheim, Germany
Typesetting SPi Global, Chennai, India
Printing and Binding

Printed on acid-free paper

10 9 8 7 6 5 4 3 2 1

I dedicate this book to my HUSBAND and PARENTS.

Contents

Preface

In the last decades, photocatalysis has been demonstrated to be one of the most promising approaches to environmental protection, solar energy conversion, as well as in the sustainable production of fuels from water and carbon dioxide. Visible-light-induced photocatalysis is relatively a new area of material science, but the major problem remains as poor solar energy conversion efficiency. The development of novel nanoscale structures as visible-light-responsive photocatalysts causes a dramatic improvement in energy conversion and generation. This book includes the visible-light-active photocatalysis to cover the entire field, focusing on fundamentals, size and shape tunable nanostructures, and the evaluation of their effectiveness as well as perspectives, technologies, applications, and the latest developments, including pollutants degradation by oxidative or reductive processes, organic transformations, CO_2 reduction to produce low-carbon fuels, water electrolysis for hydrogen generation, and photoelectrochemistry for water splitting to produce hydrogen and oxygen and put forward future directions in solar light harvesting.

The book begins with a brief introduction of visible-light-induced photocatalysis by various nanomaterials in chapter 1, followed by chapters 2–15 dealing with the organic pollutants degradation, water detoxification, organic transformations, water splitting, and CO_2 reduction. There are chapters 2, 5–9, 12 devoted to metal-oxide-based photocatalysts, plasmonic catalysts, heterogeneous inorganic semiconducting materials such as metal oxides, nitrides, sulfides, oxynitrides, etc., heterostructures-based catalysts, conducting polymers nanostructures, organic polymeric semiconductors, and metal–organic complex. Effects of bandgap engineering of photocatalysts, mechanistic studies, particularly, roles of the active species on photocatalysis are covered in a separate chapter 16, 17, 18. Chapter 19 is dedicated to the computational modeling of photocatalysis, with an emphasis on reactive dynamics and quantum effects. This book also promotes the idea about solar photocatalytic reactor designs and their broader impact on the environment for large-scale applications in chapter 20. Finally, the last chapter 21 outlines a brief summary of the work and puts forward future directions in perspective of the solar light harvesting.

In order to make each contribution complete in itself, there is some unavoidable overlap among the chapters.

We believe this book endows with essential reads for university students, researchers, and engineers and allows them to find the latest information on visible-light-active photocatalysis, fundamentals, and applications.

Kolkata, 2018 *Srabanti Ghosh*

Part I

Visible-Light Active Photocatalysis – Research and Technological Advancements

1

Research Frontiers in Solar Light Harvesting

Srabanti Ghosh

CSIR – Central Glass and Ceramic Research Institute, Fuel Cell and Battery Division, 196, Raja S.C. Mullick Road, Kolkata 700032, India

1.1 Introduction

In continuously growing technology-driven society, an urgent need for efficient solar light harvesting to achieve sustainable solutions in science and industry exists [1, 2]. The rapid growth of industries and some unavoidable human activities cause environment pollution to be a threat to the society. Solar-energy-mediated advanced oxidation process in water purification is a highly desirable approach [3]. To use the solar light, energy harvested from the sun needs to be efficiently converted into chemical fuel that can be stored, transported, and used upon demand. Over the last few decades, a significant effort has been made to develop active materials including inorganic, organic, ceramic, polymeric, and carbonaceous, their composites with tunable size and structures [4–6]. A broad range of materials including metal oxides, chalcogenides, carbides, nitrides, and phosphides of various compositions such as heterogeneous, plasmonic, conjugated polymers, porous carbon-based materials, and graphene-based materials has been explored to address/solve energy and environment-related research challenges [7–10]. In this context, oxide-based semiconductors, in particular, TiO_2, have been recognized as efficient and widely explored photocatalysts. Semiconductor-oxide-based catalysts is essentially limited by low quantum yield which results from the fast charge carrier (e^-/h^+) recombination, and the necessity to use UV irradiation (5% of total sun energy) having wide bandgap [11, 12]. To overcome these limitations, surface-tuning strategies and modification of oxides on the nanometer scale have been developed via doping or surface modifications to produce visible-light-responsive photocatalysts. Indeed, TiO_2 doped with N, C, or S or its modification with metal nanoparticles (Ag, Au, Pt, Cu, Bi) has extended its activity toward the visible region [13–16]. However, the photocatalytic activity of the modified materials in the visible light is still not sufficient for commercial applications. Research efforts are therefore increasingly being carried out to design and develop more efficient novel visible-light active catalysts for photocatalysis and solar energy conversion. A considerable number of novel synthetic strategies including

Visible-Light-Active Photocatalysis: Nanostructured Catalyst Design, Mechanisms, and Applications,
First Edition. Edited by Srabanti Ghosh.

fabrication of plasmonic-based novel catalysts, heterojunctions, and cocatalyst have been proposed to offer new visible-light-active photocatalytic materials as potential substitutes of TiO_2 for the most relevant photocatalytic applications such as detoxification and disinfection, removal of inorganic pollutants, water splitting, and organic synthesis [17–19]. In this regard, the loading of cocatalysts or secondary semiconductors, which can act as either electron or hole acceptors for improved charge separation, is a promising strategy for enhanced catalytic activity. A more innovative implementation of this idea would be based on the use of polymer-based composites, which could allow enhanced charge separation with respect to the photocatalytic activity of the inorganic component alone. In this chapter, the state of the art on development of novel nanostructures and the concept of heterojunction for efficient visible-light-driven water splitting, organic or inorganic pollutant degradation, and organic transformation have been discussed. The structural features of various nanostructured catalysts and their correlation are explained in detail. An overview of recent research efforts in the applications of visible-light-active photocatalysts, which include semiconductor metal oxides (TiO_2, Fe_2O_3, Cu_2O, etc.), polymeric graphitic carbon nitride (C_3N_4), plasmonic nanostructures (Au, Ag, etc.), conducting polymers nanostructure (PEDOT, PANI, PDPB, etc.), heterostructures, and other novel materials in degradation of photocatalytic pollutants , hydrogen generation, CO_2 reduction, and selective redox organic synthesis are summarized.

1.2 Visible-Light-Driven Photocatalysis for Environmental Protection

Environmental pollution issues prompted the finding of potential solutions to clean up water and environmental detoxification via exploring clean energy routes through solar-light-induced photocatalysis. Extensive research has been done in the area of photocatalytic removal of organic, inorganic, and microbial pollutants using semiconductor photocatalysts (e.g., TiO_2, ZnO, and CdS) for wastewater purification [20–23]. The key to the success of solar energy conversion is the development of high-performance materials of well-matched photo absorption with solar spectrum (visible-light-harvesting capability), efficient photoexcited charge separation to prevent electron–hole recombination, and adequate energy of charges that carry out the photodegradation of dye and other toxic molecules. Continuous efforts have been made to generate active photocatalysts under visible light, but their efficiency is low due to fast charge recombination [24]. Many excellent reviews have also come up regarding the development of oxide-based semiconductors, in particular, TiO_2, via fine-tune of several electronic characteristics (e.g., atomic configuration, bandgap energy, band position, and lifetime of electrons and holes) [25–27]. In addition to dye sensitization, doping with metals and nonmetals, formation of heterojunctions have been extensively used to enhance the visible-light response of TiO_2 materials and discussed in detail in Chapters 2, 5, 6, 11, and 16. For example, TiO_2 doped with N, C, F, or S or its modification with metal nanoparticles has

extended its activity toward the visible region [15, 28–30]. Visible-light activities arise from the changes of bandgap structure of semiconductor via adsorbed modifiers (surface modification) or bandgap narrowing (doping). Synthesis of different materials, such as M/TiO_2 (M=Cu, Ag, Au, Pt, Pd, Bi, Ag—Au, Ag—Cu, Au—Cu, Ag—Pt), and the effect of metal modification on the photocatalytic activity have been discussed in Chapter 6. Moreover, Chen *et al.* reported disordered TiO_2 nanophase derived from hydroxylation through hydrogenation treatment, which marked as black TiO_2 and a considerable enhancement in visible-light-induced photocatalytic activity [31]. It has been reported that hydrogenation treatment induced the oxygen vacancies and Ti^{3+} sites in black TiO_2, resulting in the bandgap narrowing and the separation of photogenerated electrons and holes, which enhanced solar absorption and significantly improved the photocatalytic activity of TiO_2 [32, 33]. A variety of synthetic strategies of black TiO_2 are outlined, and the structural and chemical features, electronic properties, and catalytic activity of the black TiO_2 nanomaterials are described in Chapter 5. Furthermore, oxygen-rich layered titanium oxide is also useful for enhanced visible-light photoactivity [34, 35]. Kong *et al.* reported Ti—O—O coordination bond in layered titanium oxide (composed of TiO_6 layers, and interstitial hydrated H^+ ions) initiated visible-light-driven photocatalytic activity [36]. Presence of Ti—O—O coordination bonds lowers the bandgap and promotes the charge separation of the photoinduced electron–hole pairs.

Another important example is combination of nanostructured plasmonic metals with a oxide-based semiconductor, which significantly enhanced the photocatalytic activity due to the local surface plasmon resonance (LSPR) effect with very large absorption and scattering cross sections [28, 29]. In fact, LSPR causes an optical antenna effect, which efficiently harvests light and localizes electromagnetic waves at the nanoscale, and the charge carrier formation with efficient separation is obtained at the semiconductor/liquid interface, which benefits the photocatalytic reactions [37–40]. A series of reactions have been tested on Ag, Au, and Cu surfaces, illustrating that low-intensity visible-photon illumination can significantly enhance the rates of chemical transformations as well as control reaction selectivity with different mechanisms as discussed in Chapter 6. Direct plasmonic photocatalysis is believed to occur through the transient transfer of energetic electrons to adsorbate orbitals and the nature of the adsorbate may have a significant impact to control selectivity in plasmon-driven reactions [17]. These heterogeneous oxide-based semiconductor photocatalysts have been also explored for the removal of inorganic wastewater pollutants including cyanide-containing waste and heavy metal pollutants, such as arsenic species and hexavalent chromium [41–43]. Notably, due to high toxicity and carcinogenicity of hexavalent chromium (Cr(VI)), the concentration of Cr(VI) in wastewater should be controlled in acceptable levels before its release in order to protect potable water supplies [44, 45]. Although, molecular CO_2 has a very low electron affinity and is chemically inert as well as very stable, photogenerated energetic electrons from photocatalysts can reduce CO_2 to methane (CH_4) and carbon monoxide (CO). The photocatalytic reduction of CO_2 using solar energy has drawn considerable attention, which mimics the biological photosynthesis in plants [46–48]. It combines the reductive half reaction of CO_2 fixation with

a well- matched oxidative half reaction of water oxidation, in order to achieve a carbon neutral cycle, which accomplished with the environment protection. Over the last few decades, various semiconductor photocatalysts, including metal oxide, sulfide, and oxynitride, have been investigated [49, 50]. However, the overall efficiency of the CO_2 photocatalytic reduction has been limited by the purification and separation of products. Consequently, efficient and selective production of highly valuable fuel compounds is a vital issue for practical CO_2 photoreduction systems. Despite of huge attempts to enhance visible-light activity by narrowing the bandgap of TiO_2 through doping, large-scale application is limited due to defect-induced charge trapping and recombination sites of photoexcited charge carriers. In this regard, plasmon-based photocatalysts have demonstrated significantly higher photocatalytic performance in comparison to other known visible-light photocatalysts (e.g., N-doped TiO_2); however, the poor photostability of silver salts reduced the photoactivity of the doped TiO_2 material, which limits its extensive use as a visible-light photocatalyst [15, 51–53]. Hence, a dopant-free, pure catalyst with a bandgap that matches the visible-light energy would be ideal. Numerous efforts have been made for the development of new visible-light-induced photocatalysts, and some oxides have shown visible-light-driven catalytic activity, such as $InVO_4$, $BiVO_4$, Bi_2MoO_6, WO_3, and Bi_2WO_6. Recently, visible-light-responsive photocatalytic activity of conjugated polymer nanostructures (CPNs) such as poly(diphenylbutadiyne) (PDPB) nanofibers, poly(3,4-ethylene dioxythiophene) (PEDOT) nanospindle, and poly(3-hexyl thiophene) (P3HT) nanospheres have been reported for degradation of organic pollutants [54–56]. These CPNs demonstrated high photocatalytic activity under visible light without the aid of sacrificial reagents or precious metal cocatalysts. These novel photocatalytic materials have been proposed as potential substitutes of TiO_2 for the most relevant photocatalytic applications, such as detoxification and disinfection, water splitting, and organic synthesis.

Compared to individual semiconductor photocatalysts, composites of two or more semiconductor systems, that is, heterostructures, are advantageous in terms of more efficiently facilitating charge separation and charge carrier transfer, thereby substantially improving photocatalytic efficiency. A very large number of different semiconductor combinations have been investigated, such as metal/semiconductor, carbon group materials/semiconductor heterostructures, semiconductor/semiconductor heterostructures with different models including type I and type II heterojunctions, p–n heterojunctions, and Z-scheme [57–61]. Chapter 8 summarizes the recent strategies to develop such heterostructures and highlights the most recent developments in the field. For charge carrier separation, TiO_2 has been commonly used to form heterostructures with CdS [62, 63], CdSe [64], CuO [65], AgBr [66], PbS [67] for enhanced photocatalytic activities, such as degradation of organic molecules, H_2 generation, and CO_2 reduction. For example, the integration of a potential semiconductor nanocrystal, ZnO, with a narrow band-gap conducting polymer has also shown to be an effective means of promoting charge carrier separation and improving the utilization of solar light [68]. A deep understanding of the charge transfer process through fundamental studies toward the rational design of heterostructures exhibiting high visible-light-harvesting efficiency is addressed in Chapter 9. Similarly, the

use of multiple inorganic domains within these heterostructures enables a rapid dissociation of excitons into a spatially separated pair of charges that bears a minimal probability of the backward recombination, with a high extinction coefficient in the visible range and a low exciton binding energy, which is beneficial to photocatalytic applications [69]. In addition to metal oxides, metal sulfides or chalcogenides have been employed for photocatalytic applications [70]. Ganguli et al. reported a type II semiconductor, ZnO/CuS heterostructure, to increase the absorbance in the visible-light region and successful charge separation from CuS to ZnO through the hexagonal nanotubes (NTs) of ZnO, leading to enhanced visible-light-induced photocatalysis for the degradation of organic pollutants due to the efficient separation of photoinduced carriers [71]. Wang et al. synthesized mesoporous yolk–shell SnS_2–TiO_2 and applied them for the visible-light-driven photocatalytic reduction of Cr(VI) [72].

The two-dimensional (2-D) structure of graphene possessing the large surface area can accommodate semiconductor nanoparticles, and the injection of photoexcited electrons from the semiconductor particle can readily be transported along the graphene surface due to its superior electronic conductivity and high mobility of charge carriers [73–76]. Hence, graphene is a promising component to create efficient composite photocatalysts for dye degradation, organic transformations, and reduction of carbon dioxide (CO_2) [77, 78]. For example, Liang *et al.* prepared less defective graphene-P25 nanocomposites for the photocatalytic CO_2 reduction under visible light [79]. Yu et al. synthesized CdS nanorod/r-GO heterostructures, which demonstrated high catalytic activity for the CO_2 reduction with 10 times higher CH_4 production rate compared to pure CdS and even better than Pt loaded CdS [80]. Moreover, Meng *et al.* established the concept of photogenerated electron transfer from α-Fe_2O_3 nanoparticles to the graphene surface through transient absorption spectroscopy and time-domain terahertz spectroscopy, which increases the lifetime of charge carriers and, consequently, improve the photocatalytic activity [81]. Li *et al*. showed bandgap engineering and enhanced interface coupling of graphene–$BiFeO_3$ nanocomposites by the formation of Fe—O—C bonds, which demonstrated enhanced photocatalytic activity under visible-light illumination [82]. Yang *et al.* synthesized functionalized graphene sheets/ZnO nanocomposites that exhibited an enhanced photocatalytic activity for the degradation of rhodamine [83]. Zhang *et al.* showed the excellent performance of CdS–graphene nanocomposite photocatalyst for selective oxidation of alcohol to corresponding aldehyde [84]. Moreover, Han *et al.* successfully prepared ternary CdS/ZnO/graphene composite, which showed enhanced visible-light-induced photocatalytic activity in comparison to binary composites and pure ZnO and CdS [85]. Hence, this study highlights the significance of charge transport on graphene surface of heterostructures during catalysis reaction. Recently, another graphene-like material, layered structures of MoS_2 have been used as a cocatalyst to modify different semiconductors for hydrogen production and pollutant removal [86–88]. Zhou *et al.* prepared few-layered MoS_2 nanosheet-coated TiO_2 nanobelt heterostructures to increase the visible-light absorption ability of TiO_2, and MoS_2/TiO_2 composites showed high photocatalytic activity in the degradation of organic dyes [89]. Another example, few-layered MoS_2/BiOBr hollow microspheres demonstrated superior

visible-light-response photocatalytic activity for ciprofloxacin and rhodamine B removal in comparison to BiOBr alone [90]. The conduction band (CB) edge potential of MoS_2 (−0.09 eV) is more negative than that of BiOBr (0.29 eV), and the valence band (VB) of BiOBr (3.06 eV) is more positive than that of MoS_2 (1.81 eV). The energy difference between the CB edge potentials of MoS_2 and BiOBr leads to the transfer of the electrons from the CB of MoS_2 to that of BiOBr. Hence, the photogenerated electrons can be collected by BiOBr, and holes can be collected by MoS_2, which causes effective charge separation and can be reflected in enhanced photocatalytic activity. Graphitic carbon nitride (g-C_3N_4) considered as a low-cost photocatalytic system having a graphene-like structure consisting of two-dimensional frameworks of tri-*s*-triazine connected via tertiary amines with a bandgap of ∼2.7 eV, corresponding to an optical wavelength of 460 nm in the visible-light range [91, 92]. Hence, two-dimensional g-C_3N_4 nanosheets having a graphene-like structure consisting of two-dimensional frameworks of tri-*s*-triazine connected via tertiary amines also offers large surface area and active sites, which are beneficial for photocatalytic oxygen evolution and CO_2 photoreduction [93, 94]. Moreover, transition-metal-based inorganic compounds have also been coupled with g-C_3N_4 for the fabrication of noble-metal-free heterostructured photocatalysts. The composites of g-C_3N_4 and metal oxides (e.g., TiO_2, ZnO, In_2O_3, and Bi_2WO_6) have been investigated by various research groups for CO_2 photoreduction [95–98]. Chapter 15 covers the current progress of visible-light-induced conversion of CO_2 to fuels by heterogeneous photocatalysts over the metal oxides, sulfides, phosphides, oxynitrides, and organic semiconductors as well as highlights the importance of graphitic carbon nitrides as emerging photocatalyst.

Another way to extend the range of TiO_2 activity to the visible region is modification with visible-light-absorbing dyes such as rose bengal, chlorophyllin, porphyrins, or phthalocyanines [99–101]. Dye-modified TiO_2 can be used for visible-light-assisted photocatalytic degradation of a great variety of organic pollutants from wastewater effluents either by oxidative or reductive processes. Sensitization of TiO_2 and other photocatalysts by modification with dyes has been reviewed in Chapter 10, with an emphasis on the physicochemical properties of the modified photocatalysts, the mechanisms involved in the transformation of pollutants, and the possible technological applications. However, the use of organic dyes as sensitizers of semiconductors has the disadvantage of gradual degradation of organic molecules, which in turn affects the stability of catalysts.

1.3 Photocatalysis for Water Splitting

Solar H_2 production by photocatalytic water splitting appears to be an attractive route to store solar energy in chemical bonds from renewable resources (water and sunlight) [102, 103]. However, the complexity of resolving the complete water splitting problem, structure–property relationships of photocatalysts for the two half reactions of water splitting, hydrogen and oxygen evolution reactions in the

presence of sacrificial reagents have been studied extensively [104, 105]. Hence, light-driven water splitting is recognized as one of the major scientific challenges for hydrogen production. Since the first pioneer report of photocatalytic water splitting using titanium dioxide by Fujishima and Honda , numerous research studies have been conducted on semiconductor materials with proposed mechanisms of photocatalytic water splitting [47]. A photocatalytic system for the photoreduction of protons to produce H_2 consists of a photosensitizer, a catalyst, and sources of protons and electrons [104]. The reaction is first initiated by photon absorption, which generates numerous electron–hole pairs with sufficient potentials. The relevant photoreduction processes involve

i) absorption of light by the photosensitizer and subsequent internal charge separation
ii) intermolecular charge transfer (i.e., reduction of the catalyst by the photosensitizer and reduction of the photosensitizer by direct hole donation from a sacrificial electron donor)
iii) catalytic formation of H_2 by the reduced catalyst.

Sacrificial electron acceptors ($S_2O_8^{2-}$, $Ce(SO_4)_2$, $FeCl_3$, Ag^+ from $AgNO_3$, etc.) and donors (ethanol, methanol, triethanolamine, Na_2S, $Na_2S_2O_3$, and Na_2SO_3) control the production of either hydrogen (electron donor) or oxygen (electron acceptor) by combining with the respective charge carrier. The fundamental aspects of direct photoelectrochemical (PEC) water splitting at semiconductor electrodes are discussed along with recent experimental progresses in Chapter 3. The roles of different experimental parameters for successful water-splitting systems are also included. An overview of recent research progress in photochemically induced water splitting into hydrogen and oxygen with emphasis on new electrode materials, theoretical advances, and the development of experimental methods for light-driven water-splitting reactions has been discussed in Chapter 13 to identify stable, efficient, and cost–effective light-driven Photocatalytic systems. Now the challenge is to fabricate earth-abundant photoelectrodes and catalyst materials with high efficiency, good durability, and low cost. Recently, new visible-light-responsive photoelectrodes, including α-Fe_2O_3, $BiVO_4$, WO_3, CdS, C_3N_4, and photoanodes have been tested for water splitting [106–109]. However, severe recombination of photogenerated electron–hole pairs on the surface results in poor performance of photocatalysts. Various attempts have been made to improve the performance of photocatalysts via doping, loading of cocatalysts, and heterojunctions [19, 57, 110–113]. Alivisatos and co-worker reported the design of multicomponent nanoheterostructures composed of platinum- tipped cadmium sulfide rod with an embedded cadmium selenide tips as highly active catalysts for hydrogen production with an apparent quantum yield of 20% at 450 nm [114]. Zhang *et al.* fabricated two-dimensional titania/cadmium sulfide heterostructures through a controlled sol–gel method with an excellent hydrogen evolution activity under visible-light irradiation and an apparent quantum yield of 6.9% at 420 nm [115]. Cao *et al.* developed a highly efficient and robust heterogeneous

photocatalytic material for hydrogen generation (254 000 μmol h^{-1} g^{-1} for the initial 4.5 h) using the CoP/CdS hybrid catalyst in water under solar irradiation [116]. Kozlova *et al.* synthesized a multiphase photocatalyst $Cd_{1-x}Zn_xS/TiO_2$ with 3D ordered meso-/macroporous structure for H_2 evolution reaction from aqueous solutions of Na_2S/Na_2SO_3 under visible-light irradiation [117]. Zong *et al.* have employed MoS_2/CdS hybrid structure as a catalyst for photocatalytic H_2 evolution under visible-light irradiation [118].Wang and co-workers developed shish-kebab-like multiheterostructured metal chalcogenides (CdS—Te, NiS/CdS—Te, and MoS_2/CdS—Te) photocatalysts to exhibit enhanced efficiency and stability toward photocatalytic H_2 generation due to intimate interactions between CdS and multicomponent cocatalysts, together with improved separation of photogenerated carriers due to the presence of Te nanotubes and trace CdTe [119]. A series of MoS_2-based heterostructures, such as MoS_2/TiO_2 and MoS_2/graphene, have been tested for enhanced visible-light photocatalytic activities [87, 120]. Shen *et al.* showed one-dimensional MoS_2 nanosheet/porous TiO_2 nanowire hybrid nanostructures that facilitated charge separation and enhanced hydrogen generation rate of 16.7 mmol h^{-1} g^{-1} in visible light. Chang *et al.* synthesized MoS_2/G-CdS composite with an unexpected hydrogen evolution reaction activity. MoS_2/G-CdS demonstrated as a promising photocatalyst with high efficiency and low cost for photocatalytic H_2 evolution reaction with a 1.8 mmol h^{-1} H_2 evolution rate in lactic acid solution corresponding to an apparent quantum efficiency (AQE) of 28.1% at 420 nm, which is much higher than that of Pt/CdS in lactic acid solution. Graphitic carbon nitride, another carbon-based π-conjugated semiconductor material with a planar phase analogous to graphite, is also suitable for photocatalytic hydrogen production from water splitting made catalytic applications [121, 122]. However, quantum yields under visible light for H_2 production from water using g-C_3N_4 is still limited (not exceed 4%) due to the high recombination rate of the photoinduced electron–hole pair [91, 93]. Synthesis of porous g-CN, heteroatom-doped g-CN, metal-doped g-CN, structural modification with organic groups, metal oxide-g-CN composites, g-CN-graphene/CNT composites, and g-CN-based Z-scheme with enhanced photocatalytic activity for either H_2 or O_2 generation has been discussed in Chapter 12. Different nanostructured g-CN materials, such as nanosheets, nanospheres, and quantum dots, covalent organic frameworks (COFs), such as hydrazone COFs, donor–acceptor heptazine systems, and conjugated microporous polymers (CMPs) based on pyrene prepared from various C—C coupling reactions for water-splitting applications have also been focused in detail. Excellent performance was realized by hybridization of g-C_3N_4 with other cocatalysts. For example, metal sulfides, such as NiS, MoS_2, WS_2, and hydroxides, such as $Ni(OH)_2$ and $Co(OH)_2$, have been successfully deposited on g-C_3N_4 as cocatalysts for improved photocatalytic hydrogen production [123–126]. Meng *et al.* incorporated g-C_3N_4 into Ag_3PO_4, which exhibited an improved catalytic activity for the degradation of methylene blue under visible-light irradiation [127]. The synergic effect between between g-C_3N_4 and Ag_3PO_4 led to structural stability for silver phosphate and high separation efficiency owing to the well- positioned CB and VB and consequently improved photocatalytic activity. Besides the single-phase and heterostructure-based photocatalysts,