Chapter 4
Turning Sunlight into Fuels: Photocatalysis for Energy

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Environmental and socioeconomic considerations are forcing us to change our energy scheme. The search for primary energy sources alternative to fossil fuels and nuclear power, suitable to maintain the sustainability of the planet and the whole economic system, is therefore of prime interest for scientists and governments. In this context, renewable energy technologies (solar radiation, wind, rain, tides, biomass, geothermal heat, etc.) are called to play a key role in the close future. The strong economic and political global effort in research, development, and implementation of renewable energies has been continuously reducing the existing gap in efficiency and cost optimization compared to conventional technologies.

4.1 The Sun as Energy Source

Sunlight is by far the most abundant energy source on the Earth. The sun, basic element for the existence of life in our planet, is like a nuclear fusion reactor that generates a continuous power of 3.8 × 1,023 kW as a result of the permanent conversion into energy of part of its mass. The major part of this energy arrives to the Earth by radiation. When the radiation reaches the atmosphere, a part is reflected to the outer space again, but the 70 % is absorbed and used to maintain

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the ambient temperature, to evaporate water in the hydrological cycle, for photosynthesis, or dissipated in wind and ocean currents. Therefore, the sun is responsible for the Earth's climate, and most renewable energies are directly or indirectly powered by the sun.

4.1.1 Components of the Solar Radiation

Before reaching the ground, the solar radiation is modified by absorption and scattering due to the interaction with the gas mixture and small suspended particles that constitute the atmosphere. The Global (G) solar radiation reaching the Earth surface has three components:

$$G = I + D + R \tag{4.1}$$

- Direct radiation (I), which arrives without any alteration of direction.
- Diffuse radiation (D), which arrives from all directions after being scattered in the atmosphere. Its proportion varies from 10 % in a clear day to 100 % in a very cloudy day.
- Reflected radiation (R) or albedo, which arrives as a consequence of reflections on the ground or on vertical surfaces. It can be up to 40 % of the global radiation in the case of white surfaces.

4.1.2 The Solar Spectrum

The energy of the solar radiation (E) is inversely proportional to its wavelength (λ), according to Planck's equation for electromagnetic radiation:

$$E = \mathrm{hc}/\lambda \tag{4.2}$$

where c is the speed of light (c = 299,792,458 m s^{-1}), and h is the Planck's constant ($h = 6.626 \times 10^{-34}$ J s).

The solar radiation spectrum (Fig. 4.1) can be divided into three main wavelength regions:

- Ultraviolet (UV) radiation, at $\lambda < 400$ nm, accounts for only a 2–3 % of the radiation reaching the Earth's surface on clear days and 8–10 % in cloudy days (Escobedo et al. 2009). This region is compressed by three subregions:
  - UVA, or near ultraviolet (320–400 nm), the less energetic. Most of UV radiation reaching the Earth's surface is in this range.
  - UVB or far ultraviolet (290–320 nm). It has enough energy to damage the cellular DNA, yet not enough to be completely absorbed by the atmosphere.

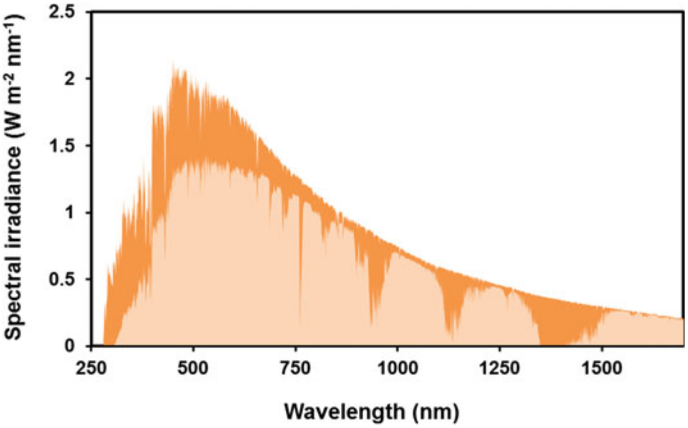

Fig. 4.1 Solar radiation spectrum showing the absorption bands of the atmosphere. *Curves* based on the American Society for Testing and Materials (*ASTM*) terrestrial reference spectra

  - UVC or extreme ultraviolet (220–290 nm). Completely absorbed by stratospheric ozone before reaching the surface.
- Visible radiation, approximately with $\lambda = 400$–750 nm, the wavelengths to which the human eye is sensitive.
- Infrared (IR) radiation, with $\lambda > 750$ nm. This region is commonly subdivided into:
  - Near infrared (NIR), between 750 and 1,400 nm.
  - Short-wavelength infrared (1,400–3,000 nm).
  - Mid-wavelength or intermediate infrared (3,000–8,000 nm).
  - Long-wavelength infrared (8,000–15,000 nm).
  - Far infrared (15,000–10^6 nm).

Oxygen and nitrogen absorb very short-wavelength radiation, effectively blocking it below 190 nm. Molecular oxygen photodissociation by UVC absorption leads to the production of the atmospheric ozone layer, which absorbs most UVB and some visible radiation. Water vapor, carbon dioxide and, to a lesser extent, oxygen, selectively absorb in the near infrared. Wavelength-dependent Rayleigh scattering and scattering from aerosols and other particulates, including water droplets, change the spectrum as well and are responsible for the blue color of the sky.

4.1.3 Uses of Solar Energy

The solar constant, $1{,}353 \pm 21$ W m^{-2}, is the radiant power received per unit area on top of the Earth's atmosphere (ASTM E 490-73a). However, the irradiance on the Earth's surface varies widely, depending on latitude, time (month, day, and

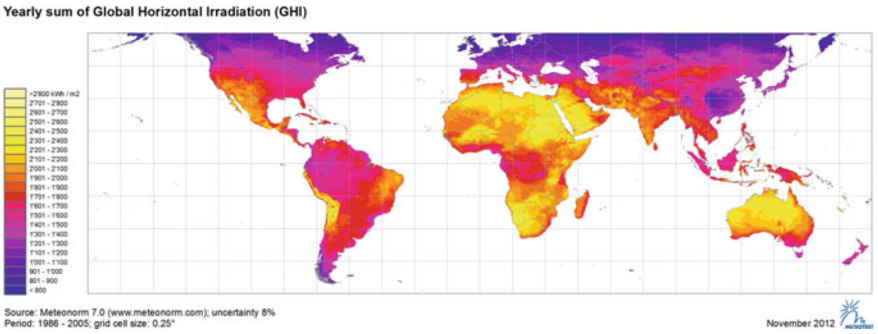

Fig. 4.2 World map of the annual solar irradiation, showing the extensive areas of high insolation in Africa, Australia, the Arabia peninsula and some areas of America. Reproduced from http://meteonorm.com/download/maps/

hour) and atmospheric effects (reflection, absorption, and scattering). The world map of yearly solar irradiation is shown in Fig. 4.2. The solar radiation that reaches the Earth surface can be collected, and even concentrated, by means of absorbents, reflectors, lenses or semiconductors, and employed in different, more or less complicated, technological processes. The main applications of solar energy include passive solar technologies, which reduce the energy demand, (for example bioclimatic designs and greenhouses), and active solar technologies, which supply energy, and are expanding nowadays. But the history of solar energy applications is not as recent as one might believe. According to the U.S. Department of Energy, already in the seventh century B.C. magnifying glasses were used to make fire (The history of solar, http://www1.eere.energy.gov/solar/pdfs/solar_timeline.pdf), and it is well known that in the first centuries A.D. the Romans took advantage of the solar heat by means of south facing windows in the bathhouses. In 1515, Leonardo da Vinci showed how solar energy could be industrially used to heat water by employing concave mirrors, and during the 1830s, Sir John Herschel used a solar cooker in his expedition to South Africa (Butti and Perlin 1980). The photovoltaic effect, that allows the direct conversion of radiation into electricity, was discovered by Edmund Becquerel in 1839 (Williams 1960), although no application was developed until one century later. In the 1860s, Augustin Mouchot started the development of the first solar motor, using heat from a solar collector to power a steam engine (Mouchot 1869). Later, Mouchot connected the steam engine to a refrigerator to make ice and continued making solar cookers, solar water pumps, and even water distillation.

After those pioneers, many researchers have explored these and other applications, including solar disinfection and photochemical and photoelectrochemical processes. Today, even though the technology is continuously being optimized, the conversion of solar radiation into electric and thermal energy is a reality. Meanwhile, CO_2 photocatalytic reduction and the production of solar fuels remain the big challenges for researchers, especially in the field of materials science, for the forthcoming years. The three basic routes for production of storable and transportable fuels from solar energy are the following:

- Electrochemical: Solar electricity obtained either directly—from photovoltaic cells—or indirectly—with concentrating solar thermal systems followed by turbines—is used in an electrolytic process. Considering typical yields of commercial PV modules (about 18 %), the variations in incident solar light, the electrical losses and the electrolyzers efficiency (ca. 80 %), an overall efficiency of 10–11 % in water splitting can be achieved (Blankenship 2011). This is probably the most mature way to storage solar power in the form of the chemical vector hydrogen, but the overall yield of these transformations is still too low for being economically competitive. Nevertheless, the rising efficiency of new PV modules can modify completely this situation in the near future.
- Photochemical/photobiological: The energy of the solar photons can be directly used for powered photochemical and photobiological processes. This is the case of the photocatalytic route discussed below, but also of the biomass growth in photosynthetic organisms by using chlorophyll, carotenoids, and other pigment molecules. In terrestrial plants, maximum efficiencies of about 4.3 % are achieved with species of C4 metabolism, whereas microalgae in controlled laboratory conditions can achieve up to 7 % efficiency (Blankenship 2011). Surprisingly enough, although photosynthesis sustains life on the Earth, it is not a very efficient process in terms of energy. This fact casts significant doubts about the feasibility of biofuels, which in last instance come from photobiological transformations, to provide a long solution for energy supply in transportation.
- Thermochemical: Concentrated solar radiation provides heat at very high temperatures (>1,100 °C) for endothermic chemical process, which can be applied to fuel production. In this respect, the use of thermochemical cycles such as those based on reducible oxides, for instance ZnO or CeO_2, can produce solar fuels with elevated theoretical efficiencies (>30 %) (Romero and Steinfeld 2012). This turns concentrating solar power into a very promising approach for sun power storage. However, due to the technical difficulties (materials stability, large thermal losses, etc.) associated with the elevated operation temperatures of these processes, this route for solar fuels production will require further development before becoming a reality.

4.2 Water Splitting

4.2.1 Hydrogen as Energy Vector

Hydrogen is by far the most common element in the Universe, but on Earth it does not occur to a significant extent in its free molecular form, H_2. However, it constitutes a major component of water, biomass, and hydrocarbons such as oil and natural gas. Leaving apart its importance for the chemical industry, in the last decades, hydrogen has gathered a great deal of interest because it can be used as a sort of "energy currency" or, in more conventional terms, as a suitable energy vector. The reason for that lies on this apparently simple transformation:

$$\frac{1}{2}\,O_2(g) + H_2(g) \rightarrow H_2O\ (l) \quad \Delta G^0 = -237\,\mathrm{kJ\,mol^{-1}} \tag{4.3}$$

which shows that hydrogen oxidation releases an important amount of energy without production of any chemical but water (Navarro et al. 2009). The energy stored in H–H bonds can be utilized by combustion in specially designed engines, but is more frequently connected to electricity production in fuel cells. These electrochemical devices are provided with an anode made of Pt on conductive carbon. H_2 dissociates in the anode to yield H^+ and electrons, which are conducted to the cathode through an external circuit, where they reduce O_2. At the same time, the protons are driven through a thin H^+ exchange membrane (generally made of Nafion, a perfluorinated polymer with sulfonic groups) to the cathode, where they combine with the reduced oxygen species to form water. These devices can have high efficiency (>30 %) in the transformation of chemical to electrical energy. Therefore, the use of hydrogen in combination with fuel cells has the potential to provide flexibility to the regulation of the energy flow from generation sites to consumers. This fact is particularly relevant in an electricity production scheme that, at a global level, is progressively incorporating a rising number of renewable energy plants (wind, photovoltaics, thermosolar, etc.). Since these energy sources are intrinsically intermittent, they require some type of storage to buffer the mismatch between generation and demand, and in this context, the flexibility of hydrogen as energy vector may play a significant role in the near future. Nevertheless, relevant technological and economic barriers, such as the prize of the Pt used in the electrodes or the need for a hydrogen distribution infrastructure, are slowing down the deployment of the so-called hydrogen economy (Armor 2005).

Hydrogen can be produced from a variety of primary sources, such as natural gas, naphtha, heavy oil, methanol, biomass, wastes, and coal, generally via a reforming process, which for the case of methane is given by:

$$CH_4 + 2\,H_2O \rightarrow CO_2 + 4\,H_2 \quad \Delta H_{298} = 165\,\mathrm{kJ\,mol^{-1}} \tag{4.4}$$

This equation accounts for the overall process that also implies the water gas shift for increasing the hydrogen ratio. In fact, natural gas reforming is currently the main industrial route for hydrogen production. This process operates at high temperature (700–1,100 °C) using Ni-based catalysts, generating a stream that typically contains 75–78 % H_2, 30 % CO_2, traces of CH_4 and 10–20 ppm CO (Heinzel et al. 2002). This gas composition highlights the two main challenges of hydrogen production for a sustainable energy system: the need to reduce CO_2 emissions, in order not to aggravate the greenhouse effect in the atmosphere, and the requirement of an additional purification process for removing CO impurities. This last constraint is imposed by the fact that the Pt component of fuel cell electrodes is deactivated by CO adsorption. The reformed gas can be upgraded by

CO preferential oxidation (CO-PROX) using catalysts typically based on CuO/CeO_2 (Caputo et al. 2008).

In this framework, the development of alternative routes for CO_x-free H_2 production is crucial for both environmental and practical reasons, and the use of solar energy, either directly or indirectly, can play a remarkable role in the activation of the water molecule. In this regard, the photocatalytic dissociation of water constitutes one of the most promising routes for the generation of solar hydrogen.

4.2.2 *Photocatalytic Production of Hydrogen*

The water molecule is very stable and its thermal dissociation, according to the inverse process to that described in Eq. 4.3, is highly endothermic. As a consequence, a temperature of 2,500 K is required to obtain about 5 % dissociation at atmospheric pressure. In contrast, considering only the thermodynamics of the process, photochemical decomposition of water is potentially feasible by applying photons with a wavelength shorter than 1,100 nm (equivalent to approximately 1.3 eV). However, this photochemical reaction has to overpass a very high activation energy. Therefore dissociation is only significant for irradiation with wavelengths lower than 190 nm, and consequently (and fortunately!), it does not take place under sunlight (Hernández-Alonso et al. 2009).

The use of photocatalysts reduces appreciably the energy barrier and turns the process viable with photons of the solar spectrum. At this point, it is important to recall that, as it was stated in Sect. 2.5, water splitting, as well as CO_2 photoreduction, is not spontaneous, but an uphill process ($\Delta G > 0$), and thus accumulates energy in the bonds of the generated chemicals. Considering only the photons with the required energy for water molecule photodissociation, about 2.8 mmol s^{-1} m^{-2} H_2 (equivalent to 800 W m^{-2}) could be potentially produced using solar radiation. Obviously, this value represents an unattainable limit, because activation losses throughout the process will reduce the efficiency. Figure 4.3 illustrates the capacity of storing solar energy as hydrogen at different quantum yield levels. In addition, this plot emphasizes the crucial influence of the wavelength on the efficiency, because shifting the absorption edge of the photoactive component from 400 to 600 nm improves the harvesting of solar power in one order of magnitude. Accordingly, the utilization of efficient visible light–responsive materials is a key aspect of any application of photocatalysis, but especially of those related to the production of fuels.

The classical work by Fujishima and Honda (1972) established that photoelectrochemical decomposition of water was possible over TiO_2 electrodes. Subsequent investigations evidenced that no external potential was required to split the water molecule, and that the photoactivity could be boosted if a noble metal (e.g., Pt) was incorporated (Nozik 1977). However, in contrast to the photoelectrochemical process, which yields oxygen and hydrogen separately, photocatalytic water splitting produces a mixture of both gases, which should be subsequently

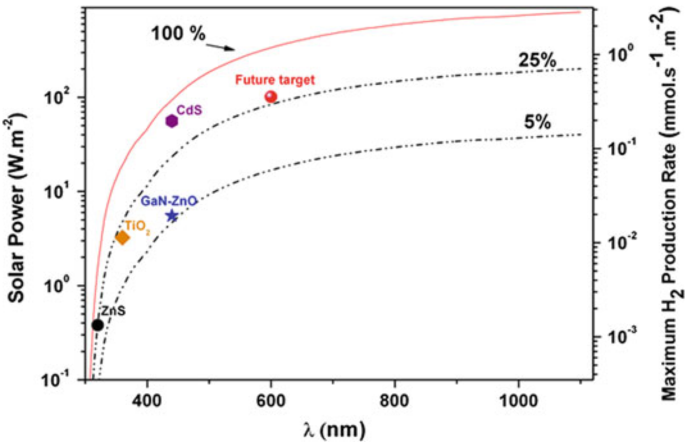

Fig. 4.3 Incident solar power and maximum hydrogen production rate as a function of the photons wavelength as obtained from the integration of the 1.5 AM solar spectrum. *Dashed lines* represent the solar power accumulated at each wavelength considering photonic efficiencies of 5 and 25 %. *The different symbols mark* some of the current or future achievements of photocatalysis for H_2 production using TiO_2, ZnS, CdS, or $(Ga_{0.88}Zn_{0.12})(N_{0.88}O_{0.12})$ as photocatalyst. It should be noted that these values are upper limits and, consequently, H_2 production rates would be appreciably lower in practice. Reproduced with permission from Hernández-Alonso et al. (2009). Copyright Royal Society of Chemistry

separated. After this groundbreaking works, the interest in photocatalytic water splitting has not decreased. Furthermore, in the last few years, it has revitalized due to the growing concern about global warming and the development of novel photocatalysts with enhanced performance, which holds the promise of the future implementation of solar hydrogen plants. These recent advances have been brought about by a continuous quest for more efficient photoactive materials. The fact that more than 150 different semiconductors, many of them described in this book, have been tested for water splitting reflects the magnitude of the research effort undertaken by the scientific community (Osterloh 2008).

Interestingly, according to their redox potentials, some materials, such as WO_3 or $BiVO_4$, are only efficient for O_2 evolution, while others, like TiO_2, are more active for H_2 production. This fact opens up a new opportunity to dissociate water combining photoactive materials using what is called a Z-scheme. The basic mechanism of this two-step approach is schematically depicted in Fig. 4.4. The existence of a redox mediator, in order to connect both components by shuttling the photogenerated electrons, is crucial for the functioning of the Z-scheme (Sayama et al. 2001). In water solution, this can be achieved by the IO_3^-/I^- redox couple. The advantage of using two semiconductors for the water splitting system is that the energy of the photons required to power each photocatalyst can be reduced when compared to the one-step water splitting system. In addition, the evolution of H_2 and O_2 takes place separately, and this hampers the reverse reaction to form water. Unfortunately, the redox mediator can also participate in

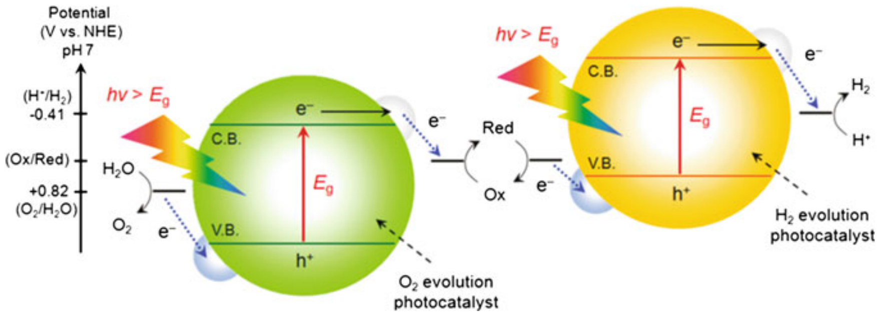

Fig. 4.4 Schematic energy diagrams of photocatalytic water splitting by using a Z-scheme with two separated photocatalytic systems. Reproduced with permission from Maeda and Domen (2010). Copyright American Chemical Society

backward reactions, decreasing the photoactivity. A successful example of a Z-scheme is the combination of Pt/ZrO_2/TaON and Pt/WO_3 systems, which attain a quantum yield of 6.3 % under irradiation at 420 nm (Maeda and Domen 2010).

Incorporation of a second component, usually referred to as co-catalyst, to the photoactive semiconductor is normally required to generate H_2 at a significant rate. It is believed that co-catalysts, based on metals oxides such as NiO_x and RuO_2 or noble metals like Pt or Rh, contribute to stabilize photogenerated charge carriers and provide additional reaction sites that further catalyze O_2 and H_2 evolution (Maeda and Domen 2010). The incorporation of these active components must be thoroughly controlled to maximize the dispersion and facilitate the electronic transference from the semiconductor. However, it is important to mention that, despite their significant promotion of water splitting, some of them, for instance noble metals, can also catalyze the reaction of O_2 and H_2 to yield water again. The role of these components will be discussed in detail in Chap. 10, but it can be mentioned here that a fine engineering of $Rh_{2-x}Cr_xO_3$ co-catalyst has allowed to achieve the record quantum yield of 5.9 % for water splitting using $(Ga_{0.88}Zn_{0.12})(N_{0.88}O_{0.12})$ under visible light illumination (at 600 nm) (Maeda and Domen 2010; Ohno 2012).

Although a very large photonic efficiency can be achieved with some photocatalysts such as NiO/$NaTaO_3$:La (QY = 56 % at 270 nm), one of the difficulties of hydrogen photocatalytic production is that the process with pure water is in general inefficient (Kato 2003). This is related to the fact that water oxidation is a multistep reaction, which involves four electrons and requires the reaction of two hydroxyl intermediates to form one hydrogen peroxide molecule, according to:

$$2\ OH\cdot \rightarrow H_2O_2\cdot \rightarrow H_2O + \tfrac{1}{2}O_2 \qquad (4.5)$$

The use of electron donors as sacrificial agents may enhance H_2 production, since holes are scavenged by this molecules and recombination is greatly reduced. Furthermore, as O_2 is not produced, gas purification is simplified and the back reaction is suppressed. Simple alcohols, like CH_3OH, or NaS/Na_2SO_3 mixtures are

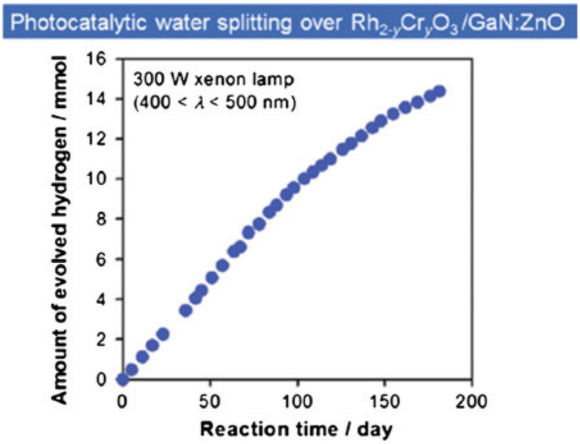

Fig. 4.5 Accumulated H_2 evolution from photocatalytic water splitting as a function of visible light illumination time. Reproduced with permission from Ohno (2012). Copyright American Chemical Society

incorporated to the aqueous solution with this purpose (Hernández-Alonso et al. 2009). However, these additives generate waste products, which have to be disposed, and consequently, their use reduces the sustainability of the process. A more ecological alternative is the use of wastewater pollutants as sacrificial agents, because this very promising approach combines in a single-step water purification and hydrogen production (Patsoura et al. 2007). On the other hand, it is important to keep in mind that a future implementation of photocatalytic hydrogen production will require not only efficient, but also durable photocatalysts. Although this aspect has received still relatively low attention, some long terms studies, as those carried out with GaN:ZnO, have revealed that the photoactivity does not change significantly for the first 3 months, but is almost halved after 6 months operation. This can be appreciated in the plot of Fig. 4.5. The main reason for the deactivation is the loss of the co-catalyst and the hydrolysis of the nitride (Ohno et al. 2012).

Although the use of this technology is not foreseen in short term, it is interesting to theoretically explore its potential to fulfill the energetic needs of the society. In this way, a preliminary estimation indicates that approximately 10,000 solar plants of 25 km^2 of extension working with an efficiency of 10 % would be necessary to provide the projected global energy demand in 2050 (Maeda and Domen 2010). Under these conditions, 570 t H_2 would be produced per day, assuming the standard incident solar energy (AM1.5[1]). Although the extension of land required for these solar hydrogen factories is huge, it corresponds to 1 % of the Earth's desert area and, therefore, it can be achievable through a multinational initiative. In this context, the utilization of simple, cost effective reactors, such as shallow pools with plastic components, will be clearly advantageous for reducing the investment. Anyhow, as shown in the picture of Fig. 4.6, after its separation

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[1] AM refers to Air Mass, and AM1.5 considers a longer atmospheric path length with a zenith angle of 48°

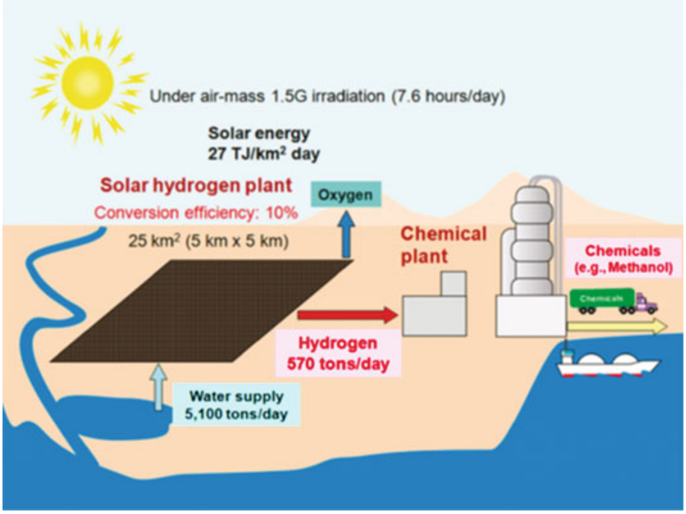


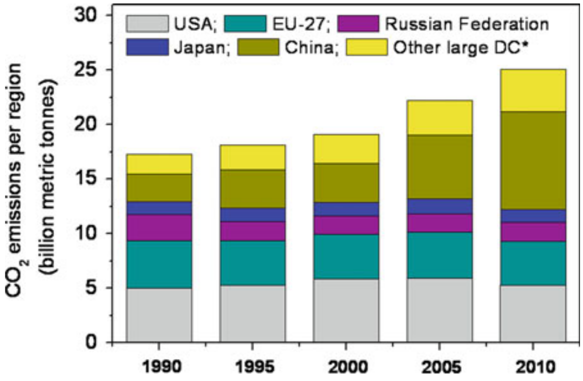
Fig. 4.6 Pictorial diagram for large-scale H_2 production via solar water splitting. Reproduced with permission from Maeda and Domen (2010). Copyright American Chemical Society

from oxygen, the produced hydrogen could be used in fuel cells to produce electricity, or transformed into liquid chemicals like methanol for transportation.

4.3 The Photosynthesis Challenge: Photocatalytic Reduction of CO_2

As the concentration of CO_2 in the atmosphere continuously increases due to anthropogenic causes (Fig. 4.7), mainly derived from deforestation and the use of fossil fuels, the possibility of converting the thermodynamically stable CO_2

Fig. 4.7 Trend in the CO_2 emissions of different countries/regions for the 1995–2010 period. Data extracted from the 2011 report “Long-Term Trend in Global CO2 Emissions” of the JRC European Commission. (* DC: Developing Countries)



molecule into useful hydrocarbon products is becoming a challenging goal and a research priority in environmental catalysis. The interest in CO_2 reduction lies in the ecological problems derived from this gas, since it is one of the major contributors to the greenhouse effect. By means of photocatalysis, this process can proceed under mild conditions, mimicking the photosynthesis in green plants, although producing partially reduced compounds, such as methanol, instead of sugars.

However, CO_2 reduction into hydrocarbon compounds is not spontaneous, but an endergonic reaction which needs energy input. In a photocatalytic process, it would be provided by irradiation and, ideally, solar irradiation. In this respect, semiconductors have proved to be effective as photocatalysts for CO_2 transformation into useful chemical compounds, in both aqueous and gas phases (Inoue et al. 1979; Indrakanti et al. 2009). In a simplified manner, the photosynthetic production of hydrocarbons requires radiation as energy source, a material that can be oxidized to act as source of electrons (e.g., water), and a compound that can be reduced by those electrons (e.g., CO_2) to yield the desired chemical compound. The principles and mechanisms of the natural photosynthetic process can be used as basis for a rational design of solar energy conversion systems.

The challenge of artificial photosynthesis represents a direct pathway to produce fuels from solar energy, being at the same time an attractive method for solar energy storage. An effective recycling of CO_2 into a hydrocarbon fuel using sunlight as energy source would be of great interest, since the product would use the current energy infrastructure. In this respect, methanol constitutes the most valuable product since it can be directly employed as a replacement of fossil fuels both in internal combustion engines (ICEs) and in the so-called direct methanol fuel cells (DMFCs). In these electrochemical cells, methanol is directly oxidized with air to produce electricity. Besides, it is used on a large scale as a source of hydrocarbons for the chemical industry (e.g., formaldehyde or acetic acid). Despite the investment that would represent nowadays the transition to a "hydrogen economy", H_2 is still considered by many as the ideal fuel for the future, due to its clean energetic transformation and its high energy content. However, the extensive safety precautions required for its handling, storage, and distribution could turn "methanol economy," as proposed by Nobel Prize Olah (2005), into a more feasible alternative. Nevertheless, although artificial systems have been reported to produce fuels using sunlight as energy source at laboratory scale, the low quantum yields achieved in these multielectron processes mean a drawback to implement the photocatalyzed reduction of carbon dioxide. So far, alternative routes to produce solar C-containing fuels, consisting in water splitting for H_2 evolution and its subsequent reaction with CO_2, have demonstrated to yield considerably higher production rates than the direct photoreduction of carbon dioxide (Indrakanti et al. 2009).

Additionally to solar fuels production, as H_2 or methanol, photoreduction of CO_2 could constitute an ecologic alternative for the chemical industry for obtaining added-value hydrocarbons, such as formaldehyde, formic acid, or methane, and therefore converting solar into chemical energy. The utilization of CO_2 as a one-carbon building block would represent a benefit from a safety point of view, compared to other raw materials used in the industry, such as carbon monoxide (CO) or phosgene ($COCl_2$). For instance, formic acid is industrially produced at high pressures from methanol and carbon monoxide in the presence of a strong base or certain amines. The photoreduction of CO_2 could represent an interesting replacement (Leitner 1995).

In nature, photosynthesis is carried out by different energetically coupled systems through several steps (Gust et al. 2009). In artificial photosynthesis, the photocatalytic system is expected to carry out the whole process in a more direct way, absorbing light, generating electron–hole pairs, and allowing the separation and migration of the generated charges to redox sites for water oxidation and CO_2 reduction. Any inhibition of electron–hole recombination would increase the CO_2 photoreduction rate, since it has to be taken into account that electron–hole recombination is several orders of magnitude faster than any other electron transfer process (Zhou et al. 2011). As described by Indrakanti et al. (2009), the energetic position of the valence and conduction bands, along with the local structure at the photocatalyst surface, determines the feasibility of these processes. Surface area, CO_2:H_2O ratio, and light intensity are some of the factors that can also influence the reactivity.

The equilibrium reduction potentials of CO_2 reduction and H_2O oxidation reactions, at pH 7 and 25 °C, are presented below (Indrakanti et al. 2009):

$$H_2O \rightarrow 1/2O_2 + 2H^+ + 2e^- \quad E = +0.82\,\text{V} \tag{4.6}$$

$$CO_2 + e^- \rightarrow CO_2^{\cdot -} \quad E = -0.49\,\text{V} \tag{4.7}$$

$$CO_2 + H^+ + 2e^- \rightarrow HCO_2^- \quad E = -0.49\,\text{V} \tag{4.8}$$

$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O \quad E = -0.53\,\text{V} \tag{4.9}$$

$$CO_2 + 2H^+ + 2e^- \rightarrow HCO_2H \quad E = -0.61\,\text{V} \tag{4.10}$$

$$CO_2 + 4H^+ + 4e^- \rightarrow HCHO + H_2O \quad E = -0.48\,\text{V} \tag{4.11}$$

$$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O \quad E = -0.38\,\text{V} \tag{4.12}$$

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2\,H_2O \quad E = -0.24\,\text{V} \tag{4.13}$$

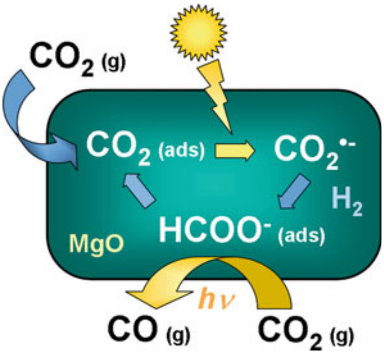
It has to be taken into account that the photoreduction of CO_2 competes with that of protons to H_2 or H_2O_2:

$$2H^+ + 2e^- \rightarrow H_2 \quad E = -0.41\,\text{V} \tag{4.14}$$

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad E = +0.30\,\text{V} \tag{4.15}$$

H_2, H_2S, and CH_4, as well as solvents such as propanol, ethanol, or methanol, among others, have been used as reductants. Replacing water by other reductant induces changes in the mechanism of the reaction, modifying the yields and selectivities that can be obtained (Usubharatana et al. 2006). Thus, it has been observed that using H_2 as reductant leads to the formation of CO as the main

Fig. 4.8 Pictorial scheme showing the proposed mechanism of CO_2 photoreduction over MgO or ZrO_2, using H_2 as reductant



product. As schematically represented in Fig. 4.8, in the particular case of the photoreduction of gaseous CO_2 to CO over MgO in the presence of H_2, it has been proposed that CO molecules are produced from the surface formate species generated in a previous step, after the photoactivation of adsorbed CO_2 (Kohno et al. 2001; Hernández-Alonso et al. 2009).

On TiO_2-based photocatalysts, the proposed activation mechanism involves the interaction of the stable CO_2 molecule with a photogenerated electron to form $CO_2^{\bullet -}$ species adsorbed on the catalyst surface, which utterly undergo further reactions to yield different CH_xO_y products. This one-electron activation of CO_2 is highly endergonic. To ensure this electron transfer, an electronic interaction between CO_2 and the photocatalyst surface is necessary. When acting as an electron acceptor, CO_2 can be adsorbed on the surface as carbonate and bicarbonate species through electrophilic interaction between the C atom and the surface oxygen atoms. Doping with alkali and noble metals may promote CO_2 activation, by means of favoring the formation of $CO_2^{\cdot -}$ species. Besides, the modification of the photocatalyst with noble metals can hinder electron–hole recombination by acting as charge carriers trap (Brause and Kempter 2001; Indrakanti et al. 2009). In the literature, the presence of Pd, Rh, Pt, Au, Cu, or Ru has been reported to improve the performance of the photoreduction process, increasing the selectivity to products that consume more electrons, such as formaldehyde, methanol, and methane (Usubharatana et al. 2006). For instance, Cu/TiO_2 photocatalysts have been observed to yield methanol as the major product (Tseng et al. 2004). Recently, a relatively high CO_2 conversion rate has been achieved on nitrogen-doped TiO_2 nanotube arrays, co-catalyzed with Cu and/or Pt nanoparticles under solar irradiation. The addition of a co-catalyst enhanced the hydrocarbon production rates and allowed modifying the product selectivity (Varguese et al. 2009). The role of the co-catalyst is to promote the charge carrier transfer between the semiconductor and CO_2. Dye sensitization of TiO_2 is another approach for decreasing recombination rates while shifting the absorption coverage into the visible range of the solar spectrum, by acting as a photon antenna and injecting electrons into the conduction band of the semiconductor (Nguyen et al. 2008; Wu 2009). As it will be described in detail in Sect. 13.2, doping with

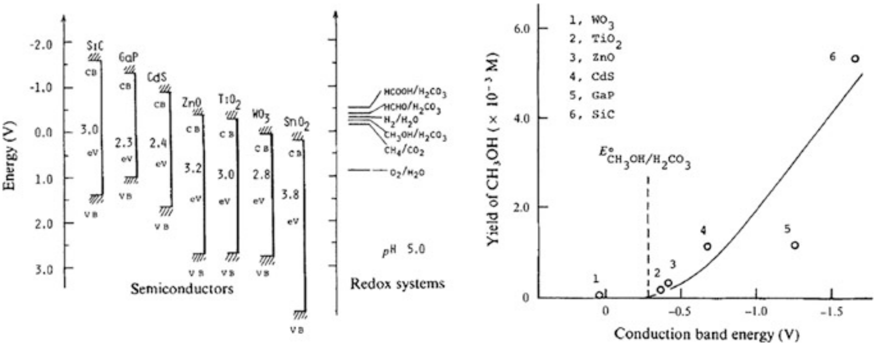


Fig. 4.9 *Left* Schematic representation of the energy correlation between semiconductors and redox couples in water; *Right* correlation between the yield of methanol and the conduction band energy of different semiconductors. Redox potentials are expressed against NHE (Inoue et al. 1979). Reproduced with permission. Copyright Nature Publishing Group (Division of Macmillan Publishers Limited)

transition metals can also lead to a shift of the absorption spectrum to lower energies.

Although most of the research works deal with the use of TiO_2-based photocatalysts, other materials have proved to be able to catalyze CO_2 photoreduction, as is the case of metal complexes. Admitting that the yields obtained with photocatalysts based on metal complexes are higher, besides being expensive and usually unstable under UV light, the consumption of a sacrificial electron donor is usually required (e.g., trimethylamine). On the other hand, the use of semiconductors such as TiO_2 allows the oxidation of inexpensive reductants, as is the case of water (Usubharatana et al. 2006).

In 1979, Inoue et al. (1979) first probed the photocatalytic reduction of carbon dioxide into formic acid, formaldehyde, methanol, and methane, in the presence of a suspension of different semiconductors in water. They observed that the methanol yield increased as the conduction band became more negative with respect to the redox potential of H_2CO_3/CH_3OH. Consequently, a higher yield was obtained on semiconductors such as SiC than on TiO_2 (Fig. 4.9).

As it will be discussed in following chapters, the efficiency of different semiconductors for the photoreduction of CO_2, such as ZrO_2, ZnS, NiO, and Ga_2O_3, has been subject of later studies (Hernández-Alonso et al. 2009). In large band gap semiconductors, the energy position of the valence and conduction bands makes them more suitable for acting as acceptors and donors of electrons in the photocatalytic reduction of CO_2. However, the larger the band gap, the higher the energy input that will be required in the process. Under visible light, NiO-/$InTaO_4$- and $K_2Ti_6O_{13}$-based photocatalysts have proved their ability to reduce CO_2. Theoretically, CuO and Cu_2O band positions make these oxides suitable for, in combination with TiO_2, achieving direct photocatalytic CO_2 conversion (Roy et al. 2010). In the case of supported systems, a screening of different metal oxides on supports of acid/basic nature led to the conclusion that basic supports are more suitable for the selective conversion of CO_2 into hydrocarbon compounds (Subrahmanyam et al. 1999).

CO_2 photoreduction can be performed in gas–solid systems, avoiding the inconvenience of the low solubility of CO_2 in water. In these cases, the use of nanoparticles and highly dispersed TiO_2 has shown to give rise to higher efficiencies than the use of bulk TiO_2. The application of isolated Ti species on microporous and mesoporous materials, the so-called *single-site* photocatalysts which are the focus of Chap. 9, has been extensively studied. In this case, as it will be commented, the reaction rates also depend on factors such as the dispersion and coordination of the Ti species and the hydrophilic–hydrophobic properties of the porous support (Anpo et al. 1997; Yamashita et al. 1998; Ulagappan and Frei 2000; Ikeue et al. 2001). High selectivities to methanol are obtained in the presence of highly dispersed tetrahedrally coordinated titanium oxide species in zeolites, in contrast to the selectivity to methane exhibited by bulk TiO_2, constituted by octahedral species (Anpo et al. 1997; Yamashita et al. 1998). Besides a high dispersion of the titanium oxide species, the use of zeolites, with a large pore size and a three-dimensional channelled structure, has proved to benefit the activity of these materials in the CO_2 photoreduction reaction (Anpo et al. 1998). The affinity for water of the zeolite has also shown to influence the reactivity and selectivity (Ikeue et al. 2001). High methane and methanol production rates have been obtained over Ti-porous materials such as Ti-ZSM-5, Ti-SBA-15, and Ti-MCM-48, just to mention some of them (Yamashita et al. 1995; Anpo et al. 1998; Hwang et al. 2005). For CO_2 activation under visible light, the use of two different metals (e.g., Ti^{4+}–Sn^{2+}or Ti^{4+}–Fe^{4+}) grafted in the porous material has been explored (Indrakanti et al. 2009).

Today, the implantation of this technology for carbon dioxide recycling is still a long-term perspective. In order to improve the low yields (in the order of $\mu mol\ g^{-1}\ h^{-1}$) and selectivities obtained so far, significant advances on the fundamental research on carbon dioxide photoreduction processes are extremely desired. Besides the design and selection of the appropriate photocatalysts and reductants, optimization of the reactor design and operating conditions (e.g., temperature, pressure, light intensity) can lead to improved yields and higher selectivities to the desired products (Usubharatana et al. 2006).

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