1

Photocatalytic Hydrogen Production in the Context of Sustainable Energy

Alberto Puga

Universitat Rovira i Virgili (URV), Department of Chemical Engineering, Av. Països Catalans 26, 43007 Tarragona, Spain

1.1 The Transition to Sustainable Energy

1.1.1 Trends in Primary Energy Production

The production of energy has not ceased to increase during the last two centuries [1]. This fact is rooted in the Industrial Revolution since the machinery representing its very heart was (and still is) powered by the exploitation of massive amounts of fossil carbon resources [2]. One key consequence of the industrial economy has been the improvement of living conditions, which, in turn, has resulted in sustained population growth worldwide. A greater population then needs more energy, leading to ever-increasing energy production. Therefore, it is not surprising that the general trend is still clearly upward for the last few decades (Figure 1.1).

Despite transient declines due to contingencies such as the credit crunch of 2007–2008 or the coronavirus pandemic in 2020, this steady and relentless increment in energy demand experienced in recent times is expected to continue for several more decades, in parallel to global demography. This is because world population growth might not reach a plateau until the end of this century, even if natural increase rates are slowing down. Although energy use is extraordinarily unequal across the planet, the overall current trend is also one of increasing energy demand in relative terms, that is, each generation consumes more energy per person than the previous one. In terms of sustainability, and considering that an excess of energy use above a certain threshold does not lead to improved living standards, an optimal and reasonable average annual per capita energy consumption at 2.8 tons of oil equivalent (toe) has been advocated [4]. Along these lines, global energy production would have to almost double up to almost 3×10^5 TWh in 2050. It is apparent that coping with demand from our near-future energy-hungry societies will represent a gigantic challenge. Therefore, energy security will also require judicious consumption and smart and efficient production, distribution, and use systems [5].
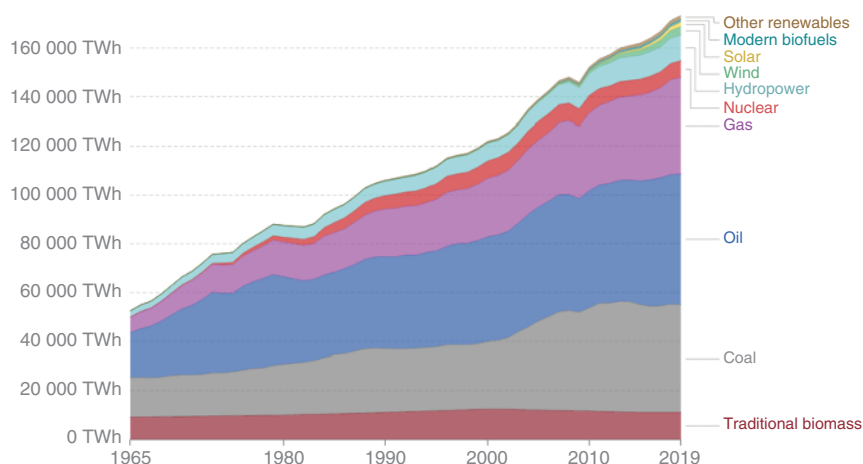
Figure 1.1 Global primary energy supply by source since 1965. Traditional biomass represents raw or gently processed solid fuels such as wood, peat, or charcoal. Modern biofuels include biomass-derived liquid fuels such as biodiesel or bioethanol. Source: OurWorldInData.org/energy, based on data from Refs. [1, 3]; Creative Commons 2022 Our World In Data.

Regarding the shares of different sources in our energy mix, it is striking to note that little has changed in the last half century besides the surge of nuclear power and the rather modest development of renewables. In fact, fossil fuels represented almost 80% of all primary energy supply in 2019 (Figure 1.1). This situation is evolving along a decarbonization pathway owing to the formidable improvement of solar and wind energy technologies, which are becoming cost-competitive at a rapid pace, motivated by the depletion of fossil fuels and the dreadful negative effects of CO_2 emissions on the global climate (see following sections). However, it is naive to assume that the enormous amounts of fossil fuel in use today (see Figure 1.1) will be easily replaced with renewables.

1.1.2 Fossil Reserves

The depletion of reserves of carbon-based fossil fuels, chiefly natural gas, crude oil, and coal, is proceeding at a rapid pace due to our obstinate dependence on them. Proponents of persisting on their mass extraction and exploitation argue that technological advances are constantly enabling new discoveries. Therefore, the so-called proven reserves – i.e. those accessible with current technologies – have been increasing, being hitherto able to meet demand in a satisfactory fashion. It should be noted, though, that most of the newly discovered oil and gas fields are nonconventional and/or extremely difficult to reach, such as extra heavy crude, tar sands, shale oil and gas, or deep offshore fields.

The data in Table 1.1 establish a comparison of reserves and consumption data. Proven reserves in present times are significant, but somewhat lower than total reserves by the end of last century. These numbers must be taken with care due

Table 1.1 Comparison of total reserves, proven reserves, and consumption of fossil fuels.

	Amounts of fossil fuels/Gt(C)			
	Total reserves[a]	**Proved reserves in 2020**[b]	**1965–2020 Consumption**[b]	**Reserves-to-production ratio**[b]/y
Gas	140	96	60	49
Oil	230	208	155	54
Coal	3510	752	162	139

a) According to geological inventories performed in the late twentieth century [6].
b) According to the BP Statistical Review of World Energy [3].

to the uncertainty in their estimation methods, but it is important to note that most of the existing oil and gas (coal is an exception) can be accessed using current means. What is even more relevant is assessing how much of the fossil fuel reserves have been already used and how much is still left. Only during the last 55 years, a significant proportion of all initially available crude oil and natural gas has been used by humanity (e.g. 155 and 60 Gt(C) equivalent, respectively, as compared to 208 and 96 Gt(C) in predicted reserves as of 2020, see Table 1.1). It should be emphasized that proven reserves are expected to be progressively more challenging for future extraction, and hence, less efficient and more expensive. Another matter of concern is their concentration in certain areas of the planet, creating dramatic geopolitical tensions and conflicts for the control of production [7, 8].

Data in Table 1.1 clearly reveal that almost half of our underground battery of stored fossil oil and gas energy is already gone, and for obvious reasons, it will not be replenished to any practically meaningful extent on a human timescale. An unavoidable question follows: how long can we still rely on fossil fuels? One straightforward way to calculate this is the reserves-to-production ratio based on current data, which points to only another half century until total depletion of oil and gas (54 and 49 years, respectively, Table 1.1), and somewhat longer for coal. Future events may of course alter such projections, but based on all the above data, it would not be surprising if production of fossil fuels will stop being able to cope with world energy demand at some not-so-distant point, probably within the next couple of generations.

1.1.3 Carbon Dioxide Emissions and Global Warming

The finite nature of fossil fuels should be a strong enough argument in itself to seriously and strategically plan our economies ahead of their inaccessibility or depletion. In addition to that, their mass consumption is noticeably affecting global carbon cycles, especially with regard to emissions, and consequent atmospheric accumulation, of carbon dioxide [6, 9]. As illustrated in Figure 1.2, anthropogenic emissions pump more CO_2 into the atmosphere than nature is able to fixate into biomass or to store into oceans (9 Gt(C) emitted, vs. 3 and 2 Gt(C) used by plants and algae to grow or absorbed by oceans, respectively, Figure 1.2).
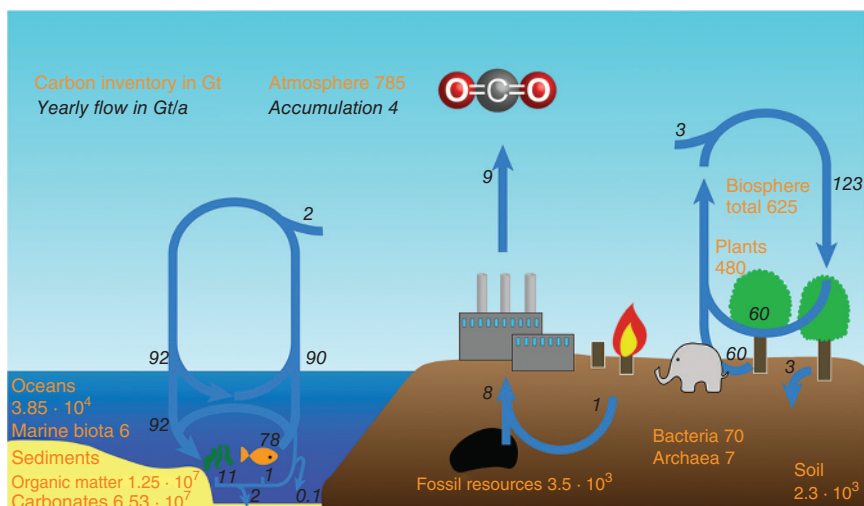
Figure 1.2 Global carbon inventories and flows on Earth, showing natural carbon cycle events and the influence of human activities. Source: P, Müller [9]/with permission of Royal Society of Chemistry.

Among the effects of CO_2 accumulation in the atmosphere, global warming is the most threatening and worrisome. The correlation of average temperatures with atmospheric CO_2 levels has been established even in a pre-industrial time frame with little influence from human activities, confirming its greenhouse effect [10]. Moreover, the extraordinary buildup of carbon dioxide in the Earth's atmosphere from burning fossil fuels in recent times is now completely out of doubt [6, 11]. The extent to which this will affect global climate is a matter of intense debate, but many different models predict a dangerous rise in temperatures, probably leading to other uncharted consequences such as extreme weather events.

1.1.4 Strategic Low-carbon Goals and Energy Sustainability

Both eventual shortages of fossil fuels and global warming due to the greenhouse effect of anthropogenically emitted CO_2 will sooner or later force humankind to a determined decarbonization. The sustainability of future energy schemes will thus largely depend on a successful transition from the current overexploitation of fossil fuels to the efficient and judicious use of renewable energy sources. Developing low-carbon, circular-carbon, or carbon-free energy sources are in principle valid options to strive on this ambitious goal.

The European Union has committed to become completely carbon-neutral, that is, to reduce its CO_2 emissions to net-zero, by 2050 [12]. In this context, the International Energy Agency has set out a comprehensive scrutiny of a range of technological options to effectively transition to decarbonized energy schemes within the same time span, emphasizing on the convenience of solar and wind electricity generation as key tools [13]. It should not be forgotten that containment of energy use to judicious per-capita amounts will be also crucial to achieve any

sustainability goals, albeit equality should also be ensured in fairness toward currently less favored communities, which require improvement of their living standards, as stressed in the United Nations' Sustainable Development Goals [14].

During such a challenging journey, the prevalence of natural gas over crude oil and coal as a low-carbon – yet still fossil – fuel and a renewed focus on nuclear power as an emissions-free way to produce electricity are also emerging as temporary means to maintain CO_2 emissions as low as possible.

Whatever the route chosen, a significant portion of energy demand that is currently met by fossil fuels will most likely require a shift toward electrification systems. This is a grand challenge considering that this amounts to more than 80% of global energy supply (Figure 1.1). Sectors such as transportation, especially by air and waterborne means, are extremely difficult to electrify. A more realistic option in this regard would be the use of nonfossil, low-carbon, storable chemical fuels of sustainable origin, among which, hydrogen is expected to play a major role.

1.2   Hydrogen as Renewable Energy Carrier

1.2.1   The Colors of Hydrogen: Toward Clean Hydrogen

Hydrogen is regarded as a versatile and potentially cost-competitive energy carrier, which may complement and even replace electrical grids and batteries for a number of final applications, especially in heavy industry and transportation sectors [15]. Not surprisingly, both public institutions and private corporations (alone or allied) are turning their efforts to consolidate hydrogen development projects. For example, the European Green Deal decidedly relies on decarbonization via its Hydrogen Strategy [16].

Most hydrogen currently produced is derived from fossil resources (*ca.* 95%), whereas some is obtained by electrolysis, historically as a by-product of the chlor-alkali process (*ca.* 5%) [7, 17]. This situation is rapidly evolving with the advent of a myriad of new green hydrogen projects. But what do we mean by green hydrogen? This term encompasses a set of technologies based on the production of hydrogen using renewable energy sources and involving zero-carbon or at least low-carbon emissions [15]. By contrast, hydrogen from fossil fuels has been given other color codes depending on its source and production process (Figure 1.3), such as:

– black hydrogen: from coal gasification,
– gray hydrogen: from natural gas reforming, or
– blue hydrogen: from natural gas reforming with carbon capture and storage.

Not further commented herein, other color codes have been proposed:

– brown hydrogen: by the gasification of lignite or other low-quality coal feedstocks,
– turquoise hydrogen: by thermal methane splitting (solid carbon as a by-product instead of CO_2),
– pink hydrogen: by water electrolysis using nuclear power, or
– yellow hydrogen: by water electrolysis using grid energy.

	FOSSIL			RENEWABLE				
	Linear carbon economy			Circular carbon economy			Carbon-free	
H_2 color code	Black	Gray	Blue	Camouflage green	Forest green	Pond green	Green	Aquamarine
Feedstock	COAL	NATURAL GAS		SOLID WASTE	BIOMASS	WASTE-WATERS	FRESH WATER	
Process	Gasification	Reforming	Reforming + Carbon Capture	Gasification	Gasification	Photo-reforming	Electrolysis	Photocatalytic water splitting
Hydrogen Cost (€/kg)	1.5–2.0	0.8–1.5	1.5–2.5	3–5	2.5–3.0	3–20*	2–7	2–20*

Figure 1.3 Comparative diagram summarizing different hydrogen production technologies according to the sustainability of the processes, defined by the H_2 color codes. Sustainability increases from left to right. The feedstocks used as hydrogen precursors range from fossil to waste, biomass, and ultimately pure water, representing the paradigm of green hydrogen. Costs of hydrogen have been collected from Refs. [15, 18–22]; asterisks indicate estimates based on techno-economic assessments.

Genuinely, green hydrogen refers to hydrogen that is produced by water electrolysis using renewable electricity, chiefly derived from solar or wind energy. Other renewable hydrogen production processes have not been unambiguously categorized. It is herein proposed (see Figure 1.3) to code them as follows:

- forest green hydrogen: from biomass gasification,
- camouflage green hydrogen: from the gasification of solid waste (e.g. mixed plastic, unrecyclable fraction of municipal solid waste, food waste, or dried sludge),
- pond green hydrogen: produced by the photoreforming of wastewaters, and
- aquamarine hydrogen: produced by photocatalytic water splitting.

1.2.2 Costs of Hydrogen Production

Prices of green hydrogen are in the range of €3–7/kg(H_2) in most common cases, whereas hydrogen from fossil fuels is still somewhat cheaper, with levelized costs as low as *ca.* €0.8–1.5/kg(H_2) for production by steam reforming of natural gas, and less than €2/kg(H_2) for coal gasification (Figure 1.3). So-called blue hydrogen, that is, produced by steam reforming of natural gas coupled with carbon dioxide capture and sequestration, is around or slightly above €2/kg(H_2) [15]. It is convenient to remark here that, as global prices of fossil fuel raw energy materials are sharply rising as this book is being written, the estimated costs of black, gray, and blue hydrogen listed in Figure 1.3 are also expected to increase significantly. This might well be a transient situation due to tensions in the geopolitical arena and, consequently, in the fossil fuel market, but the unavoidable scarcity of natural gas, crude oil, and coal in the mid-term future will most likely drive nonrenewable hydrogen costs to permanently uncompetitive levels.

Current green hydrogen costs are rapidly approaching an acceptable target for competitiveness as compared to processes fed with fossil fuels. With the

formidable development in and deployment of solar photovoltaics and wind turbines, renewable electricity is becoming cheaper than that obtained by power plants based on the combustion of fossil fuels. Moreover, continued electrolysis scale-up and optimization are bringing green hydrogen production costs down at an unprecedented pace. In favorable situations, renewable hydrogen can be even below €1.5/kg(H_2) [15]. This represents a change of paradigm toward green energy being more affordable than that produced from fossil fuels. Photocatalytic water splitting, whereby direct conversion of solar energy into hydrogen takes place, might represent a breakthrough in sustainable energy schemes given its simplicity. The technology is still immature, and efficiencies are rather low. For a typical solar-to-hydrogen efficiency at 0.75%, photocatalytic hydrogen would be expensive using state-of-the-art materials and reactors (€17/kg(H_2) [22]), but projections indicate encouraging reductions in costs if performance and durability issues can be overcome, especially in the case of photoelectrochemical approaches (Figure 1.3).

In an intermediate category of hydrogen production processes between fossil- and water-derived, a series of alternative emergent approaches can be considered. The most relevant examples are the gasification of either biomass or solid waste; some initiatives have achieved commercialization of such technologies. The reforming of organic matter, entailing its conversion into hydrogen and carbon dioxide under anaerobic conditions, is a milder catalytic route enabling energy recovery. Interestingly, the process can be activated by light in the presence of photocatalysts, as further commented below (Section 1.3.3). These waste valorization, circular-carbon, processes can result in remarkably competitive hydrogen production (below €3/kg(H_2), see Figure 1.3).

1.2.3 Solar Fuels and Synthetic Fuels

The production of solar hydrogen is a milestone of renewable green energy since it unifies the harnessing of solar light as a primary energy source and the use of a, theoretically, carbon-free fuel. Not only these sustainability credentials, but also the fact that the relentless reduction in photovoltaic electricity generation costs encourages investment, are resulting in a burgeoning wave of solar green hydrogen projects. Therefore, the production of hydrogen by photovoltaics-electrolysis represents a perfect embodiment of solar fuel technologies.

Photocatalysis offers the advantage of using and/or converting solar irradiation for the production of hydrogen in one step, that is, without the requirement of firstly generating electricity and transporting it to an electrochemical device. Unfortunately, overall efficiencies are still lower for photocatalytic hydrogen production than for the two-step photovoltaics–electrolysis process [22]. Hybrid photoelectrochemical systems are at a more advanced technology readiness level than purely photocatalytic counterparts, although engineering complexity and durability are still hurdles to overcome for their consolidation [23].

Other renewable solar fuel technologies are being investigated and on occasions tested on pilot plant demonstration levels. The most relevant examples are summarized herein. Thermosolar catalysis can be applied to water splitting and a range of

other processes leading to solar fuels [22, 24]. Carbon dioxide reduction is a truly sustainable option if performed from the artificial photosynthesis perspective [25]. The solar conversion of waste into fuels is an emerging field of research offering interesting energetic valorization and circular-carbon opportunities [26]. Finally, and obviously based on or inspired by natural photosynthesis, a myriad of sunlight-powered photobiological processes can be designed to produce fuels [22]. Not all these processes involve carbon-free hydrogen production, but most are aligned with a circular-carbon economy.

Green hydrogen is undeniably the cornerstone of decarbonization strategies. However, carbon-based solar fuels may also hold a prevalent position in future energy schemes. Circular-carbon strategies such as the capture and conversion of CO_2 into fuels, or waste-to-fuels valorization, will be useful to achieve sustainability goals. Moreover, the use of green hydrogen for the production of synthetic fuels and chemicals (e.g. methane, methanol, liquid hydrocarbon fuels, olefins, or ammonia) is gaining ground with the advent of affordable renewable energy. The hydrogenation of CO_2 is reminiscent of Fischer–Tropsch processes and readily leads to recycled carbon substances that can be stored more easily than hydrogen itself [27–29]. For example, synthetic methane or methanol produced via this route can thus be directly distributed by existing infrastructure such as pipelines and tankers, and eventually utilized by chemical sites, other industries, or even households [30].

1.3 The Opportunity for Photocatalytic Hydrogen

Hydrogen production by photocatalysis was completely unknown 50 years ago. Today, research activity in this area is burgeoning, as evidenced by an exponential growth in the number of publications year-over-year [22]. This has been motivated by the frantically and eagerly pursued goal of achieving the direct conversion of solar energy into a chemical fuel using only water as the feedstock, that is, overall water splitting [8, 31]. Hundreds, if not thousands, of new materials have been synthesized and tested for such a purpose. Remarkably high photocatalytic hydrogen production efficiencies have been attained for many different systems, yet most often using reducible substances as electron donors, thus impairing the elusive oxidation half-reaction to generate O_2 as the by-product. Conversely, overall photocatalytic water splitting represents a grand challenge requiring sophisticated materials and engineering design and/or activation by highly energetic photons (mostly in the UV frequencies), which represent a relatively small fraction of solar radiation energy. In view of this, the scientific community is striving to advance on two fronts: one is to more decidedly investigate the feasibility of photocatalytic hydrogen from water (aquamarine hydrogen, as defined herein, see Figure 1.3), and the other to re-invent and re-define advantageous processes that produce hydrogen from different feedstocks using light. The following subsections briefly introduce such approaches, whereas the different chapters in this book delve into specific examples on different areas.

1.3.1 Photoelectrocatalytic Water Splitting

The electrolysis of aqueous solutions has been known and practiced widely, mostly for the production of chlorine and caustic soda, since the end of the eighteenth century [32]. A renaissance in electrolysis technologies is currently taking place in the context of green hydrogen generation from pure water (see Section 1.2.1 above). The use of light to assist the electrolytic dissociation of water was firstly discovered by Fujishima and Honda in the early 1970s, who succeeded in producing O_2 from TiO_2 photoelectrodes under UV-visible irradiation at potentials remarkably less positive (i.e. milder) than the standard potential [33]. Figure 1.4 shows the original diagram of the photoelectrochemical cell designed, showing how a typical electrolysis cell was adapted for irradiation of the photoanode through a suitably transparent window, whereas the rest of the design was essentially unchanged. This pioneering discovery marked the start of a formidably active field of research based on the promoting effect of light (and electricity) for hydrogen production via photo(electro)catalytic processes using mostly inorganic active catalytic materials.

Multiple variations of the photoelectrochemical cell shown in Figure 1.4, on occasions entailing a high degree of sophistication, have been reported [22]. The use of double light-activation (i.e. photocathode–photoanode systems) may lead to effective unassisted photoelectrochemical water splitting, and this has encouraged intense investigation. A detailed account of such systems is presented in Chapters 5 and 6 of this book.

A breakthrough in photoelectrochemical systems is the integration of photo-voltaic materials with electrocatalysts [23]. The former absorb light and enable separation of photogenerated charge carriers, whereas the latter provide kinetically feasible pathways for charge transfer to water and the subsequent hydrogen and oxygen evolutions. Integration of multijunction photovoltaics in photoanodes and electrical connection to cathodes has generally led to superior activities, although other combinations are also possible. Moreover, electrodes can be connected either
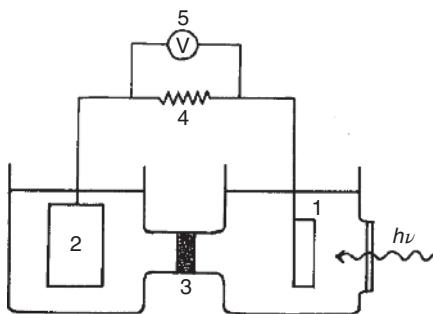

Figure 1.4 Scheme of the cell in the original article by Fujishima and Honda reporting the first photoelectrochemical process for overall water splitting. Irradiation of a TiO_2 photoanode (1) facilitated oxygen gas evolution, whereas a platinum black cathode (2) was used for hydrogen evolution in the dark; a compartment separator (3) was used for ionic transport; and an electrical circuit (4, 5) allowed electron transport from photoanode to cathode. Source: Fujishima A, Honda K. [33]/with permission of Nature Publishing Group.
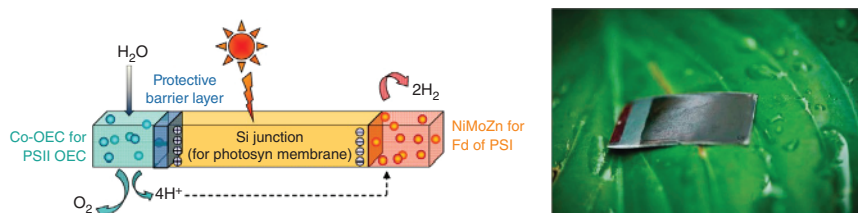
Figure 1.5 Left: Diagram of a wireless photoelectrochemical cell constructed by a back-to-back assembly of a triple junction amorphous silicon photovoltaic membrane as the light-absorbing material, and cobalt-based oxygen evolution and Ni–Mo–Zn hydrogen evolution catalysts (OEC and HEC, respectively). The OEC and HEC are inspired by photosystem II and photosystem I structures, respectively, found in natural photosynthetic organisms. Right: An aspect of an artificial leaf based on the wireless photoelectrochemical design. Source: Nocera DG. [34]/with permission of American Chemical Society.

externally (wired configuration) or in an integrated fashion (wireless configuration) [23]. A notable example of the wireless design is the artificial leaf developed by Nocera and co-workers, whereby triple junction amorphous silicon semiconductors were interfaced with appropriate Earth-abundant electrocatalysts, namely, a self-healing cobalt-based oxygen evolution catalyst and a Ni–Mo–Zn hydrogen evolution catalyst [34, 35]. The wireless photoelectrochemical cell design and an artificial leaf based on such a concept are shown in Figure 1.5. Importantly, these photoelectrocatalytic leaves split water with no electrical energy input or circuit, and can be considered closer to photocatalytic systems in practical terms.

1.3.2 Photocatalytic Water Splitting

The photocatalytic approach is presumably a distinct possibility to harness solar irradiation by directly using it to activate chemical reactions. On the other hand, overall water splitting is a convenient and clean way to store energy in a chemical fashion. For these reasons, photocatalytic water splitting is fiercely sought after as a sustainable and clean pathway to store solar energy [36–38]. The downside of this approach is that combining all efficiency requirements in a single photocatalytic material is an elusive goal [39].

The simplest possible photocatalyst configuration consists of a particulate semiconductor furnished with redox active sites for hydrogen and oxygen evolution, most commonly as deposited co-catalysts (see Figure 1.6). A clear limitation to this is related to energy levels and thermodynamics, since valence and conduction bands should lie more positive and more negative than the O_2/H_2O and H_2O/H_2 redox potentials, respectively. Moreover, overpotentials are generally required for efficiency, and hence, photon energy must be higher than that of the free energy change for water splitting plus those additional potentials. In practice, the band gaps of photocatalysts tend to be large (>3 eV), thus limiting the portion of the usable solar spectrum mostly to the UV region. An alternative solution is the combination of two semiconductors in a Z-scheme configuration inspired by the biochemical machinery of photosynthetic organisms [40]. One of the semiconductors may have lower-lying energy levels than the other, so that they are appropriately aligned with
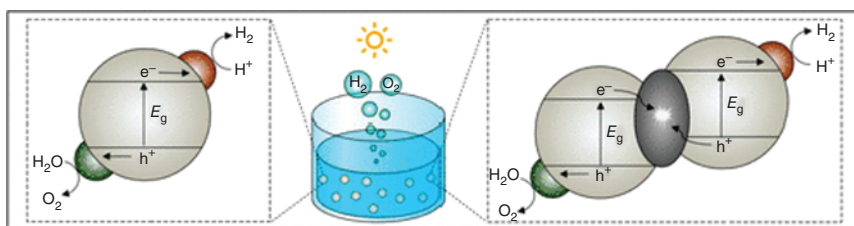
Figure 1.6 Representation of single semiconductor (left) and double-semiconductor Z-scheme (right) designs for overall water splitting photocatalysts incorporating dedicated co-catalysts for H_2 and O_2 evolution. Reproduced with permission from Ref. [22]; Creative Commons 2022 American Chemical Society.

oxygen and hydrogen evolution redox potentials, respectively, and the band gaps may be smaller, in theory enhancing visible light activation.

Excellence in photocatalytic materials has led to impressive progress in water splitting for both single particle and Z-scheme designs [41]. Record-breaking solar-to-hydrogen efficiencies exceeding 1% are being reported in recent years [22], motivating further research and development to improve performances. This is still far away from the arbitrary 10% solar-to-hydrogen energy conversion target for cost competitiveness [18], but a more reasonable medium-term goal at 5% might not be so distant provided new disruptive knowledge on photocatalytic materials and cost reductions upon scale-up can be attained.

1.3.3 Photocatalytic Hydrogen from Various Feedstocks by Photoreforming

Beyond overall water splitting, other substrates can be transformed by photocatalysis to generate hydrogen and other products. A recurring example is that of aqueous halides, which can be also split into elemental hydrogen and halogen, the latter being also a valuable commodity [42–44]. This is the case for chlorine and hypochlorite typically produced by the electrolytic chlor-alkali process, as mentioned above (see Sections 1.2.1 and 1.3.1).

In addition to halogens, nitrogen compounds are relevant since they are ubiquitous in water effluents from domestic, agricultural, and farming activities. Photocatalytic decomposition of urea or even urine [45–47], ammonia [48], and ultimately amino acids, proteins, or their metabolites [46] has been explored, also aiming at selective transformation into elemental nitrogen and hydrogen gases. Importantly, the reverse reduction of N_2 to NH_3 has also been observed [46, 49, 50]. Reduced sulfur species such as sulfides can be also used as substrates for the photocatalytic production of hydrogen [26]. Recovery of solid elemental sulfur has been proposed as a convenient way to deal with waste streams containing sulfide [51].

Needless to say, employing alternatives to water (maybe more correctly, additional substrates) as the electron donors in the overall redox reaction must be the result of a sensible choice leading to advantageous outcomes. However, many reports on photocatalytic production of hydrogen have relied on the use of sacrificial electron

donors to accelerate hydrogen production rates (otherwise limited by the generally sluggish kinetics of O_2 evolution) without caring about their fate or recyclability [52]. Examples include sulfides/sulfites and a range of model organic substances such as alcohols or saccharides, most of which are too valuable *per se* to justify their conversion into hydrogen. Notwithstanding this, if they constitute low-value streams of challenging valorization, transformation into hydrogen might be a profitable approach.

The photocatalytic production of hydrogen from organic substances under anaerobic conditions can be categorized into the so-called photoreforming processes [53, 54]. Ultimately, the organic carbon may be mineralized into CO_2. Oxidation of most organics is both thermodynamically and kinetically more favorable and straightforward than oxygen evolution from water. Early discoveries in this field using semiconductor photocatalysts were reported by Kawai, Sakata, and coworkers from the late 1970s onward. They succeeded in generating hydrogen from aqueous solutions of a range of organic compounds, and most surprisingly, also from insoluble lipids or organic solids such as fats, carbon, cellulose, synthetic polymers, algae, plants, and insects [46, 55, 56]. Photocatalysis appeared to be a powerful tool to generate hydrogen from recalcitrant organic matter of diverse origins, and under remarkably mild, nearly ambient, conditions.

Photoreforming of wastewaters [26], solid waste including plastics [19], raw biomass [57], or biomass derivatives in a biorefinery concept [53, 58, 59] is currently and increasingly considered as valorization options for otherwise challenging streams. Chapters 9 and 10 in this book deal with the photocatalytic conversion of biomass derivatives for hydrogen production, whereas Chapter 11 focuses on the photoreforming of wastewaters. Projections suggesting room for commercial opportunity are stimulating decided initiatives to develop photocatalytic waste-to-hydrogen processes from a laboratory curiosity to real technology. Teams such as those in the solar platform of Almeria (Spain) led by Malato and co-workers have paved the way by adopting their concentrating sunlight reactors for hydrogen production [60, 61]. Reisner and co-workers performed a techno-economic assessment for the photoreforming of solid plastic waste and hinted at what a solar hydrogen production plant based on such a process might look like (Figure 1.7). Finally, opportunities for photocatalytic organic synthesis giving rise to hydrogen as a co-product from diverse substrates have the incentive of generating high-value substances by a sustainable and atom-economic process [62]. Chapter 8 by Fornasiero and co-workers delves into this topic.

The preceding paragraphs outline several useful classes of photocatalytic transformations involving hydrogen production from tremendously variate substrates. The solar option is the preferred activation mode given the virtually free energetic cost, albeit the use of artificial light might prove useful or necessary in some instances. Whatever the irradiation source, a benefit must be ensured regarding the oxidation half-reaction, be it the degradation of an inconvenient waste or the generation of a valuable co-product.
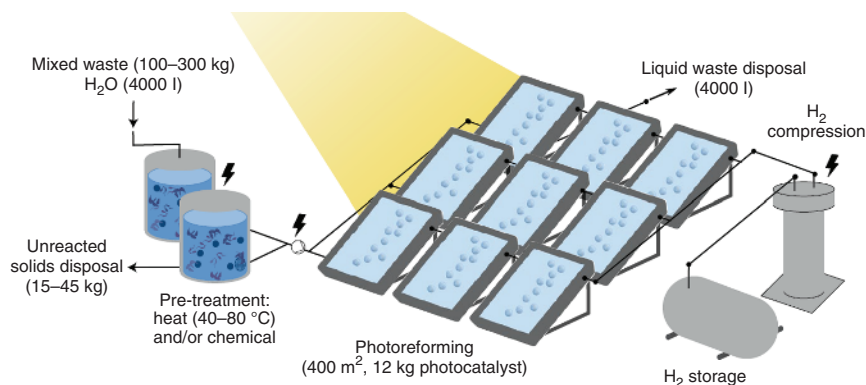
Figure 1.7 Illustration of a projected solar pilot plant for the production of hydrogen by photoreforming of solid waste in water. Source: Uekert et al. [19]/with permission of Springer Nature Limited.

1.3.4 Photobiocatalytic Hydrogen

The term photocatalysis in its broadest dimension comprises any biological transformations promoted by light, mostly sunlight, since these involve the absorption of photons, their use to generate charge carriers, and the eventual catalytic action of enzymes, thanks to an incredibly complex biochemical machinery [63]. Natural photosynthesis is probably the most sublime example of photocatalysis, and maybe also of solar energy use, allowing the creation of life on Earth. Compared with it, even state-of-the-art artificial photosynthetic processes can be viewed as rather rudimentary.

As a hybrid between photobiological and artificial photocatalytic systems, the combination of synthetic materials and reaction setups with microorganisms is a worthwhile and exciting field of research in its own right. The biological part might play a role in absorbing light, promoting chemical reactions, or both. At a lower degree of biotechnological implications, the coupling of enzymes or biomimetic synthetic organometallic substances as co-catalysts into inorganic photocatalysts has attracted significant attention [64, 65]. A typical example is the use of hydrogenases to provide active sites for the hydrogen evolution reaction.

Photobiocatalysis is a relatively unexplored technology as compared to its other photocatalytic counterparts [22, 23]. Curiously, the discovery of photobiological hydrogen production by algae in a light-promoted fermentative process was the first ever reported photocatalytic technology for the purpose, dating back to 1942 [66]. Two main approaches have been adopted: (i) biophotolysis, as a biochemical embodiment of overall water splitting; and (ii) photofermentation, whereby microorganisms thrive under sunlight irradiation in the presence of biomass-based feed, enabling the evolution of hydrogen under anaerobic conditions.

The singularity of photobiological hydrogen production deserves attention from the scientific community, although unfortunately, it is not further accounted for in this book. It would be good news should an explosion in this fascinating field of research be witnessed by future generations.

1.4 Outlook

Photocatalysis requires essentially a source of light and an appropriate redox photoactive material. On a fundamental level, electromagnetic energy is absorbed, channeled, and harnessed to drive chemical reactions. Energy can be only utilized for the activation of thermodynamically spontaneous processes (e.g. aerobic oxidation of organics) or also stored in chemical products of endergonic ones (e.g. overall water splitting or natural photosynthesis). The complexity of the photocatalytic system may vary greatly depending on the specific transformation taking place, but in general terms, activation by light proceeds under near-ambient conditions. Additional energy might be also applied in the form of, *inter alia*, electricity or heat, but mild operation conditions are a clear advantage of photocatalytic processes over their classical thermocatalytic counterparts.

Generating hydrogen by photocatalysis is certainly possible in a formidable variety of systems. However, an assessment of each process must be undertaken to ensure its merits, be they economic, environmental, or energetic. Considering a specific case, the production of hydrogen by the photoreforming of alcohols might proceed rapidly and at an outstanding quantum efficiency close to 100%, but it may be meaningless to do so since the value of the starting alcohols might be even higher than that of the produced hydrogen. Notwithstanding this, one could consider a process of this kind still useful if a simple alcohol such as methanol is used as a high volumetric energy density carrier of hydrogen for eventual use in fuel cells. From a different perspective, the photoreforming of a range of organic (or inorganic) substances can make sense for the energetic valorization of waste streams or in high-added-value synthetic processes.

The most popular and intensely sought objective of photocatalysis is the storage of solar energy into chemical energy by artificial photosynthetic processes, namely overall water splitting and carbon dioxide reduction. The former is seen as the quintessence of renewable and sustainable energy schemes, since it goes beyond the green credentials of hydrogen produced by photovoltaics followed by electrolysis, due to its presumably enhanced simplicity and affordability. Photocatalytic hydrogen by overall water splitting has been given here aquamarine as a color code denoting extreme cleanliness. The bad news lies in the fact that efficiencies using state-of-the-art systems are still far from the desirable threshold (5%) for consolidation of the technology in terms of competitiveness. Surpassing this landmark in the near future would be a game-changer, provided the environmental and societal impact of mining and supplying materials for the required photocatalysts on a gigantic scale globally to meet energy demand can be kept within reasonable levels. We should not be surprised if, in addition to technological advancements, our exorbitant thirst for energy will have to be restrained to some extent to maintain a peaceful balance with energy production. Ultimately, humankind must assume that our planet has its limits.

Acknowledgments

References

1 Smil, V. (2016). *Energy Transitions: Global and National Perspectives*, 2nd ed. Praeger.

2 Hudson, P. (2014). *The Industrial Revolution*. London: Hodder Arnold.

3 (2021). *Statistical Review of World Energy 2021*, 7th ed. BP.

4 Armaroli, N. and Balzani, V. (2016). Solar electricity and solar fuels: status and perspectives in the context of the energy transition. *Chem. Eur. J.* 22 (1): 32–57.

5 IEA (2020). *Key World Energy Statistics 2020*. Paris: International Energy Agency https://www.iea.org/reports/key-world-energy-statistics-2020.

6 Falkowski, P., Scholes, R.J., Boyle, E. et al. (2000). The global carbon cycle: a test of our knowledge of Earth as a system. *Science* 290 (5490): 291–296.

7 Armaroli, N. and Balzani, V. (2010). *Energy for a Sustainable World: From the Oil Age to a Sun-Powered Future*. Wiley.

8 Armaroli, N. and Balzani, V. (2007). The future of energy supply: challenges and opportunities. *Angew. Chem. Int. Ed.* 46 (1+2): 52–66.

9 Tomkins, P. and Müller, T.E. (2019). Evaluating the carbon inventory, carbon fluxes and carbon cycles for a long-term sustainable world. *Green Chem.* 21 (15): 3994–4013.

10 Lüthi, D., Le Floch, M., Bereiter, B. et al. (2008). High-resolution carbon dioxide concentration record 650,000–800,000 years before present. *Nature* 453 (7193): 379–382.

11 Keeling, R.F. (2008). Recording Earth's vital signs. *Science* 319 (5871): 1771.

12 Directorate-General for Climate Action (2019). *Going climate-neutral by 2050: a strategic long-term vision for a prosperous, modern, competitive and climate-neutral EU economy*. European Commission.

13 Bouckaert, S., Pales, A.F., McGlade, C. et al. (2021). *Net Zero by 2050, A Rodmap for the Global Energy sector*. Paris: International Energy Agency.

14 (2020). *The Sustainable Development Goals Report*. United Nations.

15 Gielen, D., Taibi, E., and Miranda, R. (2019). *Hydrogen: A Renewable Energy Perspective*. International Renewable Energy Agency (IRENA).

16 Directorate-General for Research and Innovation (2020). Research & Innovation key driver of the hydrogen strategy. European Commission.

17 Armaroli, N. and Balzani, V. (2011). The hydrogen issue. *ChemSusChem* 4 (1): 21–36.

18 Shaner, M.R., Atwater, H.A., Lewis, N.S., and McFarland, E.W. (2016). A comparative technoeconomic analysis of renewable hydrogen production using solar energy. *Energy Environ. Sci.* 9 (7): 2354–2371.

19 Uekert, T., Pichler, C.M., Schubert, T., and Reisner, E. (2020). Solar-driven reforming of solid waste for a sustainable future. *Nat. Sustainability* 4 (5): 383–391.

20 Navarro, R.M., Sánchez-Sánchez, M.C., Alvarez-Galvan, M.C. et al. (2009). Hydrogen production from renewable sources: biomass and photocatalytic opportunities. *Energy Environ. Sci.* 2: 35–54.

21 Pinaud, B.A., Benck, J.D., Seitz, L.C. et al. (2013). Technical and economic feasibility of centralized facilities for solar hydrogen production via photocatalysis and photoelectrochemistry. *Energy Environ. Sci.* 6 (7): 1983–2002.

22 Song, H., Luo, S., Huang, H. et al. (2022). Solar-driven hydrogen production: recent advances, challenges, and future perspectives. *ACS Energy Lett.* 7 (3): 1043–1065.

23 Liu, G., Sheng, Y., Ager, J.W. et al. (2019). Research advances towards large-scale solar hydrogen production from water. *EnergyChem* 1 (2): 100014.

24 Mateo, D., Cerrillo, J.L., Durini, S., and Gascon, J. (2021). Fundamentals and applications of photo-thermal catalysis. *Chem. Soc. Rev.* 50 (3): 2173–2210.

25 Li, K., Peng, B., and Peng, T. (2016). Recent advances in heterogeneous photocatalytic CO_2 conversion to solar fuels. *ACS Catal.* 6 (11): 7485–7527.

26 Jeon, T.H., Koo, M.S., Kim, H., and Choi, W. (2018). Dual-functional photocatalytic and photoelectrocatalytic systems for energy- and resource-recovering water treatment. *ACS Catal.* 8 (12): 11542–11563.

27 Centi, G., Quadrelli, E.A., and Perathoner, S. (2013). Catalysis for CO_2 conversion: a key technology for rapid introduction of renewable energy in the value chain of chemical industries. *Energy Environ. Sci.* 6 (6): 1711–1731.

28 Puga, A.V. (2018). On the nature of active phases and sites in CO or CO_2 hydrogenation catalysts. *Catal. Sci. Technol.* 8: 5681–5707.

29 Aresta, M., Dibenedetto, A., and Angelini, A. (2014). Catalysis for the valorization of exhaust carbon: from CO_2 to chemicals, materials, and fuels. Technological use of CO_2. *Chem. Rev.* 114 (3): 1709–1742.

30 Olah, G.A., Goeppert, A., and Prakash, G.K.S. (2009). *Beyond Oil and Gas: The Methanol Economy*, 2e. Wiley-VCH Verlag.

31 Balzani, V., Credi, A., and Venturi, M. (2008). Photochemical conversion of solar energy. *ChemSusChem* 1 (1-2): 26–58.

32 Bommaraju, T.V., Lüke, B., O'Brien, T.F., and Blackburn, M.C. Chlorine. In: *Kirk-Othmer Encyclopedia of Chemical Technology*. (Ed.), https://doi.org/10.1002/0471238961.0308121503211812.a01.pub2.

33 Fujishima, A. and Honda, K. (1972). Electrochemical photolysis of water at a semiconductor electrode. *Nature* 238: 37–38.

34 Nocera, D.G. (2012). The artificial leaf. *Acc. Chem. Res.* 45: 767–776.

35 Reece, S.Y., Hamel, J.A., Sung, K. et al. (2011). Wireless solar water splitting using silicon-based semiconductors and earth-abundant catalysts. *Science* 334: 645–648.

36 Takanabe, K. (2017). Photocatalytic water splitting: quantitative approaches toward photocatalyst by design. *ACS Catal.* 7 (11): 8006–8022.

37 Kim, J.H., Hansora, D., Sharma, P. et al. (2019). Toward practical solar hydrogen production – an artificial photosynthetic leaf-to-farm challenge. *Chem. Soc. Rev.* 48 (7): 1908–1971.

38 Chen, S., Takata, T., and Domen, K. (2017). Particulate photocatalysts for overall water splitting. *Nat. Rev. Mater.* 2 (10): 17050.

39 Idriss, H. (2020). The elusive photocatalytic water splitting reaction using sunlight on suspended nanoparticles: is there a way forward? *Catal. Sci. Technol.* 10 (2): 304–310.

40 Wang, Y., Suzuki, H., Xie, J. et al. (2018). Mimicking natural photosynthesis: solar to renewable H_2 fuel synthesis by Z-scheme water splitting systems. *Chem. Rev.* 118 (10): 5201–5241.

41 Hisatomi, T. and Domen, K. (2019). Reaction systems for solar hydrogen production via water splitting with particulate semiconductor photocatalysts. *Nat. Catal.* 2 (5): 387–399.

42 Bard, A.J. and Fox, M.A. (1995). Artificial photosynthesis – solar splitting of water to hydrogen and oxygen. *Acc. Chem. Res.* 28 (3): 141–145.

43 Teets, T.S. and Nocera, D.G. (2011). Photocatalytic hydrogen production. *Chem. Commun.* 47 (33): 9268–9274.

44 Antonietti, M. and Savateev, A. (2018). Splitting water by electrochemistry and artificial photosynthesis: excellent science but a nightmare of translation? *Chem. Rec.* 18 (7-8): 969–972.

45 Wang, G., Ling, Y., Lu, X. et al. (2012). Solar driven hydrogen releasing from urea and human urine. *Energy Environ. Sci.* 5 (8): 8215–8219.

46 Kawai, T. and Sakata, T. (1981). Photocatalytic hydrogen production from water by the decomposition of poly(vinyl chloride), protein, algae, dead insects, and excrement. *Chem. Lett.* 81–84.

47 Kim, J., Monllor-Satoca, D., and Choi, W. (2012). Simultaneous production of hydrogen with the degradation of organic pollutants using TiO_2 photocatalyst modified with dual surface components. *Energy Environ. Sci.* 5 (6): 7647–7656.

48 Yuzawa, H., Mori, T., Itoh, H., and Yoshida, H. (2012). Reaction mechanism of ammonia decomposition to nitrogen and hydrogen over metal loaded titanium oxide photocatalyst. *J. Phys. Chem. C* 116 (6): 4126–4136.

49 Schrauzer, G.N. and Guth, T.D. (1977). Photolysis of water and photoreduction of nitrogen on titanium dioxide. *J. Am. Chem. Soc.* 99 (22): 7189–7193.

50 Sakata, T. (1985). Photocatalysis of irradiated semiconductor surfaces – its application to water splitting and some organic-reactions. *J. Photochem.* 29 (1-2): 205–215.

51 Gonell, F., Puga, A.V., Julián-López, B. et al. (2016). Copper-doped titania photocatalysts for simultaneous reduction of CO_2 and production of H_2 from aqueous sulfide. *Appl. Catal., B* 180: 263–270.

52 Kamat, P.V. and Jin, S. (2018). Semiconductor photocatalysis: "tell us the complete story!". *ACS Energy Lett.* 3 (3): 622–623.

53 Puga, A.V. (2016). Photocatalytic production of hydrogen from biomass-derived feedstocks. *Coord. Chem. Rev.* 315: 1–66.

54 Christoforidis, K.C. and Fornasiero, P. (2017). Photocatalytic hydrogen production: a rift into the future energy supply. *ChemCatChem* 9 (9): 1523–1544.

55 Kawai, T. and Sakata, T. (1980). Conversion of carbohydrate into hydrogen fuel by a photocatalytic process. *Nature* 286 (5772): 474–476.

56 Kawai, T. and Sakata, T. (1979). Hydrogen evolution from water using solid carbon and light energy. *Nature* 282: 283–284.

57 Kuehnel, M. and Reisner, E. (2018). Solar hydrogen generation from lignocellulose. *Angew. Chem. Int. Ed.* 57 (13): 3290–3296.

58 Davis, K.A., Yoo, S., Shuler, E.W. et al. (2021). Photocatalytic hydrogen evolution from biomass conversion. *Nano Convergence* 8 (1): 6.

59 Granone, L.I., Sieland, F., Zheng, N. et al. (2018). Photocatalytic conversion of biomass into valuable products: a meaningful approach? *Green Chem.* 20 (6): 1169–1192.

60 Maldonado, M.I., López-Martín, A., Colón, G. et al. (2018). Solar pilot plant scale hydrogen generation by irradiation of Cu/TiO$_2$ composites in presence of sacrificial electron donors. *Appl. Catal., B* 229: 15–23.

61 Arzate Salgado, S.Y., Ramírez Zamora, R.M., Zanella, R. et al. (2016). Photocatalytic hydrogen production in a solar pilot plant using a Au/TiO$_2$ photo catalyst. *Int. J. Hydrogen Energy* 41 (28): 11933–11940.

62 Friedmann, D., Hakki, A., Kim, H. et al. (2016). Heterogeneous photocatalytic organic synthesis: state-of-the-art and future perspectives. *Green Chem.* 18 (20): 5391–5411.

63 Blankenship, R.E. (2002). *Molecular Mechanisms of Photosynthesis*. Wiley.

64 Wen, F. and Li, C. (2013). Hybrid artificial photosynthetic systems comprising semiconductors as light harvesters and biomimetic complexes as molecular cocatalysts. *Acc. Chem. Res.* 46 (11): 2355–2364.

65 Hennessey, S. and Farràs, P. (2018). Production of solar chemicals: gaining selectivity with hybrid molecule/semiconductor assemblies. *Chem. Commun.* 54 (50): 6662–6680.

66 Gaffron, H. and Rubin, J. (1942). Fermentative and photochemical production of hydrogen in algae. *J. Gen. Physiol.* 26 (2): 219–240.