

Green Chemistry and Sustainable Technology

Juan Carlos Colmenares
Yi-Jun Xu *Editors*

Heterogeneous Photocatalysis

From Fundamentals to Green
Applications

 Springer

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Green Chemistry and Sustainable Technology

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Aims and Scope

The series *Green Chemistry and Sustainable Technology* aims to present cutting-edge research and important advances in green chemistry, green chemical engineering and sustainable industrial technology. The scope of coverage includes (but is not limited to):

- Environmentally benign chemical synthesis and processes (green catalysis, green solvents and reagents, atom-economy synthetic methods etc.)
- Green chemicals and energy produced from renewable resources (biomass, carbon dioxide etc.)
- Novel materials and technologies for energy production and storage (biofuels and bioenergies, hydrogen, fuel cells, solar cells, lithium-ion batteries etc.)
- Green chemical engineering processes (process integration, materials diversity, energy saving, waste minimization, efficient separation processes etc.)
- Green technologies for environmental sustainability (carbon dioxide capture, waste and harmful chemicals treatment, pollution prevention, environmental redemption etc.)

The series *Green Chemistry and Sustainable Technology* is intended to provide an accessible reference resource for postgraduate students, academic researchers and industrial professionals who are interested in green chemistry and technologies for sustainable development.

More information about this series at <http://www.springer.com/series/11661>

Preface

Heterogeneous photocatalysis has become a comprehensively studied area during the past several decades because of its great potential for solving the problems of environmental pollution and the world energy crisis. As a green technology featured with the unique advantages of operation at room temperature and utilization of clean, renewable solar light as the driving force, heterogeneous photocatalysis continues to be an important component of modern chemistry in the twenty-first century.

The available existing literature in heterogeneous photocatalysis mainly focused on the advances of semiconductor TiO_2 for degradation of pollutants in water and air. However, recent researches have proven that heterogeneous photocatalysis is effective and promising for many other reactions, such as carbon dioxide reduction, photocatalytic water splitting and organic transformations. In addition, the research reports have also shown that a lot of alternative semiconductors and photoactive organic species can apply to these photocatalytic reactions. Therefore, in this book, we highlight and summarize recent progress in green-chemistry-oriented application fields (e.g. carbon dioxide reduction, selective organic transformations, water splitting) over TiO_2 -based and other new photocatalysts alternative to TiO_2 . The synthetic consideration of the proper design of photocatalytic reactors and modeling of light has also been discussed, which are often neglected in literature but rather important for improving efficacy and scale-up applications of photocatalytic systems.

The book *Heterogeneous photocatalysis: from fundamentals to green applications* is aimed at providing researchers with the up-to-date advances related to the field of photocatalysis in the shape of a collective work of reviews illustrative of recent advances in exploitation and green application of heterogeneous photocatalysis towards solar energy conversion and utilization. The book consists of 11 chapters including the principles and fundamentals of heterogeneous photocatalysis (Chap. 10), the mechanisms and dynamics of surface photocatalysis (Chap. 11), the researches on the TiO_2 -based composites with unique nanostructures (Chap. 5), the latest developments and new advances of exploiting

new photocatalyst materials alternative to TiO_2 (Chap. 4) and photocatalytic materials for new applications different from the traditional degradation of pollutants: carbon dioxide reduction (Chap. 1), water oxidation (Chap. 2), a complete spectrum on selective organic transformations (Chaps. 8 and 9) and water splitting by photocatalytic reduction (Chap. 6). In addition, heterogeneized polyoxometalate materials for photocatalytic purposes (Chap. 3) and the proper design of photocatalytic reactors and modelling of light (Chap. 7) have also been discussed. These progresses in heterogeneous photocatalysis provide new directions and tremendous opportunities for developing new generations of effective and selective photocatalysts towards target practical applications.

In this book the high quality and geographic distribution of the contributions are taken into consideration when inviting worldwide respected and well-known leaders in the relative field including Prof. Pierre Pichat, Prof. Leonardo Palmisano, Prof. Flemming Besenbacher, Prof. Graham J. Hutchings, Prof. Hermenegildo Garcia and Prof. Xueming Yang, as well as excellent emerging young scientists, among them Prof. Bin Liu, Prof. Nurxat Nuraje, Prof. Adriana Zaleska-Medynska, Prof. Elisa Garcia Lopez, Dr. Ren Su and Prof. Hiroshi Kominami.

The book is able to serve as a self-contained major reference for heterogeneous photocatalysis towards solar energy conversion and utilization. This book appeals to a wide readership of the academic and industrial researchers and can also be used in the classroom for undergraduate and graduate students who focus on heterogeneous photocatalysis, sustainable chemistry, energy conversion and storage, nanotechnology, chemical engineering, environmental protection, optoelectronics, sensors and surfaces and interfaces sciences.

We would like to express our sincere thanks to all authors for their excellent contributions to this impressive book. We are also thankful to the whole Springer team, especially to Heather Feng and June Tang for their priceless support in publishing this book.

Warsaw, Poland
Fuzhou, China

J.C. Colmenares
Y.-J. Xu

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Chapter 1

Photocatalytic CO₂ Reduction

Josep Albero and Hermenegildo García

Abstract In the context of finding sustainable and environmentally neutral alternatives to fossil fuels, there is much current interest in the production of chemicals that can be used as fuels using solar light (*solar fuels*). In the present chapter, we describe the fundamentals and the current state of the art for the photocatalytic reduction of CO₂, making emphasis on the importance of the co-substrate (either water, hydrogen, or other electron donors), the differences of the process with respect to the photocatalytic hydrogen generation from water, and the importance to control the selectivity towards a single product of the many possible ones. After this part describing some basic issues of the photocatalytic CO₂ reduction, some of the currently more efficient photocatalysts are described, delineating similarities and differences among those materials. The final section summarizes the main points of the chapter and presents our view on future developments in the field.

Keywords Solar fuels • CO₂ reduction • Photocatalysts • Semiconductor photocatalysts • Graphene-based photocatalysts

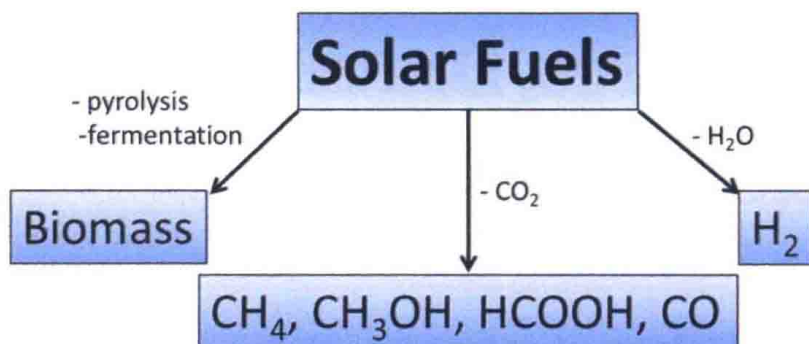
1.1 Solar Fuels: Concept and Importance

Modern societies consume an enormous amount of energy to perform their activities including transportation, industrial processes, and heating, among other main uses. The current scenario is based on the massive consumption of fossil fuels, including oil and natural gas, not only for transportation but also for the production of electricity and heating. Considering the limited resources on fossil fuels, it is clear that at the high current consumption rate these resources will become depleted, making the present energy source scheme unsustainable.

Besides sustainability, a second driving force to develop alternative energy sources is climate change and, specifically, atmospheric pollution by greenhouse effect gases. The limited resources of fossil fuels together with global warming

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Scheme 1.1 Most common chemicals considered as solar fuels

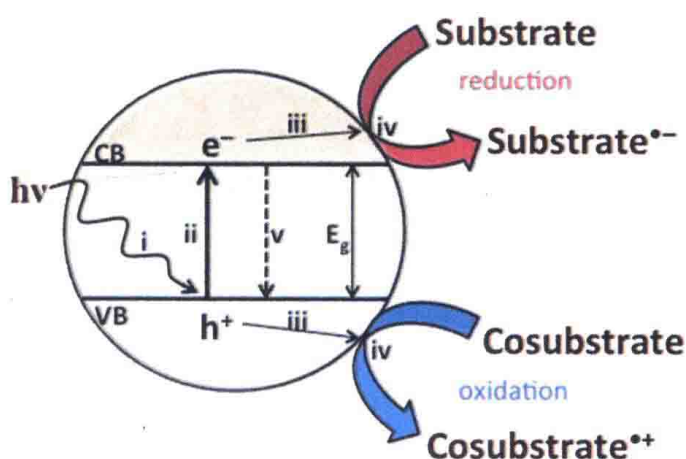
concerns as well as geostrategic considerations derived from the uneven geographical distribution of oil and natural gas reserves have motivated a strong interest in developing alternative energy resources that should be characterized by sustainability and lack polluting emissions.

In this regard, one almost inexhaustible natural energy resource is sunlight reaching the Earth's crust [1]. While there is a series of competing alternative technologies to convert solar light into other types of energy, particularly electricity, including thermal conversion and photovoltaic devices, the use of sunlight directly in transportation and many other applications is problematic due to the low energy density of sunlight, circadian cycles between day and night, and dependence on weather and seasonal conditions [2].

In this context, one possibility would be to accumulate the energy of the sunlight into chemical compounds that could later be used in transportation or when required on demand [3–7]. The use of chemicals obtained from solar light as fuels in transportation has led to the concept of solar fuels (Scheme 1.1). These solar fuel chemicals have in common to correspond to a reduced compound that when reacted with atmospheric oxygen should undergo combustion or oxidation, releasing the accumulated energy. Among the possible solar fuels, hydrogen has been identified by the US Department of Energy as an ideal energy vector since when oxidized at moderate temperatures it will form water as the only product [8]. However, the use of hydrogen as fuel cannot be readily implemented due to the lack of technology concerning its production, storage, and use. Due to the extremely low boiling point ($-253\text{ }^{\circ}\text{C}$), hydrogen has to be handled as compressed gas, and this creates problems concerning filling fuel tanks and storage of enough energy to achieve autonomy in transportation.

Besides hydrogen one alternative that is increasingly being considered is the use of C1 chemicals obtained by CO_2 reduction, including methane, methanol, formic acid, and others. Although the use of solar fuels derived from CO_2 has a major drawback in that CO_2 having a greenhouse effect is formed in their combustion, the overall CO_2 footprint should be neutral when these solar fuels are prepared from CO_2 as feedstock [9, 10].

Scheme 1.2 Elementary steps taking place in a photocatalytic cycle: light absorption (i), electron excitation (ii), electron and hole migration (iii), oxidation and reduction reactions (iv), or geminate electron recombination (v)

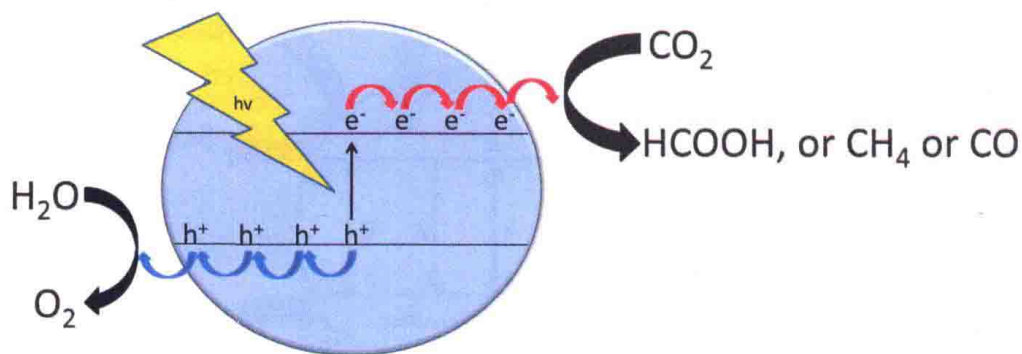


Besides hydrogen and CO₂-derived chemicals, fuels from biomass are also considered in the broad sense as solar fuels since biomass is based on natural photosynthesis by green algae and plants [11].

Solar fuels can be obtained in an indirect way by first converting solar energy into electricity and subsequently carrying out the electrochemical reduction of water or CO₂ [12]. This possibility has some advantages as a way to store the excess of electricity from renewables. However, also appealing is to devise systems for the direct conversion of sunlight into solar fuels, since this approach could require much less capital investment and is flexible enough to be implemented for small-scale production. This strategy is based on the use of materials that are capable to absorb sunlight generating a charge separation state, generally electrons and positive holes. These materials are generally termed as photocatalysts since they should perform many turnovers absorbing photons and generating a product [13, 14]. The most typical photocatalyst are solid semiconductors, such as some metal oxides, chalcogenides, and carbonaceous materials.

In photocatalysis photons, having energy higher than the bandgap of the semiconductor promotes excitation of electrons from the occupied state of highest energy to unoccupied states of lowest energy. This electronic excitation is generally described as charge separation since, very often in a semiconductor, electrons and/or holes are mobile and electronic excitation results in uncoupled electrons and holes (Scheme 1.2).

The state of charge separation can decay through different pathways, the most important ones being charge recombination of geminate electrons and holes generated in the same event of photon absorption or charge recombination after random migration of electrons or holes through the material [15]. The difference between geminate and random recombination is the time scale in which they take place, sub-microsecond for geminate recombination and microsecond time scale after random migration of the charges. During the lifetime of charge separation, the semiconducting particle behaves simultaneously as an oxidizing reagent (by capturing electrons from a substrate and placing them at the positive holes) or reductant (by transferring electrons to substrates). Scheme 1.3 illustrates the dual nature of charge-separated states as reducing and oxidizing agents. As briefly



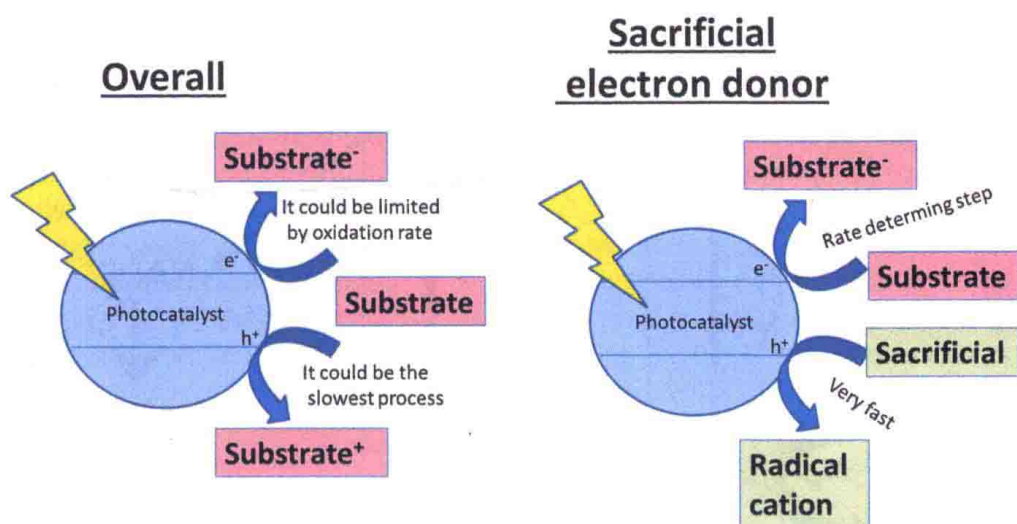
Scheme 1.3 Schematic representation of an ideal photocatalyst performing CO_2 reduction by water

indicated above, for the sake of solar fuel production, the most wanted process is reduction of a substrate (H_2O or CO_2) by photogenerated electrons at the semiconductor to form the solar fuel. However, for the sake of fulfilling the electroneutrality principle, reduction in the photocatalytic process has to occur at the same reaction rate as the oxidation reaction by holes. This requirement of simultaneous oxidation and reduction of different chemicals in the same particle makes necessary that in the photocatalytic process, besides the targeted solar fuels, some oxidized compound has to be simultaneously formed.

In order to decouple oxidation and reduction at the semiconductor, achieving the maximum possible efficiency in the reduction semireaction leading to solar fuels, it is very common that model studies use a sacrificial agent whose role is to quench efficiently at a high rate photogenerated holes, allowing the study of the reduction process as the rate-limiting step. Preferred hole quenchers in this type of photocatalytic studies are tertiary amines, particularly triethanolamine and triethylamine, and alcohols, especially methanol and ethanol, and also inorganic ions such as sulfide, sulfite, and nitrate. To differentiate those photocatalytic experiments in the absence of a sacrificial electron donor with those having present these reagents, it is common to indicate the term “overall” to denote that photocatalytic oxidation and reduction of the same substrate are simultaneously carried out without any sacrificial electron donor (Scheme 1.4). Photocatalytic generation of solar fuels has the advantage with respect to indirect strategies based on electrolysis in that they require much less infrastructure and lower capital investment in equipment, and therefore, it could be more amenable for on-site implementation in small- or medium-sized plants, rather than application in large facilities.

1.2 Advantages of Solar Fuels Derived from CO_2

As commented earlier, the current energy production is largely based on fossil fuel combustion in which vast amounts of CO_2 is formed. These power plants are an interesting source of CO_2 that at the moment has to be captured and stored. It would



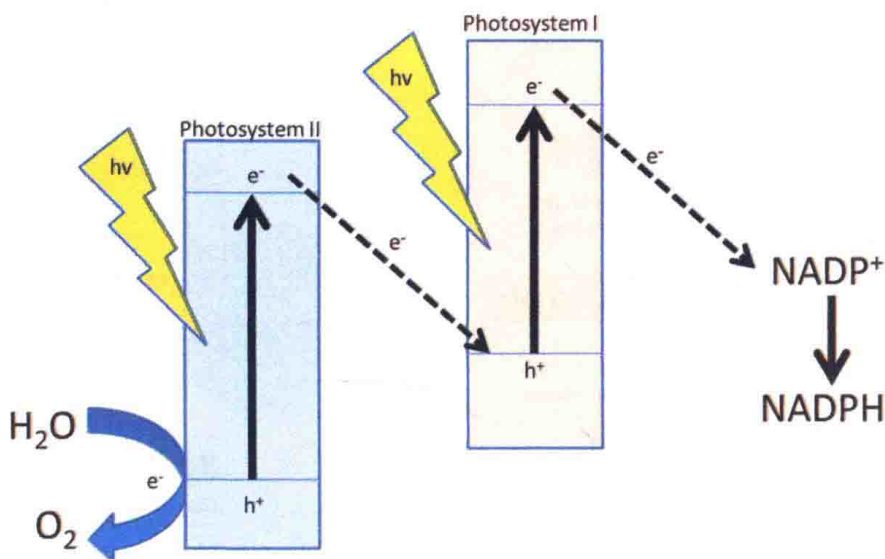
Scheme 1.4 Photocatalytic oxidation and reduction of a substrate with and without a sacrificial electron donor

be interesting to use this CO₂ as feedstock of chemical processes and, particularly, as source of solar fuels. International treaties currently enforced require a gradual reduction of CO₂ emissions to the atmosphere, and one of the most appealing ways to reduce CO₂ emissions is their use as feedstock. It should be taken into account that solar fuels based on CO₂ will be neutral from the point of view of greenhouse emission gases. Another advantage of CO₂-derived solar fuels with respect to hydrogen is that some of the possible products such as formic acid or methanol are liquids under ambient conditions and this physical state will simplify enormously their storage and all the technology involved in their manipulation. Even in the case of methane as CO₂ reduction product, there are nowadays a large number of implemented energy systems using natural gas that would be straightforwardly adapted to methane as solar fuel. Thus, solar fuels derived from CO₂ would overcome the major problems encountered in hydrogen technology related to storage and manipulation [16, 17].

However, compared to hydrogen generation from water, the use of CO₂ as feedstock for the preparation of solar fuel is extremely challenging from the photocatalytic point of view. One of the major problems related to the use of CO₂ as feedstock for the generation of solar fuels is that the “overall” CO₂ splitting has never been reported. Thus, in contrast to H₂O which photocatalytically can be reduced to hydrogen and oxidized to oxygen, in the case of CO₂, it is necessary to add another substrate that should undergo oxidation concurrently to CO₂ reduction. The most advantageous reductant promoting CO₂ reduction would be water. Equation 1.1 illustrates one of the possible stoichiometries for this reaction:



In this case water would be oxidized to oxygen while CO₂ will be reduced to methanol. This process of CO₂ reduction by water is the one that is taken place in



Scheme 1.5 Pictorial illustration of some of the processes taking place in natural photosynthesis

natural photosynthesis carried out by algae and green plants. Unfortunately, the current state in photocatalysis is very far from mimicking natural photosynthetic centers, and the present efficiency using semiconductors for CO_2 reduction from water is very low. Below in this chapter, we will describe some of the most efficient artificial photocatalyst for this process.

The reasons why CO_2 reduction by water is so inefficient are both thermodynamic and kinetic. From the thermodynamic point of view, CO_2 reduction is highly endothermic and consequently requires more than one photon to occur. It should be noted that in natural photosynthesis the transfer of one electron requires the absorption of two photons, one in each of the two photosynthetic centers (Scheme 1.5) [18]. Also from the kinetic point of view, the process of CO_2 reduction is very complex since, depending on the products formed, several steps of reduction and protonation have to take place. For instance, conversion of CO_2 into methane is a process that requires eight electrons and eight protons, and most probably this transformation has to occur stepwise, each step consisting in the transfer of one electron followed more or less synchronously by protonation. For the reaction of Eq. 1.1, formation of methanol requires the reduction of six electrons and six protons.

Besides water other reducing agents can also be considered for photocatalytic CO_2 reduction. Particularly interesting is the use of hydrogen as reducing agent. In contrast to CO_2 reduction by water, the reaction of CO_2 with hydrogen is exothermic, thus making the reaction favorable from the thermodynamic point of view (Eq. 1.2):



In fact, CO_2 reduction by hydrogen, the so-called Sabatier reaction, can be carried out thermally in the absence of light at high temperature [19]. However, the use of

sunlight to assist the reaction is interesting from the point of view of saving energy in the process. The main problem of the Sabatier reaction is the source of hydrogen that has to be supplied to the system. Hydrogen can be obtained by steam reforming of methane and fossil fuels [20], a process based on nonrenewable chemicals that cannot be considered for CO₂ reduction since it would not make sense to use methane to generate hydrogen to react with CO₂ to form methane again. However, hydrogen can be also obtained in thermal water splitting, electrolytically from alternative renewable electricity or even photocatalytically. In this scenario, the advantage of the Sabatier reaction would be to provide methane as substitute of natural gas from renewable resources and avoiding the direct use of hydrogen as fuel. In other words, since natural gas is widely used as fuel and its technology is fully developed, the shift will be in the origin of this fuel moving from nonrenewable resources to a renewable process based on CO₂ and hydrogen coming from a sustainable primary energy.

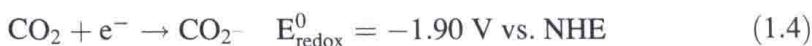
From the point of view of a desirable C1 fuel, methanol is probably the best choice since it is liquid under ambient conditions and has high volumetric energy content [21]. In addition, burners and combustion engines for gasoline can be easily adapted to use methanol as fuel. In addition, methanol can also be the fuel for proton-exchange membrane fuel cells (PEM-FC) instead of hydrogen [22]. In this regard, the use of methanol as fuel and PEM-FC as an electricity provider device could represent a temporary transition towards the complete implementation of hydrogen technology that still needs scientific knowledge and technical developments to be close to application. However, as it will be commented below, it is very unlikely that methanol could be obtained photocatalytically from CO₂ by reduction since due to its high chemical reactivity, the same photocatalytic process would decompose methanol if this molecule is present in high concentrations in contact with the photocatalyst. Thus, under batch conditions, the stationary concentration of methanol in a photocatalytic experiment has to be very low.

1.3 Differences Between Photocatalytic Hydrogen Generation from Water and CO₂ Reduction

Photocatalysis is aimed at converting light into chemical energy. However, the nature of the substrates that are going to be converted photocatalytically and the nature of the products formed are extremely important for the success of the reaction and for efficiency of the photocatalytic process. In this regard there are remarkable differences between water reduction to generate hydrogen and photocatalytic CO₂ reduction that are worth to be commented in order to understand the reasons why the level of development in photocatalytic CO₂ reduction is always lower than photocatalytic hydrogen evolution from water.

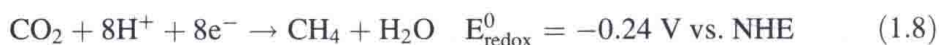
One of the first differences from the fundamental point of view is the higher reduction potential to inject a single electron to CO₂ compared to water.

Equations 1.3 and 1.4 indicate the redox potential for the simplest elementary step of one electron reduction to water or CO₂:



These represents the thermodynamic requirements of the photocatalytic process, meaning that, in order to start the photocatalytic reduction, electrons in the conduction band of the semiconductor have to have enough reduction potential to initiate the process. As it is indicated in Eqs. 1.3 and 1.4, the reduction potential required for CO₂ is considerably higher than in the case of H₂O. It should be noted that if instead of Eq. 1.4 an alternative Eq. 1.5 is considered in which electron reduction is accompanied simultaneously by protonation of the reduced species, then a significant decrease in the energy of the process from the thermodynamic point of view occurs. It has to be, however, noted that mechanistically to transfer an electron and a proton simultaneously can be rather difficult since as it is indicated in Eqs. 1.3 and 1.4 they are incompatible in the sense that protons and electrons react to give hydrogen at much lower potential without requiring CO₂.

Naturally, in certain enzymes, proton-assisted electron transfer is promoted by having one redox center near a proton donor center in a relatively rigid environment that keeps the two sites separated. The problem is that artificial photocatalysis is based on considerably simpler and not ordered systems than those occurring in natural photosynthetic systems or enzymes and artificial photosynthesis is still far behind the complexity characteristic of natural systems. Moreover, if instead of Eqs. 1.3 or 1.5 referring to single electron reduction of CO₂, assisted or not by proton transfer, other possible equations in which two electrons and two protons (Eq. 1.6) leading to formic acid or six electrons and six protons leading to methanol (Eq. 1.7) or eight electrons and eight protons leading to methane (Eq. 1.8) are considered, then the thermodynamic potential decreases gradually for each reaction. This relaxation of the thermodynamic reduction potential is, as just commented, a reflection of the assistance of protons to the electron transfer. However, from the mechanistic point of view, none of the Eqs. 1.7 and 1.8 have any sense as occurring in a single step and have to be considered only as the thermodynamic potential between reactants and products rather than having any mechanistic implication:



The previous comment on the higher reduction potential to convert CO₂ in respect to H₂O reduction raises the issue of whether or not all the photocatalysts reported