# Fuel Production with Heterogeneous Catalysis

## Edited by Jacinto Sá



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### Preface

This book describes the importance of catalysis for the sustainable production of fuels, focused primarily on the state-of-the-art catalysts and catalytic processes anticipated to play a pivotal role in the production of fuels. The growth in energy prices, environmental trepidations, and population commanded the development of new and/or improved processes to attain sustainability and energy stability, and ultimately mankind's current way of life.

Heterogeneous catalysis plays an essential role in improving industrial processes, including a water–gas shift, and coal combustion in respect to greenhouse gas emissions and profitability. Novel technologies, including solar energy harvesting and conversion, provide an attractive means toward carbon independence; however, they are not yet economical, thus requiring further research.

Herein, we compile the latest developments on fuel production processes with heterogeneous catalysis, including reaction mechanism schemes, engineering solutions, and perspectives for the field. The book is aimed for undergraduate and graduate students as well as scientists working in the area. It should be mentioned that the goal of the book is to provide an overview of the field. The examples were chosen to cover a larger range of scientific experiments as concisely as possible. Therefore, and on behalf of the authors, we would like to apologize for any work that has not been referenced or mentioned. The omission was decided simply on the basis of chapter concision. Finally, the book was written in a language that we consider accessible to most science undergraduate students. Technical terms were mentioned only when strictly necessary.

On a personal note, I thank the chapter authors for their contribution and all the scientific works that made the execution of this book possible.

Jacinto Sá Polish Academy of Sciences

## Editor

Dr. Jacinto Sá (PhD in physical chemistry) is the Modern Heterogeneous Catalysis (MoHCa) group leader at the Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland. He earned an MSc in analytical chemistry at the Universidade de Aveiro, Portugal, and did his research project at the Vienna University of Technology, Vienna, Austria. He earned a PhD degree at the University of Aberdeen, Scotland, in the field of catalysis and surface science. In 2007, he moved to the CenTACat group at Queen's University Belfast, Belfast, Northern Ireland, to start his first postdoctoral fellowship under the guidance of Professors Robbie Burch and Chris Hardacre. During his stay, he was awarded an R&D100 for his involvement in the development of SpaciMS equipment (Hiden Analytical, Warrington, UK). In 2010, he moved to Switzerland to start his second postdoctoral fellowship at ETH Zurich and the Paul Scherrer Institute. His research efforts were focused on the adaptation of high-resolution x-ray techniques to the study of catalysts and nanomaterials under working conditions. In 2013, he joined the Laboratory of Ultrafast Spectroscopy, the École Polytechnique Fédérale de Lausanne (EPFL), Switzerland, to expand the use of high-resolution x-ray techniques into the ultrafast domain and to take advantage of the newly developed XFEL facilities.

Currently, Dr. Sá's research efforts are focused on understanding the elemental steps of catalysis, in particular those taking place in artificial photosynthesis and nanocatalytic systems used in the production of fine chemicals and pharmaceuticals. His experience in using accelerator-based light sources to diagnose the mechanisms by which important catalytic processes proceed, and more recently conventional ultrafast laser sources, makes him one of the most experienced researchers in the world in this area. He has more than 70 publications in international scientific journals and more than 20 oral and 50 poster presentations at scientific congresses.

Sá is married to Cristina Paun and is expecting his first child, a boy to be named Lucca V. Sá. He is a member of Portuguese think tank O Contraditorio, which is part of the English volunteer group of the Red Cross Zurich, and a part-time DJ (DJ Sound It). He enjoys fine art, in particular impressionism and surrealism, traveling, music, cinema, and fine dining.

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## 1 Solar Water Splitting Using Semiconductor Systems

Lorenzo Rovelli and K. Ravindranathan Thampi

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This chapter deals with sustainable hydrogen production by water splitting under sunlight using semiconductor materials. We will start with a broad overview of the field, briefly dealing with its history and evolution, and thereafter present the state of the art in a logical manner by highlighting the current and future research trends, and finally conclude with a critical perspective.

#### 1.1 INTRODUCTION ON SOLAR WATER SPLITTING

#### 1.1.1 GENERAL INTRODUCTION

It is often said that artificial photosynthesis is the "Holy Grail" of chemistry. After almost two decades since the first introduction of this metaphor by A. J. Bard and M. A. Fox [1], it is still pretty common to find similar statements among the scientific community. And in some ways this is not surprising; indeed, energy is often considered to be the most important problem for mankind in the coming years [2]. In particular, the need for clean and sustainable energy sources is of high priority for at least two reasons. First, it is well known that the fossil fuel resources are limited and the extraction of such fuels will require continuously growing financial investments. Secondly, there is general agreement that threats like global warming and climate change in general are associated to the significantly huge and still growing anthropogenic emissions of greenhouse gases to the atmosphere [3]. It is also widely recognized that, being completely renewable and plentiful, solar energy is one of the best candidates to feed the energy needs of humanity. However, this is obviously an intermittent energy source and therefore needs to be associated with an efficient energy storage system. Hydrogen produced from nonfossil sources appears to be the best fuel that qualifies as a clean energy vector [4]; the ideal energy system would then associate solar light as the energy source and hydrogen produced from water as an energy storage means. Conceptually, two general configurations can be adopted to achieve such a system; the most obvious "brute-force" approach simply involves using a photovoltaic module (PV) to power a conventional dark electrolyzer. A most elegant, yet most challenging approach is the direct conversion of sunlight into hydrogen using a stand-alone integrated device, a solar water-splitting cell. Despite the several underlying challenges, as will be pointed out in this chapter, this second approach has several advantages over the conventional "brute-force" approach, in particular for decentralized energy production, still deserving the title of "Holy Grail" of chemistry.

#### 1.1.2 HISTORICAL BACKGROUND ON SOLAR WATER SPLITTING

The origins of the concept of photoelectrochemical energy conversion date back to the middle of the nineteenth century, as Antoine C. Becquerel together with his son Alexandre-Edmond Becquerel discovered the photoelectrochemical effect (which at the time was called Becquerel effect, in their honour) in 1839 [5]. In their device, a voltage and an electric current were generated upon illumination of a silver chloride photoelectrode immersed in a liquid electrolyte and connected to a metallic electrode. This setup represented the first photovoltaic device ever reported. A similar scheme, involving illumination of silver halides, was by the way utilized in the same period for photographic applications, although the underlying mechanism was not understood until about one century later [6]. Interestingly, the development of film photography and photoelectrochemical cells turned out to be tightly correlated in subsequent years, as the two technologies rely on similar photochemical mechanisms; however, extensive practical applications and widespread commercial interest turned out to be restricted only to the field of photography. The role that photochemical techniques could potentially play for power generation was however highlighted in 1912 by Giacomo L. Ciamician in his brilliant contribution in *Science*. In this paper, he already realized that the fundamental problem is "how to fix the solar energy through suitable photochemical reactions" and that a potential key to the problem would be the "artificial reproduction of [...] the assimilating processes of plants" [7].

However, significant advances, in both understanding of the photoelectrochemistry and its applications, did not occur until the 1950s, when extensive research was carried out on the optical, electronic, and photochemical properties of single-crystal semiconductors. In parallel, biochemists have made also fundamental discoveries about how natural photosynthesis occurs, notably the roles of Photosystems I and II, as well as that of the thylakoid membrane, and the unique architecture of light-harvesting chloroplasts in plants. Theoretical physicists and chemists have continuously looked for clues in natural photosynthesis in order to be able to replicate it and-ideally-improve it. Excellent reviews are available on the mechanisms underlying the plant photosynthesis [8]. Basically, the natural photosynthetic machinery involves two functional units: a light-harvesting center and a reaction center. The first unit is responsible for absorbing sunlight, converting its energy into photogenerated charges through electronic excitation, and effectively mediating their separation over large distances to the site of the second functional unit. This second unit is then responsible for the conversion of the net excitation energy into an electrochemical potential difference, which ultimately provides the driving force for all biological energetics [9]. The integration of knowledge arising from these various fields has allowed researchers to bring out path breaking progress in artificial photosynthetic systems research and exploitation.

The early advances in artificial photosynthesis are in particular due to extensive research carried out in the mid-1950s at the Bell Laboratories, where the electrochemical properties of germanium and of silicon were first investigated in aqueous solutions [10]. While the same Bell Laboratories developed the first practical photovoltaic device in the same years [11], the first actual photoelectrochemical devices were reported only many years later, and research in the field of photoelectrochemistry was until the 1970s essentially of fundamental nature. In particular, the photocatalytic properties of some metal oxide semiconductors (zinc oxide, titanium oxide, and antimony trioxide) were first studied by Sister Clare Markham in 1955 [12]. Although the most well-studied materials were  $TiO_2$  [13] and ZnO [14–16], these fundamental investigations were extended in the 1960s to other semiconductor materials such as CdS [17] and GaP [18], and allowed the development of a theoretical model to describe the junction forming at the interface between a metal or semiconductor and a liquid electrolyte. The main contributor to the understanding of such solid–liquid junction was the German chemist Heinz Gerischer. Despite devoting most of his efforts to understanding the underlying mechanisms of the photochemical processes occurring at the solid–liquid junction [19–21], Gerischer later recognized that the phenomena observed could actually lead to the realization of photoelectrochemical solar cells, for which he gave some design principles and some examples of materials, such as CdS, CdSe, and GaP [22] as well as ZnO [23]. For an exhaustive collection of the work carried out by H. Gerischer in the field of photoelectrochemistry, the interested reader is referred to one of his several book chapters [24].

The most significant advance for applied photoelectrochemistry occurred, however, in 1972 as the Japanese chemists Akira Fujishima and Kenichi Honda first reported in Nature the demonstration of electrochemical photolysis of water into hydrogen and oxygen using an illuminated TiO<sub>2</sub> photoelectrode and a dark Pt electrode [25]. This experiment represented the first successful use of a semiconductor electrode for light-driven water splitting. However, more than 10 years before this, an organic photosensitive material had already been effectively investigated for the same purpose by H. Kallmann and H. Pope, who reported in a 1960 Nature article successful photodecomposition of water into hydrogen and oxygen using an illuminated anthracene crystal [26]. After the groundbreaking article by Honda and Fujishima, the interest for metal oxides and in particular TiO<sub>2</sub> for photoelectrochemical and photocatalytic applications grew dramatically, especially in the 1970s and the 1980s. Simultaneously, a new class of semiconductor materials emerged in the fields of solar energy conversion: III-V semiconductors. The photoelectrochemical properties of these materials, in particular GaAs, InP, and GaP, were thoroughly investigated in the late 1970s and early 1980s in particular by the group of Allen J. Bard at the University of Texas at Austin [27-30] as well as several other groups [31-34]. The most significant breakthrough obtained till date with this class of materials was in 1998 as John A. Turner and Oscar Khaselev obtained a 12.4% record efficiency for a watersplitting device using GaInP<sub>2</sub>, described in Section 3.3; unfortunately, the stability of the device was limited only to few hours [35].

While the earlier studies regarded single-crystal and later polycrystalline materials, the tendency of the last two decades is to employ nanostructured materials. This was largely due to the breakthrough obtained by Michael Grätzel and Brian O'Regan in 1991, as they showed that by nanostructuring a semiconducting electrode it is possible to increase the device solar energy conversion efficiency by over an order of magnitude [36]. Although this work involved a regenerative device (i.e., a photovoltaic cell), the same concept was extended to photoelectrochemical cells for water splitting. Photoelectrodes involving the use of surface modifications and of composite materials are another direction that was allowed in the last two decades by the advances in nanotechnology; these involve in particular dye- and quantum-dots-sensitized photoelectrodes, as well as deposition of protective layers, catalytic materials, or plasmonic metal nanoparticles. In the last decade, research was also focused on finding a suitable catalyst for oxygen evolution and hydrogen evolution. This indeed represents a very old and significant problem, since the only effective catalysts traditionally involve noble metals. An important advance in this field was enabled by the discovery in 2008 by the group of Daniel G. Nocera at Massachusetts Institute of Technology of a new noble-metal-free oxygen evolution catalyst composed of inexpensive cobalt, now widely known as Nocera's catalyst [37].

#### 1.1.3 THEORETICAL PRINCIPLES OF SEMICONDUCTOR-BASED SOLAR WATER SPLITTING

In some of the solar water-splitting device types considered here, the presence of a solid–liquid junction between a semiconductor and an electrolyte plays a fundamental role. Therefore, some general considerations about semiconductors and a short description of the phenomena occurring at the solid–liquid junction between a semiconductor and an electrolyte are imperative. However, this section will be limited to a brief description of the most important concepts; for a comprehensive discussion of semiconductor properties and semiconductor–liquid junctions (SCLJs), the interested reader is referred to the available literature covering the field [38–40].

#### 1.1.3.1 Key Properties of Semiconductor Materials

Unlike metals, semiconductors are materials characterized by a gap in the density of electronic states. This gap however is sufficiently small so that electronic conduction is possible under certain conditions. At room temperature, the concentrations of electrons in the conduction band and holes in the valence band are generally very small. This is in accordance with the Arrhenius-like relation (Equation 1.1), where n and p are the concentrations of electrons and holes in the conduction band and the valence band, respectively;  $N_c$  and  $P_v$  are the corresponding density of states in the conduction and the valence band, respectively;  $E_g$  is the bandgap of the material; k is the Boltzmann constant; and T is the absolute temperature.

$$n \cdot p = N_C \cdot P_V \cdot e^{-E_g/kT} \tag{1.1}$$

However, this situation can be drastically modified by heating or illuminating the material. In the case of intrinsic semiconductors, the amount of negative charges in the conduction band always equals the amount of positive charges in the valence band. For doped semiconductors, this is no longer the case: considering the case of p-type semiconductors, the amount of holes in the valence band is significantly higher than the amount of electrons in the conduction band. In such a material, electrons and holes are therefore referred to as the minority and majority carriers, respectively.

$$E_F = \frac{E_V + E_C}{2} + \frac{kT}{2} \cdot \ln\left(\frac{n \cdot P_V}{N_C \cdot p}\right)$$
(1.2)

According to the above equation, where  $E_F$  is the Fermi level, and  $E_V$  and  $E_C$  are the energies of the top edge of the valence band and the bottom edge of the conduction band, respectively, this implies that the Fermi level of a p-type semiconductor is not in the middle of the bandgap (as is the case for intrinsic semiconductors, neglecting the contribution of the reduced mass of the electron and of the hole), but rather is shifted toward the top edge of the valence band. How close this is to the valence band depends on the doping level: the higher the p-doping level, the closer the Fermi level to the valence band. In some cases, the doping level can be so substantial that the Fermi level lies within the valence (for p-doping) or the conduction band (for n-doping). Transparent conductive oxides, such as Al-doped zinc oxide, are important examples of this family of semiconductors, which are said to be degenerate.

#### 1.1.3.2 Semiconductor-Liquid Junction and Semiconductor Photoelectrodes

It is well known that a photovoltaic device can be obtained upon contact between a p-doped and an n-doped semiconductor. Considering the simple case of a homojunction, that is, when the two sides of the junction are composed of the same material (e.g., n-Si and p-Si), it is well known that a band bending will establish at the interface upon equilibration of the Fermi levels of the two materials. An analogous situation originates upon contact between a doped semiconductor and an electrolyte. In the context of solar water splitting, this interfacial band bending and the electrical field associated can be exploited for the formation of photoanodes and photocathodes for water oxidation and water reduction, respectively. The case of a p-type semiconductor material in contact with an aqueous electrolyte (typically constituting a photocathode where water reduction can occur) will be considered here in detail, while the case of n-type photoanodes for water oxidation is entirely analogous. In commonly used photocathode systems, the Fermi level of the p-type semiconductor (and thus the electrochemical potential of the electron in the solid) turns out to be lower in energy than the redox potential of the electrolyte. This implies that upon equilibration of the electrochemical potentials for the electron, a net flow of negative charges will occur from the electrolyte to the p-type semiconductor. This will cause an increase in the energy of the conduction and the valence bands of the semiconductor; however, the energy of these bands turns out to be fixed right at the interface, due to the presence of adsorbed ions (called potentialdetermining ions) within the Helmholtz layer. Therefore, the energy of the bands will increase only in the bulk of the semiconductor; as a consequence, a band bending situation is encountered, where the bands bend "downward" from the bulk of the semiconductor toward the interface. This is exactly the situation that is needed to drive electrons toward the interface (and thus react with any adsorbed species having a suitable redox potential) and holes toward the bulk of the material (and thus be collected at the backcontact), and is therefore the desired situation for a photocathode.

However, one should note that this charge separation is only effective for electronhole pairs that are generated sufficiently close to the interface: in principle, only electron-hole pairs that are generated within the space-charge layer are readily separated by migration within the electrical field (band bending). In fact, it turns out that pairs that are generated close enough to the space-charge layer can be separated as well, provided that the diffusion of the electrons is faster than the competing recombination of the electron-hole pair. Therefore, one would ideally look for a space-charge layer as large as possible; unfortunately, a larger space-charge layer implies a lower doping level, as shown by Equation 1.3, where  $W_{SC}$  is the width of the space-charge layer,  $N_D$  is the concentration of dopants,  $\varepsilon_0$  is the permittivity of vacuum,  $\varepsilon_r$  is the dielectric constant of the material,  $V_a$  is the applied potential,  $V_{fb}$  is the flat-band potential, and e is the elementary charge.

$$W_{SC} = \sqrt{\frac{2 \cdot \varepsilon_0 \cdot \varepsilon_r \left| V_a - V_{fb} \right|}{e \cdot N_D}}$$
(1.3)

There is therefore an evident trade-off between electrical conductivity on the one side and the width of the space-charge layer on the other. Experimentally, the concentration of dopants (doping level), and therefore the width of the space-charge layer, can be found by performing a Mott–Schottky analysis from capacitance measurements. According to the Mott–Schottky Equation 1.4, where *C* is the interfacial capacitance and *A* is the interfacial area, the plot of the inverse square of the capacitance against the applied potential allows establishing the flat-band potential of the semiconductor as well, by simple extrapolation on the potential axis.

$$\frac{1}{C^2} = \frac{2}{\varepsilon_0 \cdot \varepsilon_r \cdot e \cdot N_D \cdot A^2} \left( \left| V_a - V_{fb} \right| = \frac{kT}{e} \right)$$
(1.4)

One has to note that the above equation only applies under depletion conditions, that is, it only holds for the range of applied potential leading to a depletion of majority charge carriers within the space-charge region. Furthermore, the Mott–Schottky analysis is based on the assumption that the capacitance of the electrochemical double layer is several orders of magnitude higher than the capacitance of the space-charge layer, and its contribution to the total (i.e., measured) capacitance is therefore negligible. The flat-band potential is an important characteristic of a semiconductor, as it reflects the position of its Fermi level before contact with the electrolyte. In the case of p-type semiconductors, the flat-band potential therefore gives an indication of the energy of the valence band edge. The energy of the conduction band edge can then be estimated by adding the energy of the valence band edge to the value of the bandgap, which can in turn be determined experimentally by transmittance or reflectance spectroscopy measurements.

#### 1.1.4 AN OVERVIEW OF THE MAIN APPROACHES TOWARD SOLAR WATER SPLITTING

Several different approaches have been developed toward solar water splitting using semiconductor materials. An important distinction among these approaches is the one between systems using suspended semiconductor particles and systems featuring semiconductor electrodes. The first approach is commonly and broadly referred as photocatalytic systems (described in Section 1.3.1) and is arguably the simplest conceivable type of solar water-splitting device. The second approach, on the other hand, involves both photoelectrochemical cells (presented in Section 1.3.2) and photovoltaic-based

cells (described in Section 1.3.4). In all these three approaches semiconductor materials play an essential role, as they are responsible, among the other things, for harvesting the incident sunlight. However, there is a fourth approach, namely dye-sensitized solar water splitting, where this does not happen to be the case. In this concept (presented in Section 1.3.5), the semiconductor material acts instead as a porous scaffold and as a charge transfer mediator, while the light harvesting is carried out by a dye (or another sensitizer) attached to its surface. An important common point between dye-sensitized and photocatalytic systems in that owing to the size of the particles involved, their mechanism does not necessarily rely on an SCLJ, but rather on the kinetic competition between the various charge transfer processes involved in the system.

The opposite situation is encountered with photoelectrochemical and photovoltaicbased water-splitting cells, as in both cases the semiconductors form a junction, which plays a fundamental role toward effective separation of the photogenerated charges. This can be either a solid–solid junction between two semiconductors (as in most photovoltaic-driven cells considered here) or a solid–liquid junction forming at the interface between the semiconductor and the aqueous electrolyte. There exists a fifth class of water-splitting cells, where two of these junctions are combined in the same device, known as water-splitting tandem cells. Broadly speaking, two different classes of tandem cells can be conceived, which are known as photoanode–photocathode cells and photoelectrode–photovoltaic hybrid cells, respectively (as described in Section 1.3.3).

A concept related to solar water splitting is solar-driven hydrogen evolution from wastewater and biomass; within this type of devices, hydrogen generation is coupled to degradation of organic molecules, such as dyes, sugars, and alcohols. This concept is extremely interesting from a practical point of view, as the goal of hydrogen production is coupled to decontamination of industrial effluents or efficient utilization of energy-rich biomass. Furthermore, this concept shares many aspects with solar water splitting from a mechanistic point of view. However, as the scope of this chapter is confined to overall water-splitting systems, this concept will not be discussed in detail here; the interested reader is instead referred to Chapter 2.

#### 1.2 MATERIALS FOR SOLAR WATER SPLITTING: REQUIREMENTS AND CURRENT TRENDS

#### 1.2.1 SEMICONDUCTOR MATERIALS FOR SOLAR WATER Splitting: General Requirements

In practice, a suitable semiconductor material for solar water splitting must satisfy a number of conditions. Foremost, the material has to yield a reasonable photoactivity toward water splitting; in other words, a reasonable solar-to-hydrogen conversion efficiency. Generally, the accepted energy conversion threshold for a commercial solar water-splitting system would be 10%, although the vast majority of the materials investigated so far are not capable of yielding such high performances. To achieve this high activity, the semiconductor material must be capable of absorbing sunlight over a wide range of wavelengths with photonic energy being larger than the minimum energy required to split water and to subsequently perform an efficient conversion into chemical energy. The second most critical criterion for the choice of a suitable semiconductor material for a practical solar water-splitting device is its stability. This implies that the photoactivity (and therefore the conversion efficiency or in other words the amount of hydrogen generated) has to be sustained for a sufficiently long period of time, typically several years to be practically useful. Typically, a system is considered to achieve satisfying stability if its performances do not change significantly over the course of a 1000-hour test under simulated solar light illumination. In addition, the device should ideally be composed of nontoxic, inexpensive, and readily available materials. Aspects that are even more important for a commercially viable device are that the materials and manufacturing processes involved must be easily upscalable, reproducible, environmentally safe, and relatively inexpensive.

#### **1.2.1.1** Photoactivity of Semiconductor Materials

First and foremost, photoactive semiconductor materials for solar energy conversion must be able to absorb as much light as possible from the solar spectrum. Translated in terms of electronic properties, this implies that their electronic bandgap should be sufficiently small with respect to the photon energy of the incident sunlight. Absorption of solar light allows the generation of electron-hole pairs within the semiconductor absorber that will subsequently need to be separated at its surface; in practical systems, that generally occurs at the interface with another material or another phase. But even before this can occur, however, the photogenerated charges must be able to reach the surface of the material before recombining; this implies good electrical conductivity within the material and ideally the absence of any trap states. Typically, this in turn requires the use of high purity and defect-free materials, as impurities and defects are among the major factors responsible for reduced charge mobility within semiconductors. In addition, to ensure that the semiconductor material is capable of overall water splitting, its conduction and valence band edges must straddle the relevant redox potentials for the water-splitting reaction: the conduction band bottom edge of the semiconductor must be higher in energy than the redox potential of the  $H^+/H_2$  couple, while its valence band top edge must be lower in energy than the redox potential of the  $O_2/OH^-$  couple. As the standard potential of the O<sub>2</sub>/OH<sup>-</sup> redox couple is 1.23 V/RHE, this condition imposes a thermodynamic minimum value of 1.23 eV for the bandgap of the material, which corresponds to photons having maximum wavelength of 1008 nm being absorbed. However, in addition to thermodynamic considerations, kinetic losses have to be taken into account in any practical system. In accordance to the Marcus theory for heterogeneous charge transfer, the energy difference between the band edges and the potential of the redox couples have to be sufficiently high to ensure enough driving force for the electron (or hole) transfer to happen at a reasonable rate [41]. Due to these ubiquitous kinetic losses, as well as to resistive Ohmic losses which are present within any realistic system, the optimum bandgap for a semiconductor absorber material turns out to be substantially increased, to over 2 eV [42,43]. Obviously, there is therefore a fundamental trade-off, as a large bandgap material is desirable to obtain the sufficient driving force for unassisted water splitting, while on the other hand a small bandgap material would harvest a higher amount of photons from sunlight, thus yielding more photogenerated charges. This is clearly exemplified by the wide-bandgap material anatase TiO<sub>2</sub>, which has a bandgap of 3.2 eV (thus absorbing only the UV portion of the solar spectrum), for which the maximum theoretical solar-to-hydrogen (STH) efficiency is only 1%, while hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>)—which has a bandgap of 2.2 eV (thus absorbing UV and a portion of the visible wavelengths)—features a maximal theoretical STH efficiency of 15% [44]. Since the overall efficiency of the water-splitting process is dictated by both the amount of charges generated and their driving force toward water splitting, this trade-off leads in practice to limited efficiencies when only one semiconductor material is used to harvest sunlight.

In practice, various strategies have been proposed and investigated in order to relax the various material constraints and in particular to overcome some of the fundamental trade-offs. The two most common approaches in the literature are the use of multiple absorber materials (in what are known as photoelectrochemical tandem cells and photocatalytic Z-schemes, discussed in Sections 1.3.1.2 and 1.3.3, respectively) and the sensitization of a wide-bandgap semiconductor with sunlight-harvesting dye molecules. A further possible approach is of course to simply connect the photocatalytic or photoelectrochemical cell to any external bias, in order to generate the required voltage for overall water splitting; such a configuration, however, cannot be classified as unassisted solar water splitting, unless the external bias is generated by a photovoltaic cell. In some experiments, like the Fujishima and Honda's seminal work, a wide difference in chemical potentials between the liquid medium (aqueous electrolyte) present in a twocompartment cell was maintained in order to take advantage of the fact that for every 1 pH unit about 59 mV of potential difference could be generated between the two electrodes [25]. Again, this is akin to applying an external chemical potential and involves the use of bases and acids. Finally, the use of sacrificial agents is another possible option to relax the constraints in terms of material photoactivity. In this situation the difference between two relevant redox potentials involved in the overall reaction turns out to be smaller than 1.23 eV, which allows for the use of lower bandgap semiconductors. In these systems, however, only one of the two water-splitting half-reactions is carried out by the photogenerated charges – the other half-reaction arising from decomposition of the sacrificial agent - and overall water splitting, is therefore not achieved.

#### 1.2.1.2 Stability of Semiconductor Materials

All of the aforementioned conditions are necessary to ensure a reasonable photoelectrochemical or photocatalytic activity of the material, translating into a high efficiency of the solar water-splitting cell. However, activity is far from being the only important parameter for a commercially viable device; the second most important factor being the stability of the materials, implying that the efficiency of the device should not significantly decrease with time. As pointed out by Butler and Ginley, a candidate semiconductor material for solar water splitting has to be stable on various different levels [45]; for photoelectrochemical energy conversion there are in fact three main factors which can lead to material instability. These are the nature of the electrolyte with which the material is in contact, the electrical potential applied, and the effect of light illumination. This means that the semiconductor material has to be stable against chemical dissolution, electrochemical corrosion, and photocorrosion.

The third factor, photocorrosion, is unique to photosystems and represents is in fact a self-inflicted damage caused by kinetic factors besides thermodynamic reasons

and arising from the photogenerated holes consuming the semiconductor itself. In fact, for a given combination of pH value and potential, a material can be stable in the dark according to its Pourbaix diagram but unstable under light illumination; this is because of the photogenerated holes and electrons within the material, which are strongly oxidizing and reducing species, respectively, and can thus lead to oxidative or reductive decomposition of the material. From a *thermodynamic* point of view, a semiconductor is said to be unstable against oxidative (or anodic) decomposition if the redox potential for its anodic decomposition reaction lies above the valence band edge, while it is classified as unstable against reductive (or cathodic) decomposition if the redox potential for its cathodic decomposition reaction lies below the conduction band edge. The vast majority of the materials reported turn out to be thermodynamically unstable and susceptible of photodecomposition; however, several materials appear to be relatively stable when tested in practice.

This apparent contradiction is related to favorable *kinetic* competition between the decomposition reactions and the reactions of interest (water oxidation and water reduction). In fact, what is critical from a practical point of view is the relative position of the redox potential of the decomposition reactions with respect to the water reduction and water oxidation potentials. In accordance to the Marcus theory for electron transfers, the rate at which a charge transfer occurs scales to the square of the driving force. Therefore, for a system within the normal Marcus region, if the driving force for water reduction into hydrogen is sufficiently larger than the driving force for reductive decomposition of the semiconductor material, the latter will not occur at an appreciable rate in practice. Analogously, oxidative decomposition of the material can be avoided if the driving force for water oxidation into oxygen is sufficiently larger than the driving force for reductive decomposition. The latter situation can be exemplified by TiO<sub>2</sub>, which is considered to be among the most stable and robust semiconductor materials, despite actually turning out to be unstable against photodecomposition from a thermodynamic point of view. On the other hand, CdS is perhaps the prototypical example of a material, which is unstable against photodecomposition both from a thermodynamic and a kinetic point of view. It is interesting to note here that CdS, unlike  $TiO_2$ , can absorb a considerable portion of the visible spectrum and hence would have been a suitable material to improve the spectral absorption range and thus attain higher energy conversion efficiencies in water-splitting reactions. It appears that a few general empirical rules can be drawn after decades of experience: in particular, it has been observed that oxide materials typically offer superior electrochemical stability when compared to other semiconductors and that wide-bandgap semiconductors are generally more stable than low bandgap materials. Although these rules bear some rationale associated to the electronic structure of the materials, they are not to be taken for granted as several exceptions exist; for instance, ZnO, despite being a wide-bandgap oxide, is particularly unstable when in contact with an aqueous electrolyte under light illumination. Unfortunately, ZnO is an excellent photocatalyst except for its precarious stability issues arising from its amphoteric nature.

With such unstable materials (such as ZnO or CdS) there still exist some possible strategies to overcome this problem. The most straightforward, which does not involve any modification of the semiconductor material, is to modify the electrolyte by introducing a redox couple, which owing to its appropriate redox potential

can favorably compete with the decomposition reaction, kinetically. These redox couples are known as *sacrificial agents* as they are not regenerated after their oxidation or reduction. A sacrificial electron donor is added to the electrolyte to efficiently compete against oxidative decomposition, while a sacrificial electron acceptor is introduced in the system to prevent reductive decomposition of the semiconductor. Typical examples of sacrificial donors include simple organic compounds like alcohols or inorganic chalcogenide salts or multivalent ions such as  $Ce^{4+/3+}$ . This solution however—which does not represent overall water splitting—presents two major drawbacks: besides the increased overall cost due to the utilization of the sacrificial agent, the fact that a species has to be continuously fed in the system introduces some additional complications from a technical point of view.

Two other major approaches have been pursued to overcome the stability issue, which both involve modification of the surface of the semiconductor itself: an unstable material can be made more stable by deposition of a suitable catalyst or by deposition of a stable passivating material. Owing to its chemical stability,  $TiO_2$  is a commonly employed passivating material, while prototypical examples of catalysts employed are Pt for water reduction and RuO<sub>2</sub> for water oxidation (although a wide range of alternative catalyst materials has emerged in the last decade, described in Section 1.2.3). The two approaches can be seen as fundamentally different, as the first is designed to remove highly reactive photogenerated charge carriers as quick as possible from the semiconductor material, whereas the second is mainly designed to provide a physical barrier between the unstable semiconductor material and the electrolyte. Contrary to a catalyst, which is essentially designed to prevent photocorrosion and electrochemical corrosion of the semiconductor material, a stable passivating material will therefore also be effective to prevent physical dissolution of the semiconductor in the electrolyte. Ideally, a passivating material will therefore coat the entire surface of the semiconductor, while on the other hand the presence of a catalyst will be characterized by a small surface coverage. In practice, however, these two strategies are often used in combination and in some systems a material is introduced that can behave as both a catalyst and a passivating agent; even from a mechanistic point of view, it is sometimes not straightforward to determine whether a material rather acts as a catalyst or merely as a physical barrier.

#### 1.2.2 MODIFICATION AND NANOSTRUCTURING OF MATERIALS FOR SOLAR WATER SPLITTING

In the previous section, it has been pointed out how difficult it is to develop semiconductor materials, which are both highly photoactive toward water reduction and/or oxidation and sufficiently stable in contact with an aqueous electrolyte and under light illumination. In fact, in practical water-splitting systems, surface modification of the photoactive material with one or more other materials, whether passivating or catalytic, turns out to be virtually always necessary to obtain a reasonably efficient and stable system. While surface passivation and deposition of a suitable catalyst are two major strategies toward stable photoactive architectures, various other approaches have been proposed and successfully demonstrated, in particular to improve the photoactivity of semiconductor materials and therefore the overall solar-to-hydrogen efficiency of water-splitting cells. These strategies can be classified into three major approaches: surface modification, bulk modification, and nanostructuring.

#### 1.2.2.1 Surface Modifications for Enhanced Light Harvesting

Regarding *surface modification*, besides the two aforementioned approaches involving passivation and catalysis, two additional strategies have been pursued in the last decade: surface sensitization, through anchoring of sensitizer molecules on the surface of a wide-bandgap semiconductor, and—more recently—plasmonics, through deposition of plasmonic metallic nanoparticles. These approaches are somewhat similar in that they both have as the main objective an increase of light absorption by the system in the visible spectral range, ultimately leading to an increase in the amount of photogenerated charge carriers and thus an enhancement in the rate of hydrogen production.

The idea of using visible-light absorbing molecules to sensitize wide-bandgap semiconductors is nowadays well known because of the successful development of the dye-sensitized solar cell (DSSC), a photovoltaic device which can currently reach efficiencies of over 12% [46]. Surprisingly perhaps, this concept has been around for well over a century, as it had been first used in the field of color photography in 1873 [47] and had been applied to the field of energy conversion devices already in 1887 [48]. In the 1960s dye-sensitization has been "rediscovered," in particular thanks to the work carried out by Heinz Gerischer and Helmut Tributsch [23], but it was not until the late 1980s and early 1990s, with the development of fractal and then the mesoporous films of TiO<sub>2</sub> and other semiconductor materials that dye-sensitization became a credible strategy for effective solar energy conversion [36].

Understandably, the development of dye-sensitized water-splitting cells turned out to be significantly more challenging than their regenerative counterpart (i.e., dye-sensitized photovoltaic cells) and significant progress has only been carried out in the last decade. This is essentially due to the different electron transfer kinetics involved: while in dye-sensitized regenerative cells one can choose a suitable redox couple in order to optimize the energetics and the kinetics of the system, the redox potentials of the electrolyte are obviously fixed in the case of a water-splitting cell. In a very similar way to DSSCs, this class of water-splitting cells are typically based on the absorption of visible light by ruthenium-based sensitizers, which are anchored onto the surface of a mesoporous TiO<sub>2</sub> nanocrystalline film and attached to a water oxidation catalyst (WOC), such as iridium oxide nanoparticles [49,50]; these devices are a subclass of photoelectrochemical water-splitting cells. In fact, dye-sensitized photocatalytic water-splitting systems, involving a suspension of TiO<sub>2</sub> nanoparticles, have been investigated as well. These devices are based on various scaffold materials and architectures, ranging from simple TiO<sub>2</sub> nanoparticles [51] to more complex semiconductor/zeolite composites [52] and layered metal oxides semiconductors [53], and will be described in more detail in Section 1.3.5.

The second major class of surface modification involves deposition of plasmonic metallic nanoparticles on the surface of a semiconductor. Despite the effects of metallic nanoparticles first being reported and investigated in the 1970s, their use for water-splitting purposes emerged only in the last decade and is still limited to few materials. Plasmonic effects arising from metallic nanoparticles deposited on semiconducting materials are manifold and they generally all lead to increased light

absorption and thus increased amount of photogenerated charge carriers. The two most important mechanisms involve hot carrier transfer and plasmon resonance energy transfer (PRET) from the metal to the semiconductor, although purely optical effects may come into play as well. The so-called hot carrier transfer refers to the transfer of a photogenerated electron from the conduction band of the confined metal to the conduction band of the semiconductor. This is in many ways analogous to dye sensitization, with the role of the dye molecule played here by a metallic nanoparticle, and allows for visible-light sensitization of wide-bandgap semiconductors, such as TiO<sub>2</sub>. On the other hand, PRET does not involve the transfer of photogenerated charge carriers, but rather of excitation energy. Analogous to the phenomenon of Förster resonant energy transfer (FRET), this phenomenon requires overlap of the emission spectrum of the metallic nanoparticles with the absorption spectrum of the underlying semiconductor. Therefore, this mechanism is mainly exploited in combination with lower bandgap semiconductors, such as  $Fe_2O_3$  or  $WO_3$ . Further details on the various mechanism involved in plasmonic-enhanced photocatalysis can be found in the various reviews recently published in this field [54-56].

A significant milestone on the way to plasmonic-enhanced water splitting has been achieved in 2004, as a  $TiO_2$  film immersed in an aqueous electrolyte had been reported to be photoactive in the visible range upon deposition of gold and silver nanoparticles, which was attributed to the hot carrier transfer mechanism [57]. The beginning of the 2010s showed a dramatic increase in the interest in the field, and several examples of plasmonic-enhanced water splitting have been reported. A significant number of studies have been devoted to the deposition of Au or Ag nanoparticles on Fe<sub>2</sub>O<sub>3</sub> [58-60] and N-doped [61,62] and undoped [63,64] TiO<sub>2</sub> photoelectrodes. In the case of Fe<sub>2</sub>O<sub>3</sub> and N-doped TiO<sub>2</sub>, the enhancement in the photoactivity is usually attributed to PRET because of the spectral overlap between the plasmonic nanoparticles and the semiconductor [55]. While gold and silver appear to be the best plasmonic metals so far, the approach has been extended to other semiconductor materials besides TiO<sub>2</sub>. A heterogeneous Au/CeO<sub>2</sub> composite showed enhanced water oxidation upon visible-light illumination in the presence of Ag<sup>+</sup> as a sacrificial electron donor [65]. The activity of CdS nanoparticles toward photocatalytic hydrogen evolution also appeared to be significantly enhanced when these were connected to Au nanoparticles. In order to achieve an optimum distance between the Au and CdS nanoparticles and thus avoid detrimental charge transfer from the semiconductor to the metal, both CdS and Au nanoparticles were coated with a thin insulating layer of  $SiO_2$  [66]. Enhanced water oxidation has also been reported on Ag/WO<sub>3</sub> nanocomposite photoanodes; in this study, however, the enhanced performances of the composite appeared to be mostly due to optical factors, as the plasmonic nanoparticles can also lead to enhanced light scattering and reduced reflection of light [67]. This constitutes a simple light management system, through which the photons shining on the composite remain "trapped" within the underlying semiconductor and have thus a higher probability to be absorbed by the latter.

#### 1.2.2.2 Bulk Modifications for Enhanced Light Harvesting

Besides surface modification strategies, *bulk modifications* of semiconductor materials offer an additional approach to enhance the photocatalytic activity of semiconductors

and essentially involve changing the composition and/or the structure of the material. Traditionally, most modifications of semiconductor materials generally involved a change in the composition of the material; however, in the last few years, structural modification of semiconductor materials has developed as a novel approach to enhance their light-harvesting capabilities and thus their photocatalytic activity. This approach, however, can be ascribed to nanostructuring and therefore it will be presented in the next section. The most popular approach toward modifications of the composition of a semiconductor material is by doping, that is, by purposely introducing selected impurities (known as dopants) in the host material. The dopants can be either metals or nonmetals and can be introduced into the host material through various chemical and physical techniques. Traditionally, doping of semiconductors has been used to enhance the conductivity of materials; however, more recently this approach has been widely used to extend the absorption spectrum of wide-bandgap material into the visible range. This effect is generally obtained through the introduction of intra-band states, which are additional energy states lying between the valence and the conduction band of the semiconductor. Upon light illumination, these will provide electronic states, which were forbidden in the untreated material, from or to which electronic excitation can occur. This in turn leads to the presence of additional bands in the absorption spectrum of the material, characterized by lower energies than the band arising from bandgap excitation.

This approach can be easily illustrated for the case of a polar metal oxide, such as TiO<sub>2</sub>. For this kind of materials, a suitable nonmetal will be generally used as dopant to replace oxygen atoms in the lattice and thus create new energy states lying slightly above the valence band, by virtue of its high electronegativity. On the other hand, a suitable metal will be used to replace the cation in the lattice, thus introducing new electronic states lying slightly below the conduction band. ZnO and TiO<sub>2</sub> are the two materials for which this approach has been used most extensively, owing to their lack of absorption in the visible spectrum. A comprehensive description of the various metallic and nonmetallic dopants reported for these materials can be found in several reviews [68–70]. N-doping of TiO<sub>2</sub> is the most well-studied example of anion-doping reported for TiO<sub>2</sub>, followed by C- and S-doping. A seminal report was published by Asahi et al. in 2001 [71], showing that N-doped TiO<sub>2</sub> was acting as visible-light photocatalyst. One year later, visible-light absorbing C-doped TiO<sub>2</sub> was reported to split water with application of a small external bias, with an astonishing efficiency of over 8.3% (and very good stability). However, several research groups later pointed out that the reported efficiency was probably highly overestimated and the real efficiency was more likely to be in the range of 1%-3% [72]. C-doped TiO<sub>2</sub> photocatalysts have been later prepared by several groups, although a substantial increase in the photocatalytic performances was never achieved [73,74].

It is well known in the field of semiconductor physics that impurities within a material may act as recombination centers thus reducing the mobility of charge carriers. This situation, which is typically encountered with energy states located far from the bandgap edges—so-called deep defects, can indeed lead to reduced photocatalytic activities. This problem appears to be particularly acute when metal cations are used as dopants [68], while on the other hand anions appear to be less likely to generate recombination centers [75]. To mitigate the effects of recombination introduced

by doping, a general approach is to confine the impurities to the surface of the host material in such a way that charge carriers trapped in the recombination centers are more likely to reach the surface of the material [75]. Co-doping is another strategy to reduce dopant-induced recombination, which consists in introducing two different types of dopants in the lattice of the host. Boron–nitrogen co-doping of  $TiO_2$  has been shown to reduce dopant-associated recombination, by removing the  $Ti^{3+}$  recombination centers due to charge compensation effects [76]. Density functional calculations have been used to predict the most suitable combinations of co-dopants, unveiling the potential of combinations of co-dopants involving ions of Mo, W, Nb, and Ta as electron donors, while C and N appear as the two most promising acceptor dopants [77].

Besides dopant-induced recombination, which is believed to be the main reason for the overall low efficiency of visible-light absorbing materials such as N-TiO<sub>2</sub> [78], doping of wide-bandgap semiconductors to introduce intra-band states has a second major intrinsic limitation, namely, that the charges generated at the dopant levels may not have enough driving force to reduce and/or oxidize water. This has been suggested in particular for the N-TiO<sub>2</sub> system, where holes generated by visible-light absorption appear not to have enough driving force to oxidize water into oxygen [78]. Nonetheless, the overall approach of doping wide-bandgap semiconductors to achieve visible-light sensitization is extremely promising and has been shown to be applicable to other semiconductors besides TiO<sub>2</sub>. Recently, N-doped ZnO has been demonstrated for the first time to evolve oxygen from water in a photocatalytic system without external bias under visible-light illumination [79].

#### 1.2.2.3 Nanostructuring of Semiconductor Materials

As already pointed out, that it is extremely difficult to find simple materials that are suitable for solar water-splitting cells. Chemical surface and bulk modifications of pristine materials are very important routes through which complex assemblies showing suitable photoactivity and stability can be obtained. Another fundamental route to achieve this target is offered by *nanostructuring*. In the last decades there has been a dramatic increase in the number of available synthetic routes toward nanostructured material, allowing for increasingly higher control over the morphology, the shape, the size, and ultimately the various properties of nanomaterials. On the other hand, the continuous development of new analytical tools, accompanied by the increased performances of computational chemistry, has allowed a more detailed understanding of the relations between structure and properties at the nanoscale. In the field of solar energy conversion, DSSCs are the most striking and successful example of how nanostructured materials can dramatically improve the properties of a system. In this system, the use of a nanostructured mesoporous TiO<sub>2</sub> electrode produced a 3- to 4-order of magnitude improvement in both the incident photon-to-current efficiency (IPCE) and the photocurrent of the device, when compared to a flat single-crystalline electrode [80]. Nanostructured materials can improve the efficiency of solar watersplitting cells in several different ways. The most obvious effect is an increase in the roughness factor of the material, leading to a dramatically enhanced surface area; this can in turn offer several advantages, in terms of enhanced light absorption, increased catalyst loading, and increased number of catalytically active sites.

An increasingly popular device architecture is represented by ordered arrays of nanowires or nanotubes. The potential for the improvement in the catalytic activity offered by nanowire electrodes has been estimated by Liu et al. using a simple model [81], showing that these architectures offer much reduced overpotentials for solarto-fuel conversion over their planar counterpart. In addition, these architectures are generally characterized by a very high aspect ratio, and therefore offer the additional combined advantages of long optical paths, leading to efficient light absorption and reduced charge diffusion distances, ultimately leading to reduced charge recombination. The distance that photogenerated charges have to travel before reaching an active interface is a critical factor for the separation of photogenerated carriers and thus the photoactivity; this is particularly the case for materials characterized by short charge diffusion lengths, where recombination occurs relatively fast and/or the mobility of charges is typically moderate. By exploiting these effects, significant improvements in the photoactivity of several materials have been obtained in the recent years by using arrays of various high-aspect ratio architectures, such as TiO<sub>2</sub> nanotubes [82] and nanowires [83,84], Si microwires [85], Si/TiO<sub>2</sub> composite nanowires [81,86,87], ZnO/Si nanowires [88], Ti-Fe-O nanotubes [89], Ta<sub>3</sub>N<sub>5</sub> nanotubes [90,91], Fe<sub>2</sub>O<sub>3</sub> nanorods [92], and other Fe<sub>2</sub>O<sub>3</sub> high-aspect ratio architectures [93.94].

Another avenue to improve the device performance through nanotechnology is the controlled synthesis of nanostructured materials to create complex morphologies and nanocomposites, in order to spatially separate the various components and thus decouple the various functionalities within the system. The prototypical example of this approach is represented by core–shell nanocomposites, although lamellar assemblies and other host–guest nanoarchitectures have been extensively investigated as well. The core/shell approach is extensively used in photocatalytic systems, where the inner and the outer surface of the shell can be functionalized with water reduction and WOCs, respectively. In addition to spatially separate the two watersplitting half-reactions and thus decrease the reverse reaction, this architecture has been designed to facilitate the separation of the charge carriers and thus reduce electron–hole recombination. These two effects combined can lead to significantly enhanced overall water-splitting activity as it has been recently shown, for example, with SiO<sub>2</sub>/Ta<sub>3</sub>N<sub>5</sub> core/shell photocatalysts [95].

The use of lamellar assemblies is another approach to spatially separate components for effective charge separation and reduced recombination in photocatalytic systems. This route has been pursued in particular by the group of Thomas E. Mallouk at the Pennsylvania State University. The different active components of these multilayer assemblies, such as sensitizers, redox-active electron-relays, and catalysts, are confined to individual layers and separated by the presence of inorganic spacers, typically metal-organic phosphates, or layered metal oxides semiconductors, such as niobates [96,97]. Naturally, the need for compartmentalization and spatial separation of the various components of the systems is particularly stringent for photocatalytic systems, where there is generally no electrical field that can drive the separation of charge carriers. This approach, however, can be useful in photoelectrochemical cells as well, where it is also generally introduced in order to facilitate charge separation, and thus reduce the degree of charge recombination. An important example is represented by host–guest nanoarchitectures, composed of a host scaffold and a guest absorber; this strategy has recently been successfully implemented with Fe<sub>2</sub>O<sub>3</sub> photoanodes. Photocurrents using this material, which is characterized by poor light absorption and a small hole diffusion length, have indeed been significantly increased using high–surface area hosts (consisting of various oxides, such as WO<sub>3</sub> [98], Ga<sub>2</sub>O<sub>3</sub> [99], or Nb-SnO<sub>2</sub> [100]) as a substrate for the subsequent deposition of a very thin layer of hematite. A quite different approach to achieve improved charge separation in semiconductor systems is gradient doping. This concept, very simple from a conceptual point of view, though only recently rediscovered, consists in introducing a gradient dopant concentration in a semiconductor, in order to establish an additional band bending that is not confined to the interface but can also span through the bulk of the semiconductor. Using this concept of gradient doping, the group of R. van de Krol at Delft University of Technology recently achieved record-breaking conversion efficiencies using a W-doped BiVO<sub>4</sub> photoanode in a hybrid tandem cell [101].

Finally, nanostructuring techniques also turned out to be particularly beneficial toward enhanced light harvesting of semiconductor materials, through bandgap engineering, spatial structuring, and other related concepts. It is well known that the bandgap of a nanosized material can be easily tuned according to the size and the shape of the particles; this phenomenon can be useful to enhance the light harvesting of photocatalytic systems by synthesizing particles having a suitable absorption spectrum, ideally matching the solar emission spectrum. A more subtle method recently developed to tune the bandgap of semiconductor material is through introduction of disorders in the lattice. This approach has been recently developed with hydrogenated TiO<sub>2</sub>, which has been shown to be significantly more active than pristine TiO<sub>2</sub> for photocatalytic water reduction due to the resulting absorption spectrum being extended in the visible and infrared range [102]. This system was shown to perform photocatalytic hydrogen generation from water at a high rate of 10 mmol/h per gram of photocatalyst, although using methanol as a sacrificial hole scavenger. Nowadays, bandgap engineering is a very common way for optimized light harvesting through nanotechnology; besides the aforementioned approaches of doping and disorder engineering, it should be mentioned that solid solutions represent a longknown yet still extremely valuable route toward the preparation of materials with an optimized bandgap; this has been demonstrated by the advances with photocatalytic water splitting using materials such as GaN:ZnO [103].

A more recent approach toward enhanced light harvesting in nanomaterials consists in resonant light trapping using photonic crystals. This novel strategy for light management, which has been classified as "spatial structuring" of nanosized materials, exploits the fact that photonic crystals represent resonant optical cavities, where light of selected wavelengths is reflected with very low losses and has thus an increased probability to interact with a light absorbing medium, owing to increased optical path and contact time with the latter [68,104]. This approach, initially dealing with three-dimensional periodic lattices such as zeolites [104], has been recently extended to thin films, where the resonant light trapping arises from the light being reflected from a metallic "back-reflector" substrate back into the absorbing film. By depositing an ultrathin layer of a hematite photoanode with a controlled thickness on selected metallic substrates, it has been shown that an optical gain of up to a factor of 5