SOLAR DRIVEN CHEMISTRY

Solar-driven chemistry: towards new catalytic solutions for a sustainable world

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Abstract
The topic of production of useful chemical compounds with the help of solar light has been debated at a recent meeting organized in Rome on October 18 and 19, 2018, by the Accademia Nazionale dei Lincei. Some of the contributions presented at this event are collected in this special issue of the Rendiconti Lincei. Scienze fisiche e Naturali. In this paper, we briefly discuss some recent results concerning the use of solar energy by artificial photochemical reactions for four important applications: (i) conversion of solar energy into fuels or (ii) conversion of sunlight into electrical energy, (iii) use of solar energy to perform organic synthesis that cannot be obtained by conventional chemistry, and (iv) photochemical reactions to reduce pollution.

Keywords Photocatalysis · Solar fuels · Solar cells · Artificial photosynthesis

1 Introduction

Mankind is exploiting without respite the limited resources of our planet. In the long run, we are called to reverse the present trend that converts Earth's resources into waste at an astonishing rate.

Energy is the most important resource for humanity. Several ecological, economic, and political problems of the present Anthropocene epoch are connected with the extended use of fossil fuels as primary energy resource (Armaroli and Balzani 2011). On the other hand, solar energy, an enormous, reliable, and practically inexhaustible energy source, is hardly exploited. A very small fraction of solar energy, about 0.1%, is converted by natural photosynthesis into biomass. Chemists are learning to exploit the huge amount of solar energy by artificial photochemical reactions for three important applications (Balzani et al. 2014): (i) to convert sunlight into chemical or electrical energy, (ii) to perform organic synthesis that cannot be obtained by conventional chemistry, and (iii) to remedy pollution.

Light excitation of a molecule or a semiconductor leads to an electronically excited state capable of performing as a stronger one-electron oxidant/reductant compared with the ground state. This means that light excitation promotes a primary electron-transfer reaction.

When molecules are not able to absorb light, they cannot exploit the peculiar reactivity of their electronically excited states. In such a case, it is possible to use a photosensitizer, a species capable of absorbing sunlight and then making available the excited state energy to promote reactions of non-absorbing molecules.

The primary photoinduced electron-transfer reactions, particularly when the overall process requires the transfer of more than one electron, are usually followed by several secondary reactions. Therefore, catalysts (Ghosh 2018) are also needed to speed up the useful vs useless competing thermal reactions. General concepts in thermal heterogeneous, homogeneous, and enzymatic catalysis have been recently discussed at a meeting of the Accademia Nazionale

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dei Lincei organized in Rome in 2016 (Zecchina and Groppo 2017).

2 Solar energy conversion

The actual rate of worldwide energy consumption (about 17 TW) is almost four orders of magnitude smaller than the solar energy irradiating the surface of the planet. Solar energy, however, is not useful for mankind unless it is converted into usable forms of energy: heat, electricity, and fuels. Conversion of solar energy into heat is very easy, but conversion into electricity and fuels, the noblest energy forms, can only be performed by threshold-based processes with limited efficiency. Since we cannot modify the solar spectrum, we have to find suitable materials capable of exploiting sunlight through the threshold mechanism with the highest possible efficiency. Taking into account the average spectral distribution of sunlight, the most favorable threshold is about 885 nm (1.4 eV), which in principle corresponds to 33% energy conversion efficiency (Balzani et al. 2014). The materials used as reactants for solar energy conversion should be abundant on the earth's crust, reasonably inexpensive, with low environmental impact, and recyclable (Armaroli and Balzani 2011). Their products should have a high energy content, but they should also be stable enough to be directly stored, or storable by a successive transformation, to overcome the intermittency and intensity fluctuations of solar energy. Finally, photosensitizers and catalysts should be efficient and should exhibit a high turnover number.

3 Conversion of sunlight into electrical energy

3.1 Inorganic solar cells (PV cells)

Inorganic photovoltaic solar cells (usually indicated as PV cells) are made of semiconducting materials consisting of doped silicon or combinations of different elements such as gallium, arsenic, tellurium, copper, or cadmium.

In common silicon solar cells (Fig. 1), a slice of *n*-type (e.g., phosphorus-doped) material is placed in physical contact with a slice of *p*-type (e.g., boron-doped) material, so that the "free" electrons in the *n*-side will rush to fill the "holes" in the *p*-side. An electron migration over the *p*–*n* junction creates a net negative charge on the *p*-doped material, counterbalanced by an identical positive charge on the *n*-doped material. This spontaneous process creates an electric field that stops electrons flowing in one direction, thereby producing a diode. For silicon diodes, the built-in potential is about 0.6 V. When light excitation promotes an electron from the valence (VB) to the conduction band (CB)
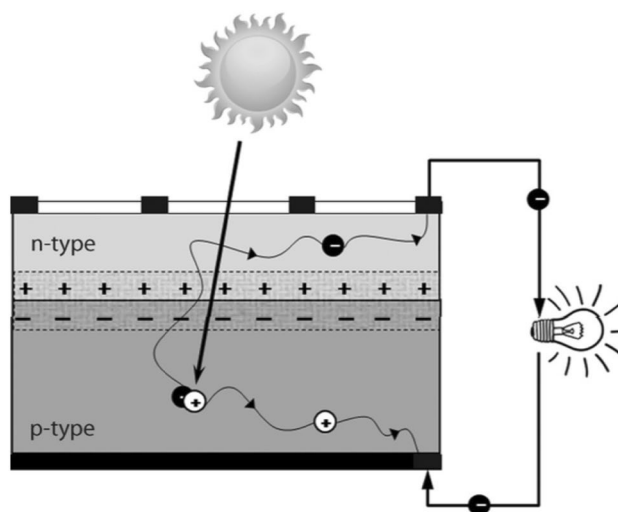

Fig. 1 Conversion of sunlight into electrical energy in a silicon photovoltaic cell (adapted from Balzani et al. 2015)

of the *p*-side silicon near the junction, the electron will be attracted on the positive side of the field, thereby flowing toward the *n*-type material through the junction. By connecting the two sides of the cell, away from the junction, the electron will travel outside the cell, thereby generating an electric current from the *n*-side to the *p*-side, which can be exploited to obtain useful work. To cope with intermittency and energy fluctuations of sunlight, storage components are required as an integral part of the system. The most common option for storing electricity is based on the reversible conversion into chemical energy by using batteries or by water electrolysis followed by the use of hydrogen in fuel cells. In designing sustainable energy conversion devices, material abundance, ecological sustainability, toxicity, and scalability should be considered.

Over 90% of today's commercial solar cells are based on doped silicon in either a polycrystalline or a single-crystal form (poly-Si and sc-Si, respectively). The band gap of silicon is 1.1 eV and the maximum theoretical efficiency is about 30%. The solar energy conversion efficiency of standard industrial cells is from 15 to 20%, but a value of about 27% has been reached at research level (NREL 2018). Silicon solar cells are reliable and robust, and their cost continues to decrease. In many countries and circumstances, PV cells are the more convenient source of electricity.

Among inorganic non-silicon semiconducting substances, a leading material is polycrystalline CdTe, whose band gap of about 1.5 eV optimally matches the solar spectrum. A drawback of CdTe is that Cd is one of the top six deadliest and toxic materials known. Earth-abundant materials such as FeS_2, CuO, and Zn_3P_2 have also been investigated (Ran et al. 2014). A novel class of materials has been developed in the last decade in the field of inorganic solar cells
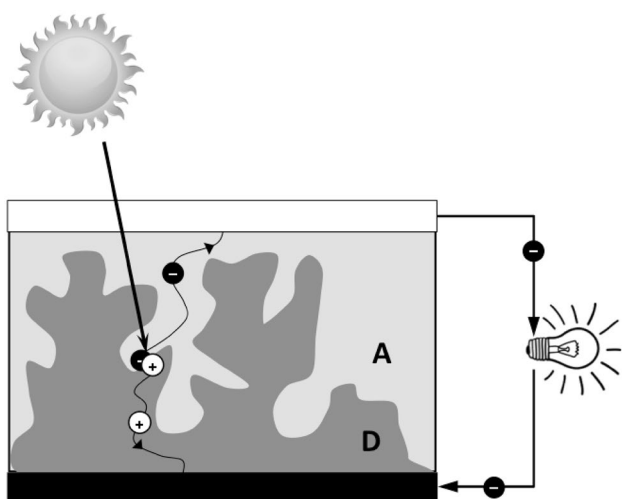
Fig. 2 Schematic representation of an organic solar cell (adapted from Balzani et al. 2015)

with good potential in PV applications. Perovskites are well-known materials, but the first use into a solar cell was reported only in 2009 (Kojima et al. 2009). It was based on a dye-sensitized solar cell that generated 3.8% conversion efficiency. Furthermore, the cell was highly unstable in the liquid electrolyte used. A few years later, stable perovskite solar cells were reported with efficiencies of almost 10% (Kim et al. 2012; Lee et al. 2012; Eperon et al. 2014).

These systems have a perovskite structure and usually consist of hybrid organic–inorganic lead or tin halide-based materials with good light-harvesting properties. They are simple to manufacture and relatively cheap, although some environmental issues are connected to the use of lead. Since the discovery of this new class of materials for applications in photovoltaics, the field has literally exploded, and efficiency has continuously increased over the years reaching 24.2% in 2019 in single-junction architectures (NRELN 2019) and, in silicon-based tandem cells, 28.0% (NREL 2018), higher than the maximum efficiency achieved in single-junction silicon solar cells.

3.2 Organic solar cells

Organic solar cells (OSCs) sometimes are called polymer solar cells. They are based on charge transfer occurring at the interface between an electron acceptor (A) and an electron donor (D) (Fig. 2), which constitute the analog of the "inorganic" semiconductor p–n junctions described above. The excited state generated by the absorption of light by either A or D is a molecular excited state ("exciton") that can either recombine emitting light or heat or migrate to the interface and produce D^+ and A^- species. These charges

then move to the respective electrodes, thereby generating a current.

A notable example is represented by PCBM, a particularly efficient fullerene derivative, mixed with conjugated polymers. These cells, called heterojunction or even plastic solar cells, take advantage of the strong electron accepting character of fullerenes (Gunes et al. 2007). Substantial absorption of light is achieved even with ultrathin devices (< 100 nm). Organic photovoltaic devices have several advantages such as low weight and high flexibility, significantly lower manufacturing costs compared to conventional inorganic cells, and manufacture of devices is performed in continuous process using printing tools. Efficiency has reached 11% (NREL 2018). A drawback is that organic materials are susceptible to chemical and physical degradation, particularly by the action of oxygen and moisture.

3.3 Dye-sensitized solar cells (DSSCs)

Sunlight can be converted directly into electrical power not only in solid-state photovoltaic devices (Figs. 1 and 2), but also in dye-sensitized solar cells, often called Grätzel cells (O'Regan and Graetzel 1991), which are based on sensitization of wide gap semiconductors by molecular species capable of absorbing sunlight.

A dye-sensitized solar cells (Fig. 3) comprises a nanocrystalline TiO_2 semi-conductor electrode of very high surface area and a counter electrode, both immersed in an electrolyte solution containing a redox mediator (*R*). A photosensitizer (PS) is anchored (usually, by –COOH, –PO$_3$H$_2$, or –B(OH)$_2$ groups) to the semiconductor surface. Light is absorbed by the photosensitizer, whose excited state injects an electron into the conduction band (CB) of the semiconductor (step 1 in Fig. 3). The oxidized sensitizer is reduced by a redox mediator R^+/R (step 2, in competition with the back electron transfer, step 4), which then diffuses to the counter electrode (step 3). A photopotential is thus generated between the two electrodes under open-circuit conditions and a corresponding photocurrent can be obtained. A great number of photosensitizers have been employed, particularly of the ruthenium polypyridine family. A variety of solvents of different viscosity have been used and the most common redox mediator is the I_3^-/I^- couple in acetonitrile solution (Bignozzi et al. 2013).

4 Conversion of solar energy into chemical energy

4.1 Natural photosynthesis

Natural photosynthesis, which is at the base of the food chain, converts light energy into the chemical energy of
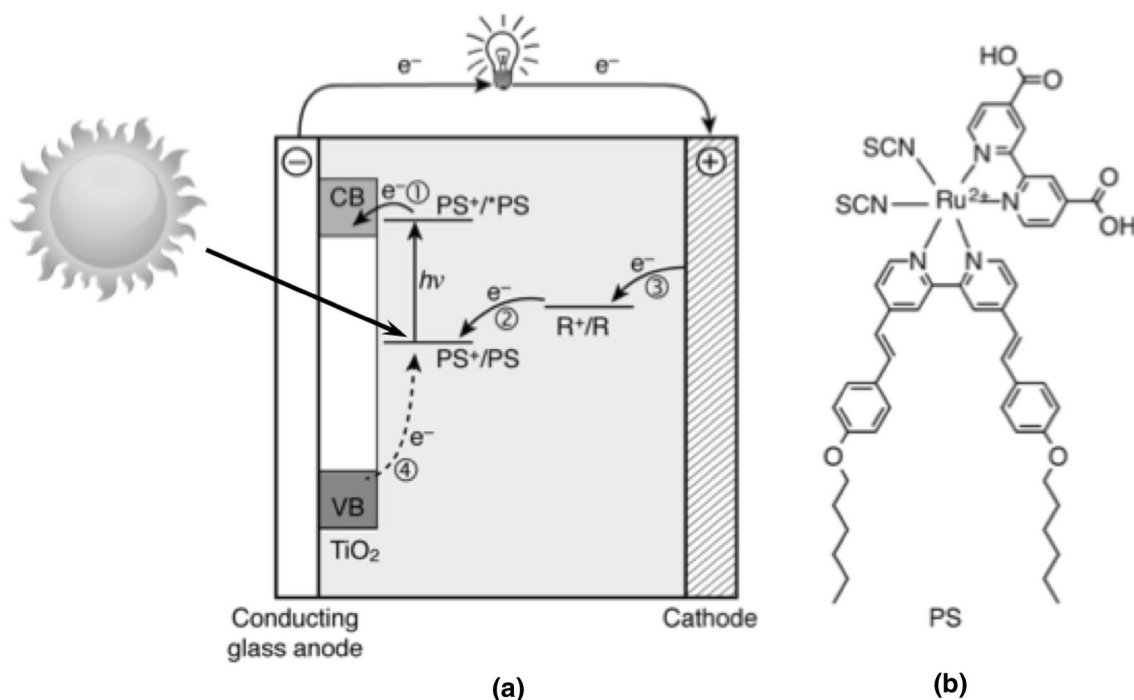
Fig. 3 **a** Scheme of a dye-sensitized solar cell. PS is a photosensitizer linked to a semiconductor electrode and R is a redox mediator. **b** A ruthenium oligopyridine complex used as a photosensitizer (adapted from Balzani et al. 2015)

plant biomass. The threshold energy to generate the photo-chemistry-driving excited state in green plant photosynthesis is about 680 nm (1.83 eV) and the two photo-systems called PSII and PSI work in series (Balzani et al. 2014), so that two photons are necessary to move an electron/proton from water to carbon dioxide. Taking into account saturation effects and leaf reflectivity, the maximum efficiency for the conversion of solar energy into stored chemical energy (dry carbon matter) is about 4.5%. Losses caused by photodamage and survival and reproduction of the photosynthetic organisms further reduce the efficiency. In fact, even under the most favorable conditions, the efficiency of biomass production is less than 1%, and often as low as 0.1% (Barber and Tran 2013).

The end product of photosynthesis, biomass, can be used to satisfy three fundamental needs of mankind: food, energy, and valuable materials (Armaroli and Balzani 2011). Biogas, a mixture of CH_4 and CO, can be obtained from sewage sludge, animal wastes, and any type of organic matter. Liquid biofuels (bioethanol, biodiesel) are produced by conventional agriculture resources rich in carbohydrates such as corn, sugar cane, sugar beet and wheat. Part of the energy stored in a biofuel had to be spent to produce the biomass (plowing, transporting, synthesizing fertilizers and pesticides). Energy must also be invested to convert biomass into the biofuel. It follows that for a biofuel, the ratio between the energy returned on energy invested (EROEI) is often close

or even smaller than 1. Furthermore, both the production and the use of biofuels are not CO_2- neutral as often asserted, but actually make the climate issue worse. Finally, using edible feedstock for making biofuels is in competition with food production.

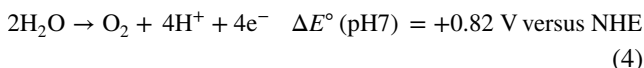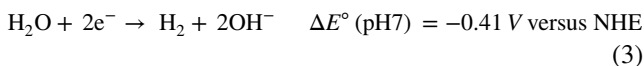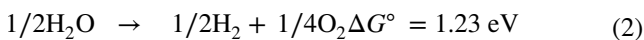## 4.2 Artificial photosynthesis

4.2.1 Homogeneous systems

Currently, studies on artificial photosynthesis are focused on using sunlight to reduce carbon dioxide in aqueous solution to CO, ethanol, or methane (Sun et al. 2018), or on water splitting into molecular hydrogen and molecular oxygen (Balzani et al. 2014; Hisatomi and Domen 2017). Since the carbon dioxide reduction is a much more difficult process from a kinetic viewpoint and, if needed, can also be performed in a conventional reaction with molecular hydrogen, the attention of most scientists is concentrated on the photochemical water splitting (reaction (1)):

$$2H_2O \ + \ 4\,h\nu \rightarrow 2H_2 + \ O_2 \qquad \Delta G^\circ \ = 4.92 \,\mathrm{eV} \qquad (1)$$
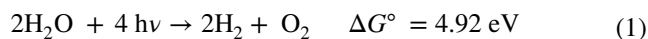
Since the electronic absorption spectrum of water does not overlap the emission spectrum of the sun, direct dissociation of water by solar energy cannot take place. From a thermodynamic viewpoint, the most convenient process for splitting water by sunlight (reaction (2) is that involving

the evolution of molecular oxygen and molecular hydrogen from liquid water. Its low-energy thermodynamic threshold (1.23 eV) theoretically allows conversion of about 30% of the solar energy. Of course, a suitable photosensitizer should be used because, as mentioned above, water does not absorb sunlight. Water splitting involves two multielectron transfer reactions [reactions (3) and (4)], the second one (reaction (4)) involving the four-electron oxidation of two water molecules:

$$1/2H_2O \rightarrow 1/2H_2 + 1/4O_2 \Delta G° = 1.23 \text{ eV} \qquad (2)$$

$$H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad \Delta E° (pH7) = -0.41 \text{ } V \text{ versus NHE} \qquad (3)$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad \Delta E° (pH7) = +0.82 \text{ } V \text{ versus NHE} \qquad (4)$$

Since in a photochemical process each photon can transfer only one electron, two catalysts must be present in a water splitting system: one to collect electrons for generating molecular hydrogen and the other to collect holes (positive charges) for producing molecular oxygen. Therefore, oxygen evolution requires, as happens in the natural photosynthetic system, four successive photoinduced electron-transfer steps (threshold: 1.23 eV) coupled with proton transfer (PCETs, proton-coupled electron-transfer processes) (Migliore et al. 2014). Artificial photosynthetic systems require also a very precise organization in the dimensions of space (location of the components), energy (redox potentials and excited-state energies), and time (rates of competing processes).

Decades of investigations have lead to substantial progress in developing essential components of artificial photosynthesis systems: photosensitizers, antenna devices, and reaction centers (Balzani et al. 2008), as well as homogeneous (Sartorel et al. 2013) and heterogeneous multielectron catalysts (Hisatomi and Domen 2019).

For several years, it was thought that water splitting could be achieved by using aqueous solutions of the required molecular components with the aid of colloidal catalysts (homogeneous systems). Appropriate bio-inspired molecular homogeneous catalysts are still a matter of intense investigation. New progress is focusing on multi-metal clusters that can replicate the perfection of the natural mechanism, i.e., a photo-assisted multi-electron–multi-proton redox cycle working at low overpotential (< 300 mV).

Recently, a supramolecular photo-system that mimics the PSII water oxidation enzyme has been obtained in water by self-assembly of positively charged perylene diimides (PDI) with a tetraruthenate polyoxometalate catalyst (Ru$_4$POM). Five PDIs are arranged around the RuPOM oxygen evolving center, thus forming a "core" photosynthetic unit, which was coined "artificial quantasome", by similarity to the natural quantasome concept (Bonchio et al. 2019). The multi-chromophore arrangement that surrounds
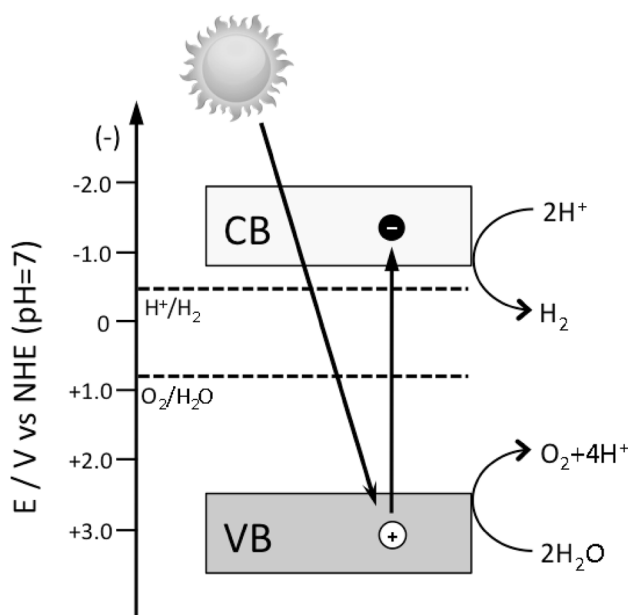

Fig. 4 Fundamental steps for the water splitting process generated by irradiation of a solid-state photocatalyst. For simplicity, semiconductor band bending and the two catalysts for water oxidation and water reduction are not shown (adapted from Balzani et al. 2017)

the catalytic cluster not only can leverage ultra-fast electron transfer, but also makes the charge-separation events to win over recombination. It turns out that the PDI-quantasome can be transferred onto nano-WO$_3$ photoanodes leading to a peak quantum efficiency using "green" photons ($\lambda > 500$ nm) with quantum efficiency up to 1.3%, i.e., similar to PSII-bioelectrodes. This result is encouraging with respect to photoelectrodes based on solid-state semiconductor materials, which generally have a dramatic performance loss using low-energy visible light, as described in the next section.

4.2.2 Semiconductor-based systems

Irradiation of a semiconductor with photons of energy equal to or greater than its band gap (Fig. 4) promotes an electron (e$^-$) to the conduction band (CB), thereby generating a hole (h$^+$) in the valence band (VB) (Balzani et al. 2017). Thanks to band bending, electrons and holes migrate to the surface of the semiconductor, where charges can be involved in thermodynamically allowed reduction and oxidation reactions.

To achieve photocatalytic water splitting with a single photocatalyst (Fig. 4), the band gap of the semiconductor must include the oxidation and reduction potentials of water (reactions (3) and (4)), which are + 0.41 V and + 0.82 V versus NHE, respectively, at pH 7. The pioneering experiment on photochemical water splitting by irradiation of a semiconductor was performed in 1972 on TiO$_2$ (Fujishima and Honda 1972). The energy gap of TiO$_2$, however, corresponds
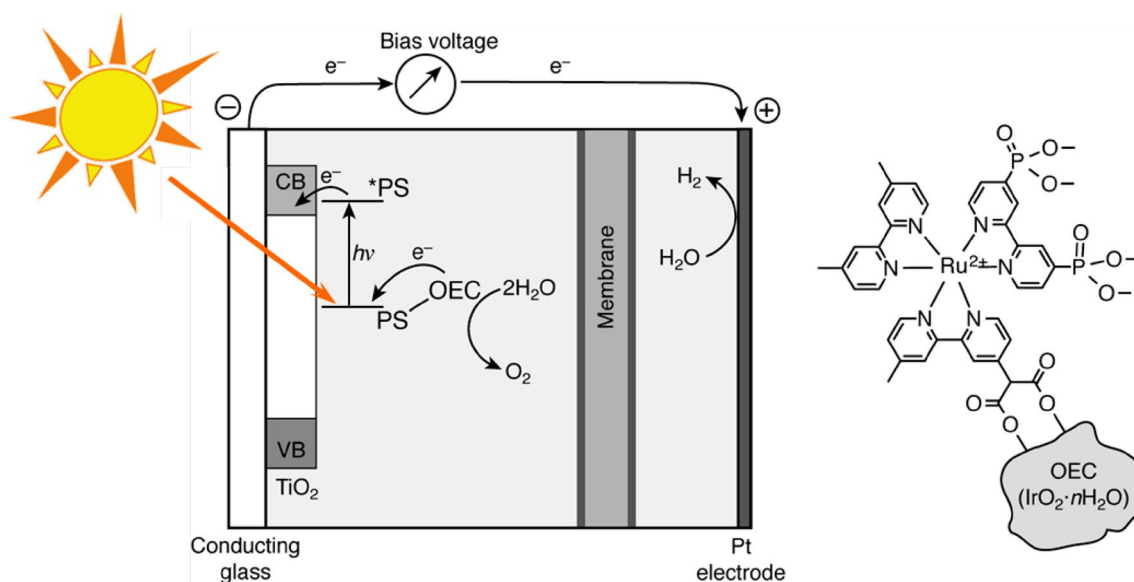
Fig. 5 Photosensitized water splitting, obtained in a DSPEC with the help of a small potential electric bias. The nanoparticulate TiO_2 photoanode is sensitized by a ruthenium polypyridine complex (right) that is covalently bound to an IrO_2 nanoparticle (Zhao et al. 2012) Adapted from (Balzani et al. 2015)

to a threshold of 390 nm. Therefore, visible light, and thus sunlight, is almost useless. In the last three decades, several hundred semiconductors have been investigated and various strategies have been adopted to improve the performances of inorganic semiconductors in photocatalysis, such as doping, nanostructuring and formation of heterojunctions (Kisch 2015). However, presently no single material meets the requirements needed for practical applications.

The major challenge in this field is not finding new ideas, but establishing whether or not the available systems have sufficient efficiency, stability, and scalability to be developed at the terawatt scale (McKone et al. 2014).

4.2.3 Dye-sensitized photoelectrochemical cells (DSPECs)

Dye-sensitized solar cells (Sect. 3.3) can be modified to construct dye-sensitized photoelectrochemical cells (DSPECs) capable of using solar energy to perform water splitting or other endoergonic reactions (Balzani et al. 2015). DSPECs differ from PECs because light absorption and charge transport are spatially separated, and from DSSCs because of the presence, in the anodic and/or cathodic compartments, of multielectron transfer catalysts that accumulate holes and electrons, respectively, created by the photoinduced charge-separation process and then use them to perform the desired endergonic reaction.

Figure 5 shows the case of photosensitized water splitting obtained in a DSPEC with the help of a small potential electric bias. The nanoparticulate TiO_2 photoanode is sensitized by a ruthenium polypyridine complex that is covalently bound to an IrO_2 nanoparticle, co-adsorbed on the TiO_2 electrode (Zhao et al. 2012).

For more efficient use of sunlight, a tandem approach can be used combining a photoanode with a photocathode. In principle, one could couple CO_2 reduction at the photocathode with water oxidation at the photoanode, with formation of oxygen and methane (Bensaid et al. 2012). DSPECs indeed represent an interesting approach toward artificial photosynthesis, but their performance is currently limited by low efficiency, instability and small turnover number of the catalysts.

4.2.4 Photovoltaic electrolysis

Hydrogen production by exploiting sunlight can be obtained by PV electrolysis in which light absorption and hydrogen formation are decoupled using a PV panel to generate electricity that is then used to power an electrolysis cell (Fig. 6) (Balzani et al. 2017). This is indeed the simplest and more efficient route toward sustainable production of hydrogen because both PV panels and water electrolyzers are commercially available (McKone et al. 2014). PV electrolysis can be carried out directly, or through the grid by appropriate converters. Currently, renewable electricity can more efficiently be used to power electric cars through batteries rather than through hydrogen conversion into electricity by fuel cells.
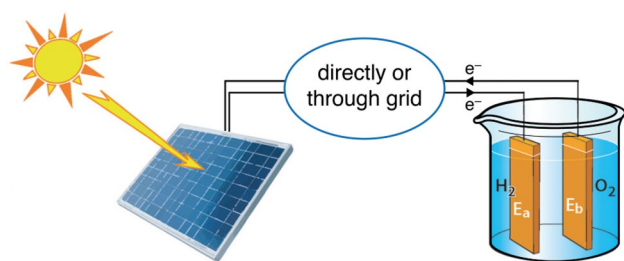
Fig. 6 Solar energy water splitting through a photovoltaic panel coupled, directly or through grid, to an electrolysis cell (adapted from Balzani et al. 2017)

5 What is the best way to make use of solar energy?

As we mentioned above, the yearly averaged solar power striking the surface of the planet is about 170 W m^{-2}. It follows that each square meter of the Earth's surface represents a potential source of energy. To make use of this energy source, we need to convert solar power into the energy forms we use every day: chemical energy (food and fuels), electricity, and heat. Conversion of solar power into low-temperature heat is an easy physical task. The conversion of solar power into food, electricity and fuels needs complex chemical processes, as described above.

An important question then arises: what is the best way to make use of the 170 W m^{-2} of solar power? (Balzani et al. 2017). We have seen that even in ideal conditions crops produce biomass with efficiency lower than 1%, and often as low as 0.1%. Improving the efficiency of natural photosynthesis by synthetic biology techniques is a very difficult, if not impossible task (Barber and Tran 2013). The low efficiency of natural photosynthesis is justified by the fact that solar energy conversion leads to chemically complex, highly organized molecules and macromolecules that are needed to feed our life. It is worth to underline that photosynthesis in the early stages of prebiotic reactions is an important area of fundamental investigation where the interaction of light with materials and small molecules plays an important role (Rapf and Vaida 2016; Nakashima et al. 2018).

The use of biomass to produce fuels (biofuels) has increased in recent years. The energy of sunlight that can be stored is less than 0.1% for biodiesel and around 0.2% and 0.3% for bioethanol and biogas, respectively (Michel 2012). Therefore, the production of biofuels is an extremely inefficient way to make use of the 170 W m^{-2} solar energy flux.

Waiting for substantial progress of artificial photosynthesis concerning efficiency, stability, and scalability (McKone et al. 2014; Balzani et al. 2017), there is little doubt that the best way to make use of solar energy is photovoltaics. PV cells are reliable and stable for about 30 years and their 15–20% conversion efficiency of solar energy into electric

energy is at least two orders of magnitude larger than the conversion efficiency of sunlight into biofuels. Furthermore, the estimated EROEI of photovoltaics continues to increase (Kittner et al. 2016; King and van den Bergh 2018).

For transportation, electric energy has to be stored in batteries, but this drawback is more than compensated by the about four times higher efficiency of electric engines compared with internal combustion engines. As we have seen above, another advantage of PV solar energy conversion is that electrical energy can be employed to generate hydrogen through electrolysis. The efficiency of water splitting using a commercial PV cell with 18% conversion efficiency and a commercial electrolyzer is around 10–12%.

In conclusion, the amount of useful energy we can get from the 170 W m^{-2} average solar power striking the earth's surface depends on our ability to construct stable, efficient, ecologically friendly, scalable, and economically sustainable solar energy conversion and storage devices by using materials available on our planet. Indeed, the limiting reactants in the photochemical processes used to exploit sunlight are not the Sun's photons, but the Earth's atoms.

6 Solar driven organic synthesis

Using sunlight to perform valuable chemical reactions is a goal pursued since Ciamician's time (Ciamician 1912). In recent years, it has been demonstrated that excitation of redox-active compounds (e.g., [Ru(bpy)$_3$]$^{2+}$, [Ir(ppy)$_3$]), and organic dyes like eosinY), or inorganic semiconductors like CdS mediates photoinduced electron transfer processes to substrates (Balzani et al. 2015; Kisch 2015). Such excited-state redox reactions occur at room temperature, without the need for highly reactive radical initiators.

Photoredox catalysis may also be used to exploit processes requiring both the donation and the acceptance of electrons at different points in the reaction sequence. Furthermore, photoinduced electron-transfer catalysis can provide access to radical ions exhibiting reactivity patterns quite different from those of their ground electronic or excited states. In these processes, enantiomerically pure products can be obtained by using a chiral photocatalyst (Huo et al. 2014) or by decoupling excitation of the photosensitizer and enantiomeric enrichment by the organocatalyst (Du et al. 2014).

As we have seen above (Sect. 4), the aim of natural and artificial photosynthesis is the conversion of light into chemical energy. Therefore, the overall chemical reaction must be endergonic and cyclic, and sacrificial reagents cannot be employed. In solar-driven organic synthesis, however, the target is to obtain a specific, high-value product, regardless of the quantum yield and the free energy change of the overall chemical reaction. Therefore, decomposition of a

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Fig. 7 Interfacial electron transfer reactions generated by light excitation of TiO_2 (adapted from Balzani et al. 2017)
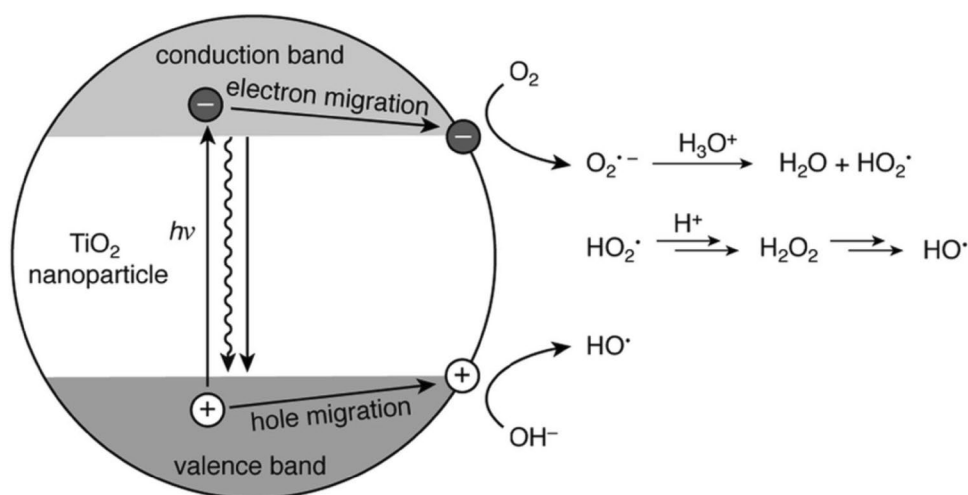
sacrificial reagent and, as an extreme case, even the partial decomposition of photosensitizers and photocatalysts are allowed when their economic value is lower than that of the target product. Nevertheless, a rational and profitable development of sunlight sensitization in organic synthesis relies on the elucidation of the reaction mechanisms and the evaluation of the efficiencies of the light-induced processes (Marchini et al. 2018).

7 Pollution remediation

Pollution remediation is presently the most important application of solar driven chemistry. It is extensively used for recovery of waters from industrial, agricultural and domestic usages, as well as for decontamination of the atmosphere and soil through the mineralization of the pollutants, or at least their transformation into non-toxic compounds (Ravelli et al. 2016).

Most of these processes are based on light excitation of a semiconductor (usually, TiO_2,) that promotes an electron from the valence to the conduction band. The promoted electron and the hole travel to the semiconductor surface where they give rise to electron transfer reactions with the solvent or other adsorbed species (Fig. 7). Electrons are scavenged by molecular oxygen to produce the $O_2^{\bullet-}$ ions that then undergo secondary reactions leading to $HO_2^{\bullet}$ and $HO^{\bullet}$ radicals, while also reactions of holes with solvent water molecules generate $HO^{\bullet}$ radicals. Reduction and oxidation of other species by the excited semiconductor can also occur, often with further formation of $HO^{\bullet}$, $HO_2^{\bullet}$, and $O_2^{\bullet-}$ (Kisch 2015; Ravelli et al. 2016). The mechanism for the photocatalytic degradation of organic pollutants over titanium dioxide has been studied in depth (Serpone and Emeline 2012).

Photocatalysis is more effective for wastewater recovery than traditional chemical oxidations, e.g., chlorination.

Further improvement can be obtained by coupling photocatalysis with a biological treatment.

Air purification can be obtained at an illuminated surface coated with a semiconductor. This principle has been applied for a variety of commercial applications, both outdoor and indoor, that destroy organic pollutants and nitrogen oxides (Gaya and Abdullah 2008). For its sterilizing, deodorizing and antifouling properties, TiO_2 is added to windows, paints, cements, tiles, or other materials (Skorb et al. 2008). A number of applications have been reported concerning surfaces that remain clean after being exposed for months to polluted urban air: for example, polymers (e.g., in tents), textiles, automobile bodies, glass covers of street lamps (even in tunnels).

8 Perspectives

We have reviewed the use of solar-driven chemistry to perform four processes that can give a determinant contribution toward the construction of a sustainable world: (a) conversion of sunlight into electricity; (b) conversion of sunlight into chemical energy; (c) photochemical synthesis of valuable molecules; (d) photochemical pollution remediation.

The conversion of sunlight into power by photovoltaic cells at the end of 2018 provided about 500 GW, 2.4% of the global electricity production (Renewables 2019). Photovoltaic conversion of sunlight has an enormous potential. The EROEI of PV continues to increase and has reached values > 20 (Kittner et al. 2016; King and van den Bergh 2018). In the next few years, higher efficiency, better stability, and use of more abundant and less expensive materials in organic and dye-sensitized solar cells will contribute to increase the production and decrease the cost of photovoltaic electricity. Once stored in batteries, photovoltaic electricity can be used to power electric engines (EEs), that are three to four times

more efficient than the internal combustion engines (ICE). If long time storage is needed, photovoltaic energy can be used to generate hydrogen by water electrolysis and then convert hydrogen back to electricity by fuel cells (Staffell et al. 2019), even on board vehicles.

Conversion of solar energy into chemical energy implies simultaneous storage of the converted energy. Therefore, it is a more difficult task than conversion of sunlight into electrical energy. Natural photosynthesis is doing well its job of supplying food, but cannot cover our energy need (Armaroli and Balzani 2011). Artificial photosynthesis represents an important breakthrough, but it is still at an early stage of development. Much work has still to be done in this field concerning efficiency, stability, and scalability (McKone et al. 2014; Balzani et al. 2017).

Solar-driven chemistry plays already an important role in pollution remediation. So far, only small amounts of a few high-value chemical products have been prepared by solar photochemistry, but we should not leave aside Ciamician's dream (Ciamician 1912): exploiting solar energy, seawater and the fundamental components of our atmosphere (oxygen, nitrogen, carbon dioxide) to pay back Earth with novel resources.[1] Interesting examples along this line are production of synthetic fuels by co-electrolysis of H_2O and CO_2 powered by renewable electricity (Ebbesen et al. 2014; Buttler and Spliethoff 2018), the electrochemical reduction of CO_2 to convert intermittent renewable energy to storable fuels and valuable chemical feedstock (Kibria et al. 2019), and photocatalytic fixation of nitrogen to ammonia (Banerjee et al. 2015; Liu et al. 2019; John et al. 2019).

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[1] "On the arid lands there will spring up industrial colonies without smoke; forests of glass tubes will extend over the plains and glass buildings will rise everywhere; inside of these will take place the photochemical processes that up until now have been the guarded secret of the plants, but that will have been mastered by human industry which will know how to make them bear even more abundant fruit than nature, for nature is not in a hurry and mankind is." (Ciamician 1912).

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