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CONCEPTS IN CATALYSIS

# Photochemistry and photocatalysis

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**Abstract** Photocatalysis is an important branch of catalysis and much more than that. To understand the potential applications and the working mechanisms of photocatalysis, it is necessary to know some important concepts of photochemistry, the branch of science that deals with the interaction of light and matter: (1) light excitation with a photon of suitable energy promotes a molecule or a semiconductor from the ground state to an electronically excited state that exhibits its own chemical and physical properties; (2) the most relevant consequence from the viewpoint of photocatalysis is that the excited state is both a better oxidant and a better reductant than the ground state; (3) some molecules or semiconductors can serve as photosensitizers, i.e., they can absorb light and then make available the excited state energy to promote reactions of non-absorbing species. Photosensitization and photocatalysis play an important role in nature and technology and they may take place in homogeneous or heterogeneous phase. Such processes can use sunlight (1) to convert solar energy into chemical or electrical energy, (2) to perform organic synthesis that cannot be achieved by thermal activation, and (3) to remedy pollution. Water splitting using sunlight and suitable photosensitizers and catalysts (artificial photosynthesis) is perhaps one of the most thoroughly investigated chemical processes. Breakthrough in this area can contribute to solve the energy and climate crisis, but substantial technological development is still needed.

**Keywords** Redox reactions · Excited state properties · Photosensitizers · Solar energy conversion · Organic synthesis

## 1 Introduction

The aim of this tutorial paper is that of presenting the relationships between photochemistry and catalysis, two very important branches of modern chemistry. We will see that photocatalysis is much more than a type of catalysis because photocatalytic processes can be used not only to change reaction rates, but also to modify chemical equilibria and, particularly, to convert light into chemical energy as it happens, e.g., in natural photosynthesis. Photocatalysis may involve processes in which light excitation and a catalyst can play separated, concerted or even entangled roles. For all these reasons it is practically impossible to give a comprehensive definition of the term photocatalysis. We will try to explain what photocatalysis is by analyzing a series of representative examples of processes that may or may not be "photocatalytic" in the literature. Although this tutorial review is mainly dealing with photocatalysis in homogeneous media, a brief non-extensive presentation of photocatalysis in heterogeneous media involving semiconductor photocatalysis and semiconductor photoelectrochemistry is also presented. For the latter cases, several accounts have been published recently that give a more comprehensive discussion of these two fields (see for example Refs. Walter et al. 2010; Hisatomi et al. 2014; Li et al. 2015).

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Processes based on the combined use of light, photosensitizers and/or catalysts are used extensively in chemistry. A look at the literature reveals that in the last ten years there has been a steady flux of more than 1300 international patents per year for various applications (Protti et al. 2014), mostly in the fields of pollution remediation (Serpone and Emeline 2012; Vione 2016), green chemical synthesis (Albini 2016; Ravelli et al. 2016), and solar energy conversion (Balzani et al. 2015; Armaroli and Balzani 2016).

## 2 Catalysis

Catalysis is the increase in the rate of a chemical reaction due to the participation of an additional substance called a catalyst.

$$A \rightarrow B \quad \text{slow (dark) reaction} \qquad (1)$$

$$A \xrightarrow{\text{cat}} B \quad \text{fast (dark) reaction} \qquad (2)$$

The catalyst is not consumed and does not affect the free energy change and the equilibrium constant. The role of a catalyst is that of offering a different path to the reaction, decreasing the activation energy (Fig. 1).

All catalytic processes are based on these principles. Nevertheless, homogeneous, heterogeneous and enzymatic catalysis have formed historically three separate branches of science that have largely developed independently.

## 3 Photochemistry

To understand the mechanisms of photocatalytic processes, we need to know some fundamental concepts of photochemistry (Balzani et al. 2014), with particular reference to photoinduced electron transfer processes that are involved very frequently in photocatalytic reactions.

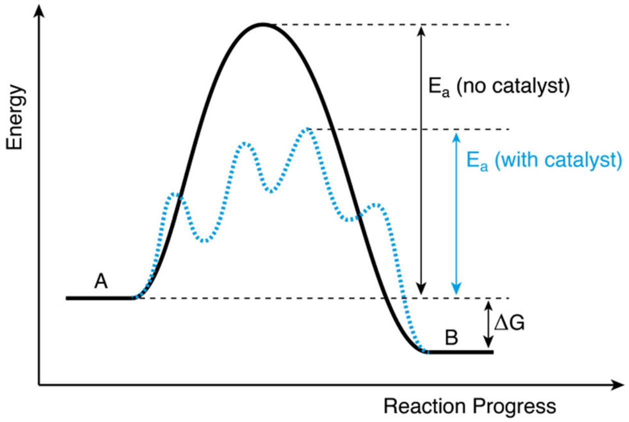


**Fig. 1** Schematic energy profiles for a reaction in the absence and presence of a catalyst

Let's consider the simple, outer sphere electron transfer reaction 3:

$$A + B \rightarrow A^+ + B \quad \text{thermal (dark) reaction} \qquad (3)$$

Why and how can light affect a process like that? The first step of any photochemical reaction is light absorption (reaction 4). Suppose that light is absorbed by reactant A: the photochemical reaction 5 involves *A and B as reactants:

$$A + h\nu \rightarrow {}^{*}A \quad \text{formation of an electronic excited state} \qquad (4)$$

$${}^{*}A + B \rightarrow A^+ + B \quad \text{photo chemical reaction} \qquad (5)$$

This is the difference: in the photochemical reaction the ground state molecule A is replaced by the excited state *A. Therefore, we need to know the properties of electronically excited states in order to understand what happens in a photochemical process.

## 4 Properties of electronically excited states

Light excitation with a photon of suitable energy promotes a molecule from its ground state to an electronically excited state (hereafter simply called as excited state, usually denoted by an asterisk, Fig. 2).

Each molecule in its ground state has specific properties, such as energy content, bond lengths, spatial structure, charge distribution, electron affinity, ionization potential, tendency to rearrange its structure, undergo bond breaking (with or without formation of ions), self-associate or associate with other molecules, and interact with solvent molecules (Klán and Wirz 2009; Turro et al. 2010; Balzani et al. 2014). All these properties depend on the electronic structure, i.e., on the distribution of the electrons in the molecular orbitals.

When a molecule absorbs light that causes an electronic transition, an excited state of the molecule is obtained. It is important to realize that an excited state differs from the corresponding ground state not only for the energy content, but also for the electronic distribution. Therefore, an excited state has to be considered not as a "hot" ground state molecule, but as an essentially new chemical species.

This is clearly shown by Table 1 that compares some properties of the ground state and the lowest excited state of formaldehyde.

From the viewpoint of photocatalysis, a more interesting example is offered by the $[Ru(bpy)_2(CN)_2]$ complex (Table 2).

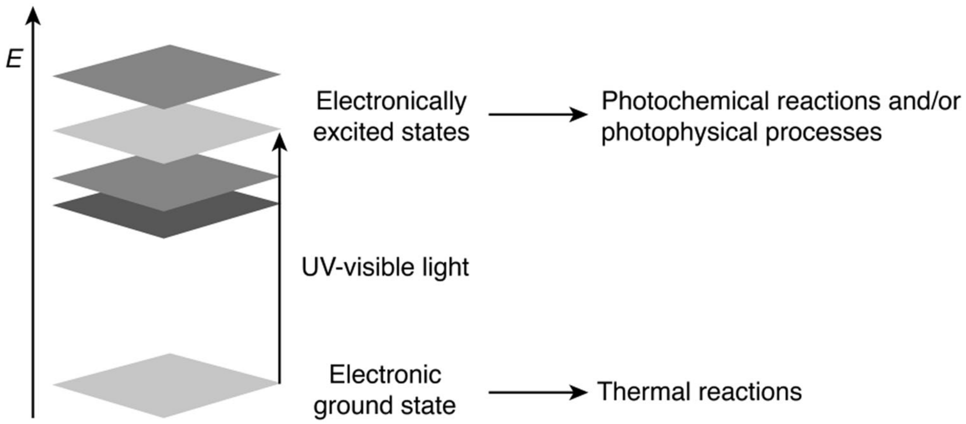


**Fig. 2** Light excitation with a photon of suitable energy promotes a molecule from its ground state to an electronically excited state, a new chemical species with its own chemical and physical properties; light excitation opens new dimensions to chemistry and physics. Adapted from (Balzani et al. 2014)

**Table 1** Comparison between ground and excited state properties of formaldehyde

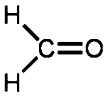
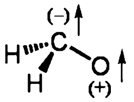
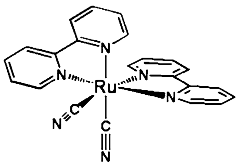
| | Ground state  | Lowest excited state  |
|---|---|---|
| Energy | 0 | +76 kcal/mol |
| Geometry | Planar | Pyramidal |
| Magnetism | Diamagnetic | Paramagnetic |
| Dipole moment | 2.3 D | 1.3 D |
| $r_{co}$ | 1.22 Å | 1.31 Å |
| $\nu_{Co}$ | 1745 $cm^{-1}$ | 1180 $cm^{-1}$ |
| lifetime | ∞ | $<10^{-3}$ s |

**Table 2** Comparison between ground and excited state properties of $[Ru(bpy)_2(CN)_2]$

|  | Ground state | Lowest excited state |
|---|---|---|
| Energy | 0 | +50 kcal/mol |
| Geometry | Slightly different | |
| Magnetism | Diamagnetic | Paramagnetic |
| Lifetime | ∞ | 0.22 μs |
| $E_{ox}$ | +1.09 V | −1.06 V |
| $E_{red}$ | −1.30 V | +0.85 V |
| $pK_a^{I}$ | −0.3 | −8.3 |
| $pK_a^{II}$ | +0.12 | −5.7 |

Not only the excited state has an extra amount of energy compared with the ground state but also, most important, the excited state is both a better reductant and a better oxidant than the corresponding ground state. At first sight such a result is surprising, but it can be easily and qualitatively understood looking at an orbital diagram such as that shown in Fig. 3 (Balzani et al. 2014). Usually, light absorption promotes an electron from a lower energy to a higher energy orbital. The electron that has been promoted can be more easily removed, which means that the excited state has a smaller ionization potential than the ground state. At the same time, the promotion of an electron leaves behind a low-lying vacancy that can accept an electron, which means that the excited state has a higher electron affinity than the ground state. Therefore, light excitation is a remarkable, double face redox process since it generates a species capable to perform as both an oxidant and a reductant.

A quantitative approach concerning the excited state redox properties is based on the extra amount of energy of the excited state compared to the ground state. In the case of a thermally equilibrated excited state and reversible redox processes, the excited state redox potentials are given by Eqs. 6 and 7:

$$E^0(A^+/{}^*A) = E^0(A^+/A) - E_{00}({}^*A/A) \tag{6}$$

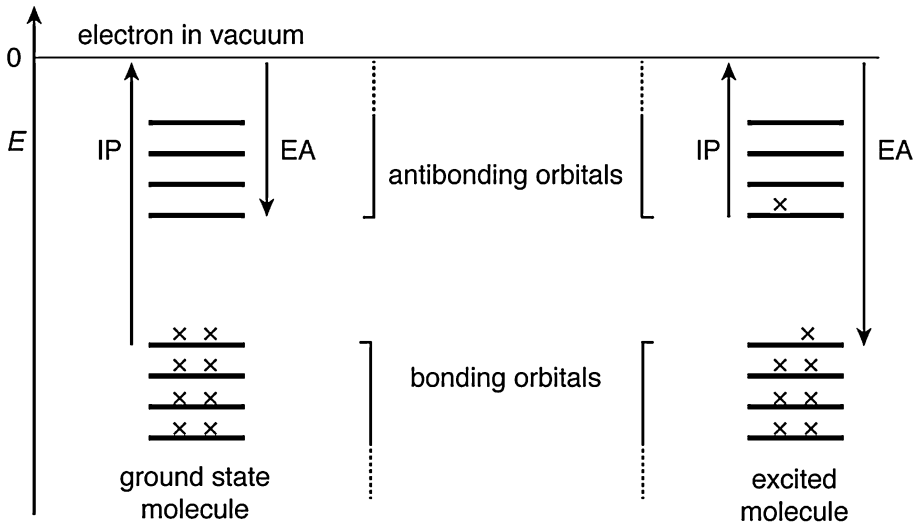
$$E^0({}^*A/A^-) = E^0(A/A^-) + E_{00}({}^*A/A) \tag{7}$$

$E_{00}(^*A/A)$ is the one-electron potential corresponding to the zero-zero spectroscopic energy of the excited state. It is worth noting that the term $E_{00}(^*A/A)$ is related to the reactive excited state that does not necessarily coincide with the excited state populated by light absorption.

When irreversible processes are involved, the redox potential values are not experimentally available; although they can sometimes be estimated from other parameters, it is difficult to forecast whether the actual electron transfer process will take place under the experimental condition used.

To illustrate the above concepts and understand why they can be exploited in a variety of processes and applications, we take as an example the extensively used

**Fig. 3** Orbital scheme useful to understand why an excited state is both a better electron donor and abetter electron acceptor than the ground state species



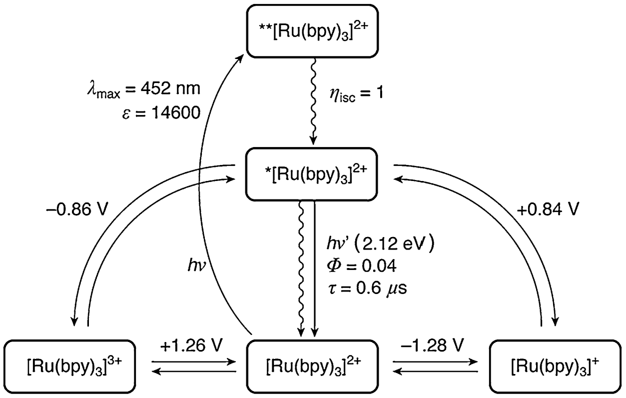


**Fig. 4** Excited state and redox parameters for electron transfer processes of $[Ru(bpy)_3]^{2+}$ relevant for electron transfer processes (Balzani and Juris 2001). $^{**}[Ru(bpy)_3]^{2+}$ indicates the spin-allowed excited state reached by light absorption and $^{*}[Ru(bpy)_3]^{2+}$ the lowest spin-forbidden luminescent excited state ($^3$MLCT). Reduction potentials in water are referred to NHE

$[Ru(bpy)_3]^{2+}$ complex (Balzani and Juris 2001). Figure 4 summarizes the energetic links between the various forms of $[Ru(bpy)_3]^{2+}$. Light excitation in the intense visible absorption band ($\lambda_{max} = 452$ nm, $\varepsilon_{max} = 14{,}600$ M$^{-1}$ cm$^{-1}$) leads to the lowest spin-allowed metal-to-ligand charge transfer ($^1$MLCT) excited state ($^{**}[Ru(bpy)_3]^{2+}$ in Fig. 4), which undergoes very fast intersystem crossing to the lowest $^3$MLCT excited state ($^{*}[Ru(bpy)_3]^{2+}$). This excited state lives long enough ($\tau = 0.6$ µs) to encounter other solute molecules before undergoing radiative or radiationless deactivation (in supramolecular systems (Balzani and Scandola 1991) a suitable reaction partner may already be nearby $^{*}[Ru(bpy)_3]^{2+}$). The extra energy available to $^{*}[Ru(bpy)_3]^{2+}$ compared with the ground state amounts to 2.12 eV and its reduction and oxidation potentials, obtained from Eqs. 6 and 7, are +0.84 and −0.86 V (vs NHE, in water). It follows that $^{*}[Ru(bpy)_3]^{2+}$ is at the same time a good electron acceptor (reaction 8) and a good electron donor (reaction 9):

$$^{*}\left[Ru(bpy)_3\right]^{2+} + Q \rightarrow \left[Ru(bpy)_3\right]^{3+} + Q^{-} \quad \text{oxidative quenching} \tag{8}$$

$$^{*}\left[Ru(bpy)_3\right]^{2+} + Q \rightarrow \left[Ru(bpy)_3\right]^{+} + Q^{+} \quad \text{reductive quenching} \tag{9}$$

The two processes are potentially in competition, but usually only one is thermodynamically allowed for a given Q. When both are thermodynamically allowed, kinetic factors establish which process wins the competition.

For reactions taking place in solution between an excited state and a solute Q (e.g., reactions 8 and 9, sometimes called dynamic quenching processes), the ratio of the excited state lifetime in the absence ($\tau^0$) and presence ($\tau$) of Q is given by Balzani et al. (2014):

$$\tau^0/\tau = 1 + \tau^0 k_q[Q]. \tag{10}$$

In this equation, known as the Stern–Volmer equation, $k_q$ is the rate of the quenching process and the product $\tau^0$ $k_q$ is called Stern–Volmer constant ($k_{SV}$). The maximum value of $k_q$ is represented by the diffusion rate constant ($k_d$) in the solvent used. Assuming that the reaction occurs at its maximum rate, $k_q = k_d$, Eq. 10 can be employed to evaluate the smallest concentration of Q required to quench an excited state with a predetermined efficiency.

A scheme of the type of that shown in Fig. 4 can be constructed, in principle, for any excited state of any molecule when the pertinent data are available (Balzani et al. 2014). Therefore, photoexcitation affords chemists with a huge repertoire of strong oxidants and reductants

(Juris et al. 1988; Kalyanasundaram 1992; Maestri et al. 1992; Flamigni et al. 2007) which, however, should be used with precaution because the necessary conditions of reversibility are often lacking in the reaction medium. Figure 5 shows the relationship between ground and excited state redox potentials for some compounds often used in redox processes involving excited states. $[Cr(bpy)_3]^{3+}$ in the excited state is a strong oxidant, perylenediimide (PDI)is even stronger, whereas *fac*-$[Ir(ppy)_3]$ in the excited state is a strong reductant. In the case of metal complexes, both the redox properties and the excited state energy can be fine- or coarse-tuned by changing the metal, the ligands and/or substituents on the ligand rings. For example, $^*[Ru(bpy)_2(biq)]^{2+}$ (biq = biquinoline) has a lower excited state energy (736 nm, 1.68 eV) compared with $^*[Ru(bpy)_3]^{2+}$ and it is easier to reduce (−0.37 V vs NHE)(Juris et al. 1988). The excited state energy 2.34 eV of *fac*-$[Ir(ppy)_3]$ moves to 2.76 eV for *fac*-$[Ir(4',6'\text{-}F_2\text{-}ppy)_3]$ and 2.64 eV for $[Ir(ppy)_2(CN)_2]^-$, while the ground state oxidation potential moves from +1.01 to +1.53 and +1.66 V (vs NHE), respectively (Maestri et al. 1992; Flamigni et al. 2007).

## 5 Catalysis by direct light irradiation

In several cases, the product of a dark reaction is different from that of the reaction performed under light excitation. When the product is the same, the photochemical reaction 11 is usually much faster than the dark reaction (reaction 1). From this viewpoint, we can say that reaction 11 is a catalyzed version of reaction 1 and that light plays the role of a catalyst.

$$A + h\nu \rightarrow B \quad \text{fast (photochemical) reaction} \qquad (11)$$

For the increase in the reaction rate upon irradiation, we could be tempted to use a diagram similar to that seen above for a (dark) catalyzed reaction (Fig. 1), assuming that, as in the case of a catalyst, light decreases the activation energy through formation of intermediate compounds. The decrease of the activation energy for the photochemical reaction, however, is usually directly connected with the free energy change caused by light excitation (Sect. 4), as rationalized by the Marcus theory for electron transfer reactions (Marcus and Sutin 1985; Balzani 2001).

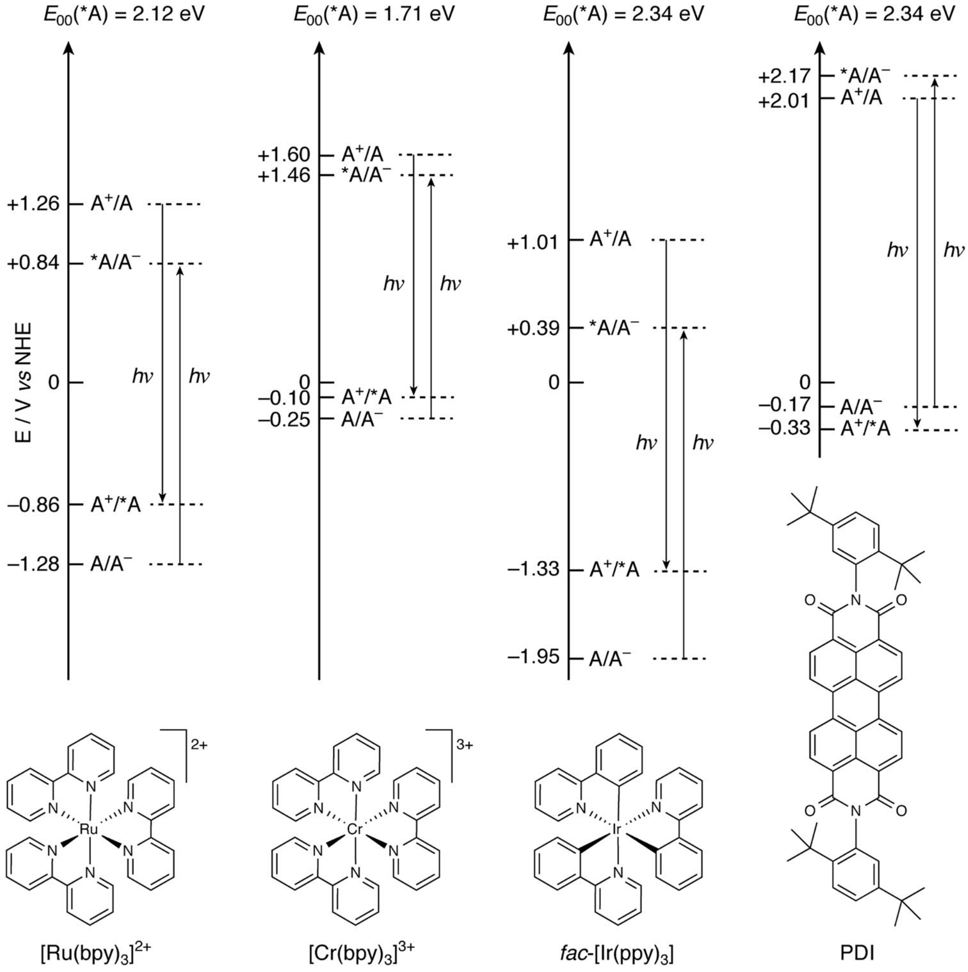


**Fig. 5** Relationship between ground and excited state redox potentials for compounds often used in redox reactions involving excited states (Balzani et al. 2015)

Therefore, the intimate mechanism of a dark reaction that becomes faster under light irradiation, reaction 11, is completely different from that of a catalyzed (dark) reaction 2.

There is also another fundamental difference in using a catalyst or light to increase the rate of a reaction: a catalyst is not consumed, whereas light is consumed. Such a difference practically vanishes when irradiation is performed with an abundant and free light source like sunlight.

An example of catalysis by direct light irradiation is given by the thermodynamically allowed oxidation of $[Ru(bpy)_3]^{2+}$ by persulfate. This reaction is very slow in the dark, but becomes very fast upon irradiation with visible light, i.e., when $[Ru(bpy)_3]^{2+}$ is replaced by its $^*[Ru(bpy)_3]^{2+}$ excited state (Fig. 6).

**1**: excited state decay ($k = 3 \times 10^5$ $s^{-1}$); **2**: photoinduced electron transfer ($k = 5 \times 10^8$ $M^{-1}$ $s^{-1}$); **3**: ground state electron transfer ($k < 1 \times 10^{-3}$ $M^{-1}$ $s^{-1}$).

As we have seen above, excited states are short lived species since they go back to the ground state with very fast deactivation processes. Therefore, the photoreaction we are interested in must be very fast to compete with the excited state decay. This underlines that the excited state lifetime is an important parameter in photocatalysis.

The rate of many reactions can be increased either by a catalyst or by light. For example, the preparation of 4-allylanisole may be performed in the dark using a metal catalyst, or by light irradiation (Fig. 7, Mordini and Faigl 2008).

Under the experimental conditions used, the metal catalyzed reaction needs longer reaction time, very high temperature, expensive reagents, and complex operations that must be carried out in a glove box, whereas the photochemical process can be performed at room temperature, in a shorter time and with a much simpler procedure (Mordini and Faigl 2008). This is often the case: with light one can use mild conditions.

Photocatalysis in its simplest form, i.e., as a means to prepare an already known product in a shorter time or even novel products, has been extensively used for organic synthesis since the beginning of the last century. The pioneer in this field was Giacomo Ciamician, the scientist who has given the name to the Chemical Department of the University of Bologna. In a series of papers on the chemical action of light (see, e.g., Ciamician 1908), he clearly demonstrated that light can play a very important role in laboratory chemistry as it does in the chemistry of plants. As shown by the very famous picture displayed in Fig. 8, Ciamician employed sunlight to prepare a great number of organic compounds. Today Ciamician is known as the father of photochemistry and the pioneer of solar energy conversion (Ciamician 1912; Balzani et al. 2014).

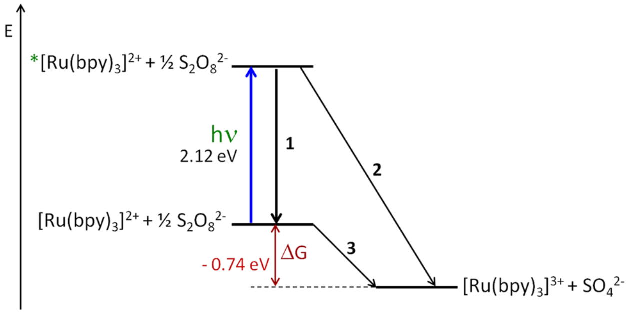


**Fig. 6** Photocatalysis of the oxidation of $[Ru(bpy)_3]^{2+}$ by persulfate (Bolletta et al. 1980)

## 6 Direct conversion of light into chemical energy

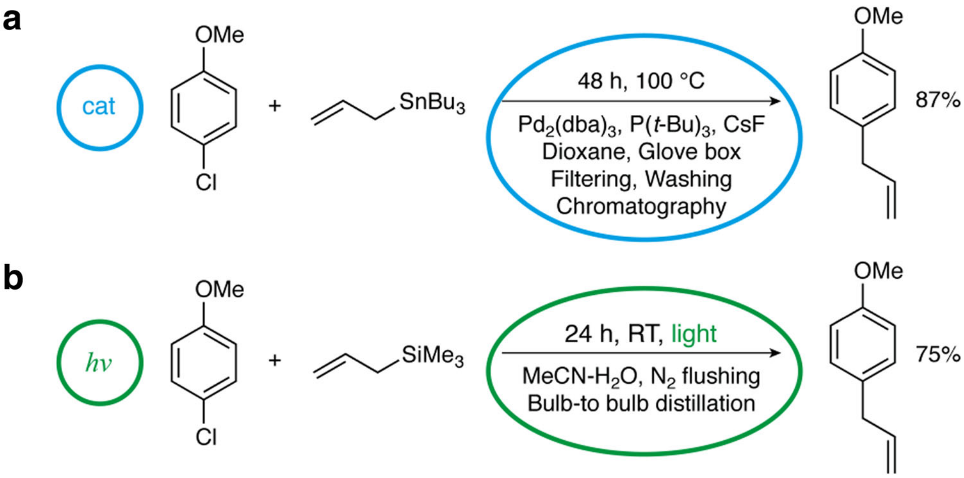
As shown by Fig. 6, the change in free energy in going from a thermal to the corresponding photochemical reaction can strongly increase the reaction rate. An even more important consequence of light excitation is that a thermodynamically forbidden reaction can become thermodynamically allowed upon light excitation. An example is shown in Fig. 9. Reduction of $Fe^{3+}$ by$[Ru(bpy)_3]^{2+}$ cannot take place in the dark, but it occurs with a very fast rate upon irradiation with visible light, i.e., when the ground state $[Ru(bpy)_3]^{2+}$ is replaced by its $^*[Ru(bpy)_3]^{2+}$ excited state, (ch. 9 in Balzani et al. 2014) which is a much stronger reductant (Fig. 4).

This photocatalytic process causes the conversion of visible light into chemical energy that, however, cannot be stored because a fast back electron transfer reaction takes place between the strongly oxidizing $[Ru(bpy)_3]^{3+}$ and the reducing $Fe^{2+}$species.

## 7 Catalysis and light energy conversion by photosensitization

Let us consider reaction (i) in Fig. 10a. Because of a high activation barrier, the reaction is very slow in the dark. To speed up the reaction we could try to inject energy in the system in the form of visible light as in the case of the reaction between $[Ru(bpy)_3]^{2+}$ and persulfate (Fig. 6), but this approach does not work if neither A nor B is able to absorb light [reaction (ii)]. If we add to the solution some $[Ru(bpy)_3]^{2+}$ (Fig. 10b), nothing happens in the dark: reaction (iii) in Fig. 10 bis slow as it was in the absence of $[Ru(bpy)_3]^{2+}$; but, if we now irradiate the solution with visible light [reaction (iv) in Fig. 10b], $[Ru(bpy)_3]^{2+}$ is excited and the reaction takes place. $[Ru(bpy)_3]^{2+}$ is not consumed. In the language of catalysis, $[Ru(bpy)_3]^{2+}$ catalyzes the reaction; in the language of photochemistry, $[Ru(bpy)_3]^{2+}$ plays the role of a photosensitizer (PS).

**Fig. 7** Preparation of 4-allylanisole by a metal catalyst (**a**) or by light irradiation (**b**). Adapted from (Mordini and Faigl 2008)



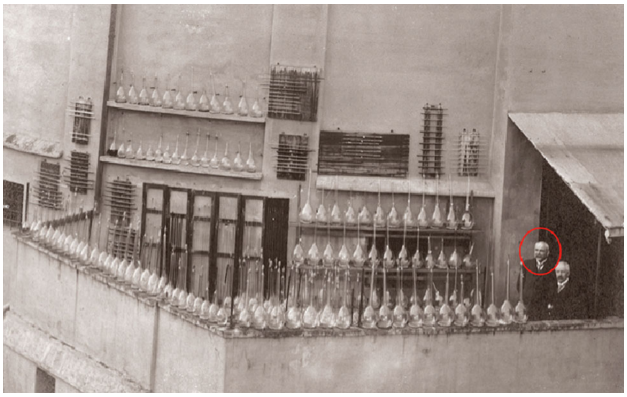


**Fig. 8** Giacomo Ciamician, pioneer of photochemistry, while watching flasks under sun irradiation on the roof of his laboratory at the University of Bologna, Italy (ca. 1910)

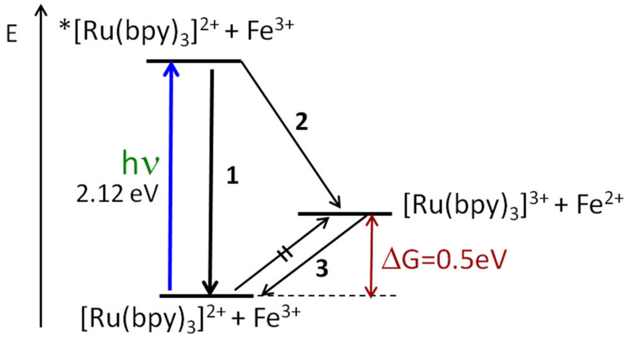


**Fig. 9** Photocatalysis of the reduction of $Fe^{3+}$ by $[Ru(bpy)_3]^{2+}$(ch. 9 in Balzani et al. 2014) **1**: excited state decay ($k = 3\times10^{5}\ s^{-1}$); **2**: photoinduced electron transfer ($k = 5\times10^{9}\ M^{-1}\ s^{-1}$); **3**: back electron transfer

Let us consider now a case of a thermodynamically forbidden reaction (i) in Fig. 11a. Again, we could try to inject free energy in the system in the form of visible light, but if A and B are unable to absorb in the visible region, nothing happens [reaction (ii) in Fig. 11a]. Addition of $[Ru(bpy)_3]^{2+}$ does not cause any effect in the dark [reaction (iii), Fig. 11b]. However, when $[Ru(bpy)_3]^{2+}$ is present, the reaction takes place upon irradiation with visible light [reaction (iv), Fig. 11b]. Again, $[Ru(bpy)_3]^{2+}$ is not consumed and behaves as a catalyst and as a photosensitizer. It is noteworthy that in this case part of the light energy is converted into chemical energy.

The reaction between methyl viologen and triphenyl amine (Young et al. 1975)

$$MV^{2} + NPh_3 \not\rightarrow MV^{+} + NPh_3^{+} \qquad (12)$$

is a real case of a reaction schematically illustrated in Fig. 11. Reaction 12 is thermodynamically forbidden in the dark (Fig. 12a). None of the two reactants is able to absorb visible light, so that we cannot make the reaction thermodynamically allowed by light irradiation (Fig. 12b). Addition of $[Ru(bpy)_3]^{2+}$ does not cause any effect in the dark, but upon irradiation with visible light the reaction takes place (Fig. 12c). $[Ru(bpy)_3]^{2+}$ is not consumed and plays the role of a catalyst as well as of a photosensitizer. The mechanism of the photosensitized reaction will be discussed later (Sect. 9.1).

## 8 Catalysts and light in chemical synthesis

### 8.1 General concepts

Catalysts and/or light are extensively used in chemical synthesis. Since organic molecules are usually colorless, photosensitizers need to be used to take advantage of sunlight.

In the last 3 years, visible light photocatalysis has been applied to at least 32 different types of reactions (Ravelli et al. 2016). Usually, the synthetic reaction is triggered by a photoinduced electron transfer process between the excited photosensitizer, which is a strong oxidant or reductant

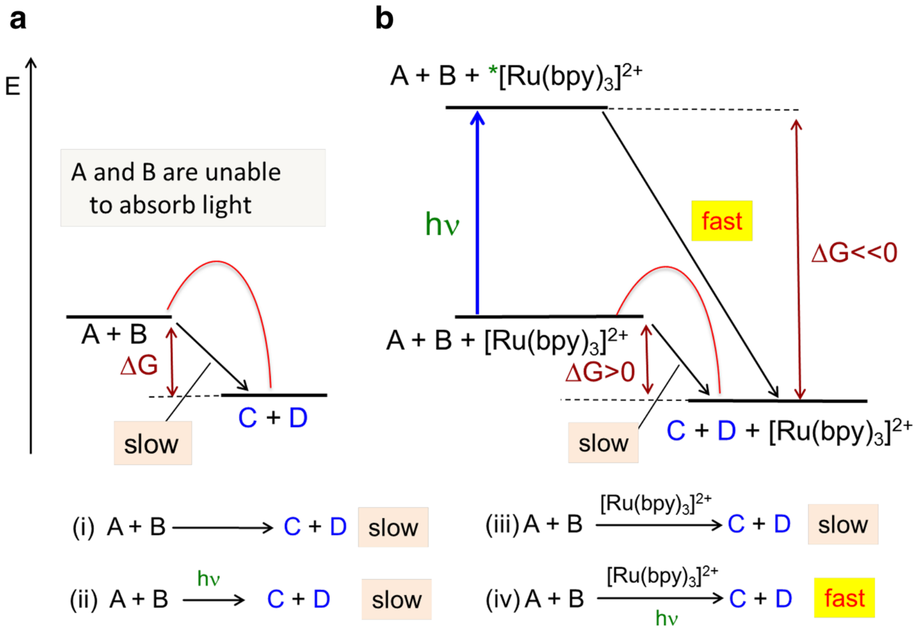


**Fig. 10** An example of photosensitized reaction. For more details, see text

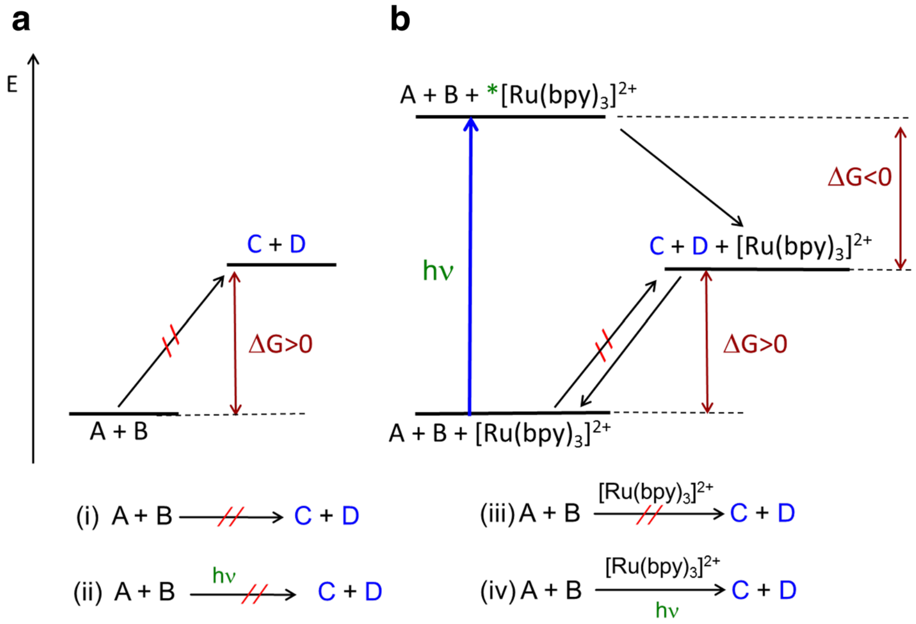


**Fig. 11** Conversion of light energy into chemical energy by a photosensitized reaction

(vide supra), and a substrate. It should be pointed out that in most cases researchers involved in photocatalyzed organic synthesis are only interested to obtain the desired product in a good yield, with little attention to reaction mechanism, turnover number of the photocatalyst and quantum yield of the photoreaction. Often the amount of photocatalyst exceeds that needed to absorb completely the incident light. In some case even saturated solutions of the photocatalyst are used, so that it is difficult to establish which compound, among different photocatalysts, is the best one.

Light and a catalyst can operate in parallel or in series. An example in which a catalyst and light operate in parallel is given by the α-allylation of amines (Fig. 13) (Xuan et al. 2015). In this process, a palladium catalyst and light, working in the same reaction medium on distinct substrates, lead to the formation of two radicals that undergo cross coupling.

When light and a catalyst operate in series, we may have two cases: first the photochemical reaction and then the catalytic one (reaction 13), or vice versa (reaction 14),

$$A \xrightarrow{h\nu} X \xrightarrow{\text{cat}} B \qquad (13)$$

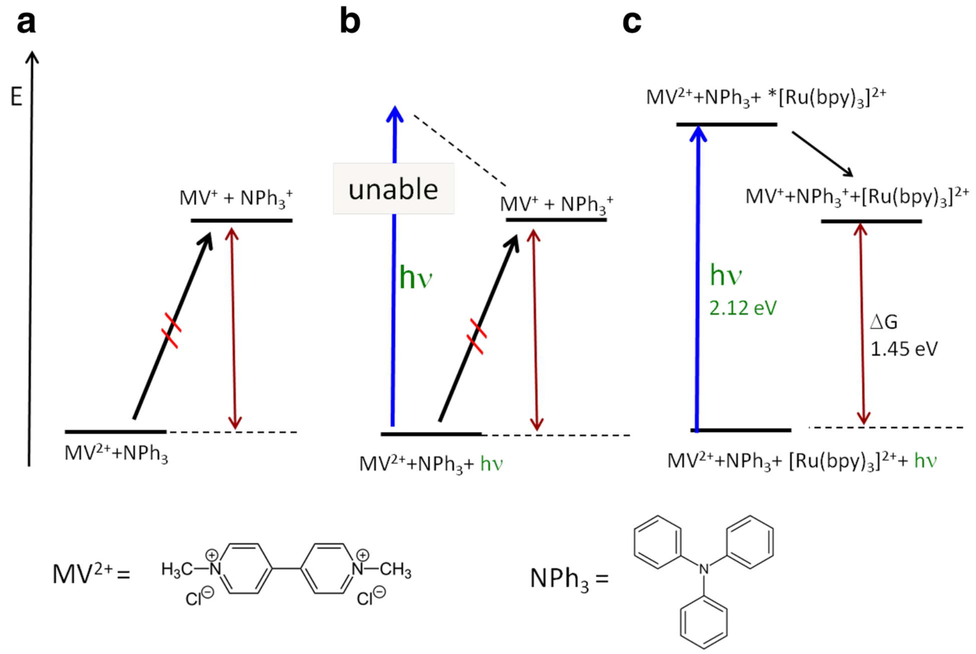


**Fig. 12** Conversion of visible light energy into chemical energy by the reaction between methyl viologen and triphenyl amine (Young et al. 1975)

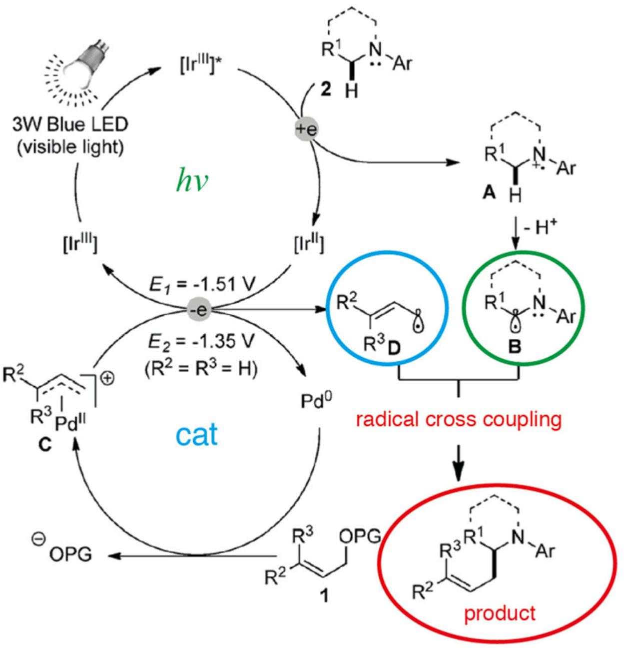


**Fig. 13** Example of α-allylation of amines in which a catalyst and light operate in parallel. Adapted from (Xuan et al. 2015)

$$A \xrightarrow{cat} Y \xrightarrow{h\nu} B \qquad (14)$$

In the simplest case, reactions 13 and 14 can be viewed as a photochemical process preparing a catalyst and/or the reactant(s) for a catalyzed reaction or, respectively, a catalytic process whose products are then involved in a photochemical reaction. In several cases, however, the catalytic and photochemical processes are entangled.

## 8.2 Photochemical control of catalytic processes

Many examples of catalytic processes controlled by a photoreaction are reported in the literature (Balzani et al. 2008; Vallavoju et al. 2014). In most cases, the photochemical reaction is a reversible photoisomerization between two forms that, for steric reasons, prevent/favor a catalytic process. The photochemical and the catalytic reactions may involve different species that are present in the same solution or different functions of the same supramolecular species.

Cyclodextrin (CD) is a catalyst for the hydrolysis of *p*-nitrophenyl acetate. The catalytic process takes place when *p*-nitrophenyl acetate is enclosed in the CD cavity (Fig. 14). A carboxyl derivative of azobenzene, which can exist in the *cis* and *trans* forms, is used to control the catalytic process. In the dark, the equilibrium is displaced towards the *trans* form, which can occupy the cavity of CD. Under light excitation, the equilibrium is displaced towards the *cis* form that is too bulky to be hosted by the CD cavity. Therefore, *p*-nitrophenyl acetate can enter the CD cavity and undergo hydrolysis (Ueno et al. 1980).

A very interesting exploitation of photocatalytic properties is given by the design of supramolecular species that carry both the catalytic and the light responsive units. As for azobenzene derivatives, molecules with a double C=C bond can exist as the *trans* and *cis* forms with the more stable *trans* isomer that can be converted into the *cis* isomer by light irradiation (Balzani et al. 2014). This is the case of the molecule shown in Fig. 15a. Functionalization of the trans isomer with

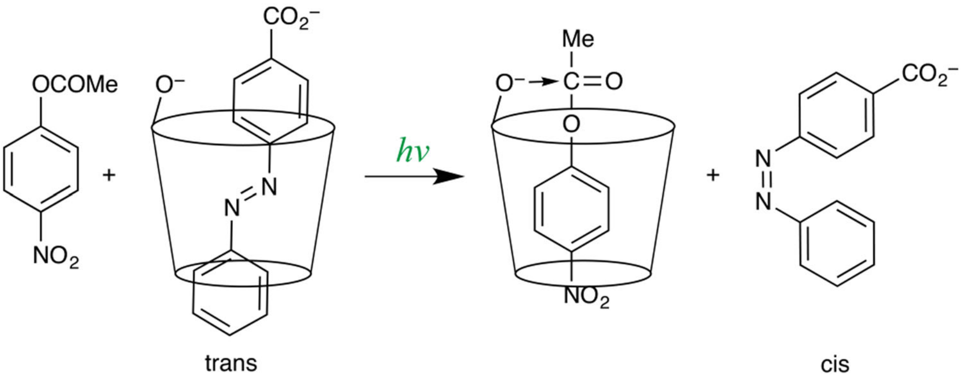


**Fig. 14** Photocontrolled catalytic activity of cyclodextrin in the hydrolysis of *p*-nitrophenyl acetate (Ueno et al. 1980)

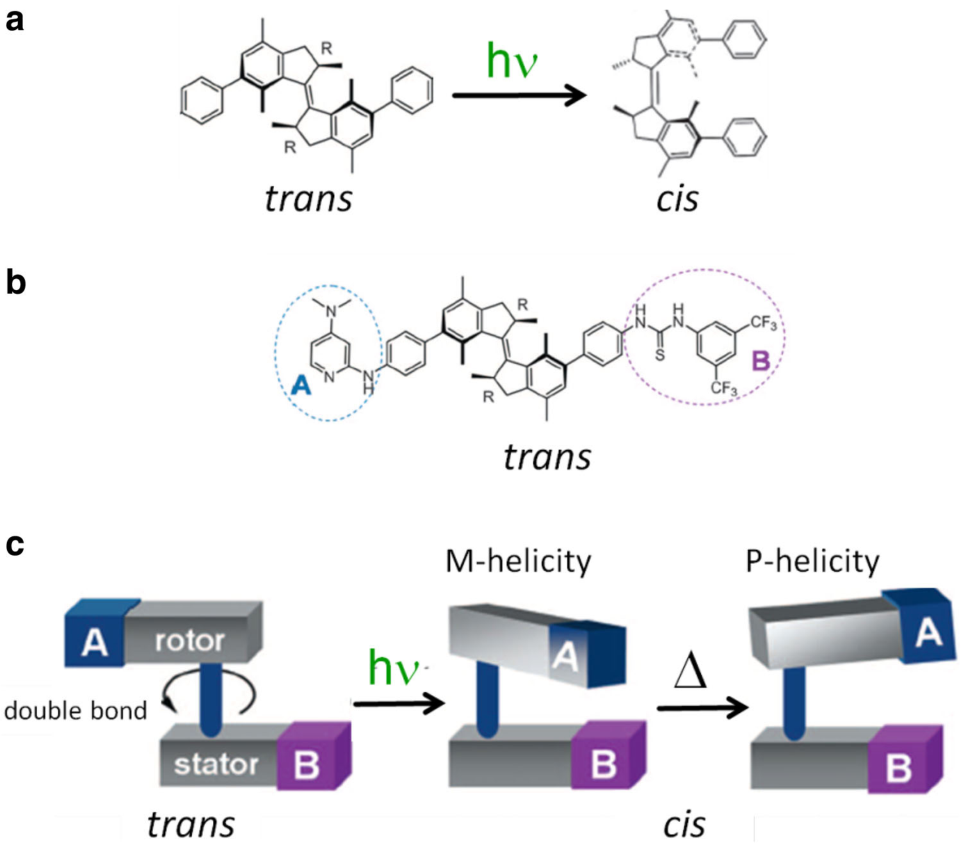


**Fig. 15** A very interesting example of photocontrolled catalytic activity (Wang and Feringa 2011). For details, see text

the A and B groups leads to the compound shown in Fig. 15b. A and B are dimethylaminopyridine (DMAP) and thiourea catalytic groups that can cooperate in an organocatalytic conjugate addition.

As schematized in Fig. 15c, in the *trans* form cooperation of the A and B groups is of course impossible, but after photoisomerization A and B are close together and can cooperate in a catalytic function. Most interesting, because of steric effects the *cis* isomer has two distinct forms that exhibit different activities and stereoselectivities (Wang and Feringa 2011).

### 8.3 Entangled reactions

Figure 16 illustrates the case in which the photochemical process precedes and, at the same time, follows the catalytic reaction (Shih et al. 2010). Light excitation of the *fac*-[Ir(ppy)$_3$] photosensitizer (PS) leads to the *[Ir(ppy)$_3$] excited state, which is a strong reductant (Sect. 4). *[Ir(ppy)$_3$] reduces benzyl bromide to the benzyl bromide radical anion which decomposes into bromide anion and benzyl radical. The latter is involved with aldeyde B in a catalytic reaction whose product Cat-B-A reduces the

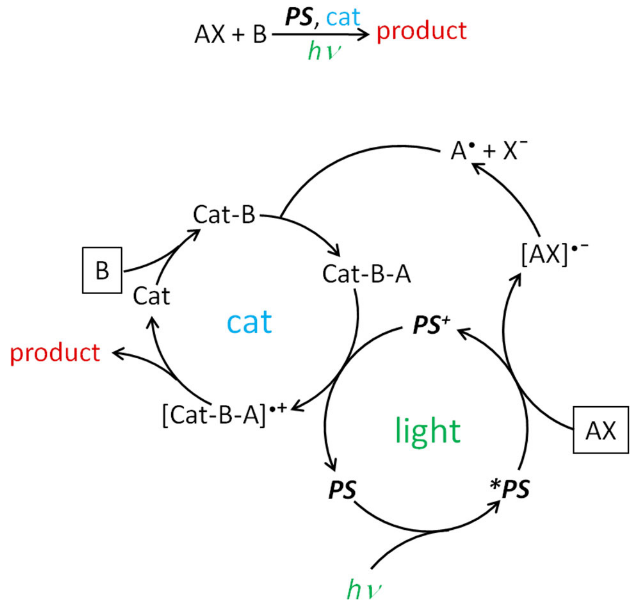


**Fig. 16** A photocatalytic cycle activated by visible light merged into an organocatalytic cycle: a prototypical example is represented by α-benzylation of aldehydes, where the photosensitizer (PS) is $[Ir(ppy)_3]$; AX = benzyl bromide; B = aldehyde; Cat = organocatalyst; product = α-benzyl-aldehyde (Shih et al. 2010)

oxidized $[Ir(ppy)_3]^+$ generated by the photoreaction, thereby closing the photosensitization cycle.

In some cases, it is not at all easy to understand which is the first step of the process and the real reaction paths. For example, in the case of arylative ring expansion (Fig. 17) (Shu et al. 2014) two different reaction paths have been proposed.

## 9 Solar energy conversion by water splitting

### 9.1 Homogeneous systems

In the system illustrated in Fig. 12, a thermodynamically forbidden dark reaction takes place thanks to the light absorbed by the $[Ru(bpy)_3]^{2+}$ photosensitzer. The reaction mechanism is illustrated in Fig. 18 (Young et al. 1975). The excited Ru complex reduces methyl viologen to $MV^+$ and the oxidized form of the complex so obtained oxidizes triphenyl amine going back to the initial $[Ru(bpy)_3]^{2+}$ species. As a result, part of absorbed light energy is converted into chemical energy. $MV^+$ and $NPh_3^+$ are indeed a strong reductant and oxidant, respectively.

The amount of chemical energy generated by the photosensitized electron transfer (Fig. 18) is larger than that needed to split water into molecular hydrogen and molecular oxygen (1.23 eV), but reactions (i) and (ii) in Fig. 19 that should lead to water splitting are multielectron transfer processes too slow to compete with the back ET reaction (iii) in Fig. 19, which is a very fast one-electron transfer process (Fig. 19).

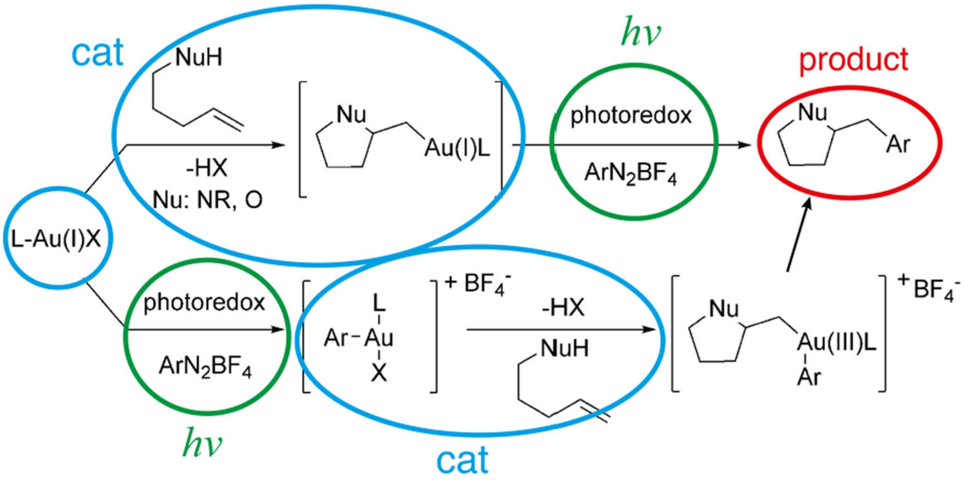
To obtain water splitting one should speed up the hydrogen and oxygen evolving reactions (i) and (ii) in Fig. 19 by suitable catalysts and, even more important, slow down reaction (iii) in Fig. 19. A strategy to slow down the back electron transfer reaction consists in linking the electron donor D and the electron acceptor A species to the photosensitizer to keep them separated from each other. In such a case, the back reaction takes place without direct contact and its rate decreases with increasing distance. In the last 20 years, a great effort has been dedicated to synthesize supramolecular systems made of three components linked together, such as that shown in Fig. 20 (Maxwell et al. 2000).

In triads, however, the distance is usually too short to prevent the back electron transfer reaction, so that systems with more than three components have then been prepared (Balzani et al. 2008).

Figure 21 shows the energy level schemes of the four-component system, a tetrad, that constitutes the reaction center of bacterial photosynthesis (Blankenship 2002).

The rate of the back electron transfer (BET) reaction decreases as the two separated charges are more distant and

**Fig. 17** Possible reaction paths of the reaction of arylative ring expansion (Shu et al. 2014)



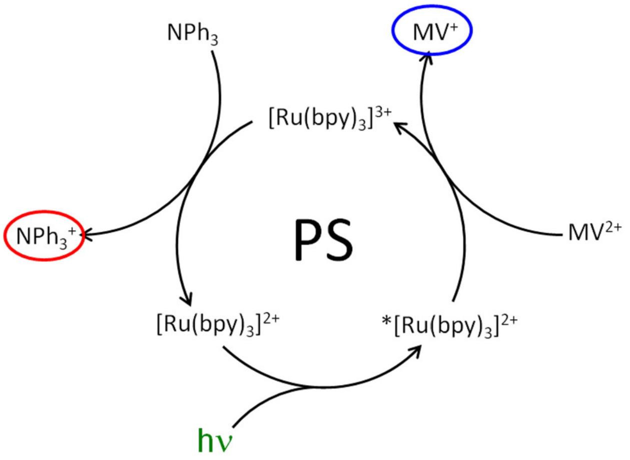


**Fig. 18** Conversion of light into chemical energy using $[Ru(bpy)_3]^{2+}$ as a photosensitizer

becomes negligible when they are far away. But it should also be noticed that any further step that increases the charge separation (CD) distance leads also to a decrease in the amount of storable energy.

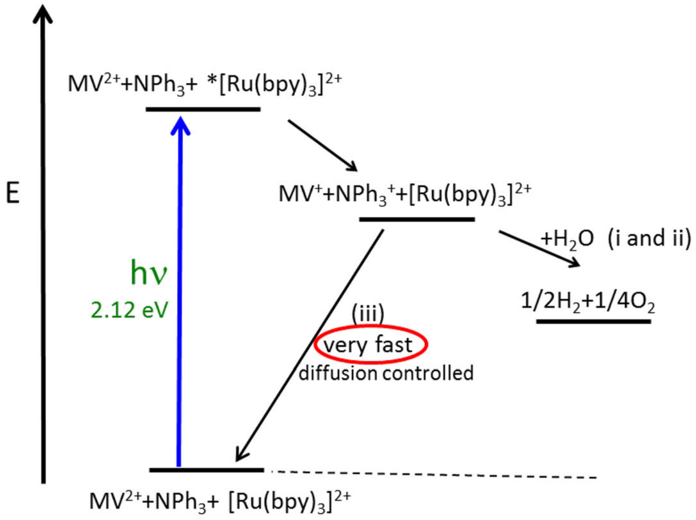
After several years of studies, it was concluded that a plausible system to achieve photocatalytic water splitting should include the basis features illustrated in Fig. 22, namely a multichromophoric system to harvest sunlight, a reaction center for charge separation, and two catalysts for hydrogen and oxygen evolution. The need for catalysts derives from the one-electron transfer nature of the photoreaction and the two (for hydrogen) and four- (for oxygen) electron transfer reactions for water splitting. In other words, oxygen evolution requires a catalyst capable of storing four positive charges originated from four successive photoinduced processes. The four charges are then used together to generate oxygen. In natural photosynthesis, oxygen evolution is mediated by the so-called oxygen evolving complex (OEC), a cluster containing four manganese atoms and a calcium atom (Siegbahn 2009; Suga et al. 2015). Much effort is currently dedicated to synthesize efficient catalysts for artificial photosynthesis. Some progress has been made, especially with complexes of expensive metals like platinum, iridium and ruthenium (Sartorel et al. 2013; Berardi et al. 2014; Sala et al. 2014).

The great number of synthetic multicomponent reaction centers (triads, tetrads, pentads) and multichromophoric systems to harvest sunlight that have been prepared and investigated (Balzani et al. 2011; ch. 11 in Balzani et al. 2014) have been very useful to develop theories on electron and energy transfer processes, but unsuitable for practical applications also because appropriate homogeneous catalysts are lacking (McKone et al. 2014).It is now believed that practical systems should be based on photoactivation of solid-state semiconductor materials.

## 9.2 Semiconductor materials

It is well known that irradiation of a semiconductor with photons having energy equal to or greater than its band gap promotes an electron to the conduction band with

**Fig. 19** Photosensitization by $[Ru(bpy)_3]^{2+}$ of the endergonic reaction between $MV^{2+}$ and $NPh_3$ leads to a strong reductant, $MV^+$, and a strong oxidant, $NPh_3^+$, which in principle could cause water splitting via multielectron transfer reactions (*i*) and (*ii*). These processes, however, are much slower than the back electron transfer reaction (*iii*)



$$\text{(i)}\quad MV^+ + H_2O \xrightarrow{cat} MV^{2+} + 1/2H_2 + OH^- \quad \text{(slow, 2 electrons)}$$

$$\text{(ii)}\quad NPh_3^+ + 1/2H_2O \xrightarrow{cat} NPh_3 + 1/4O_2 + H^+ \quad \text{(slow, 4 electrons)}$$

$$\text{(iii)}\quad MV^+ + NPh_3^+ \longrightarrow MV^{2+} + NPh_3 \quad \text{(fast, diffusion controlled)}$$

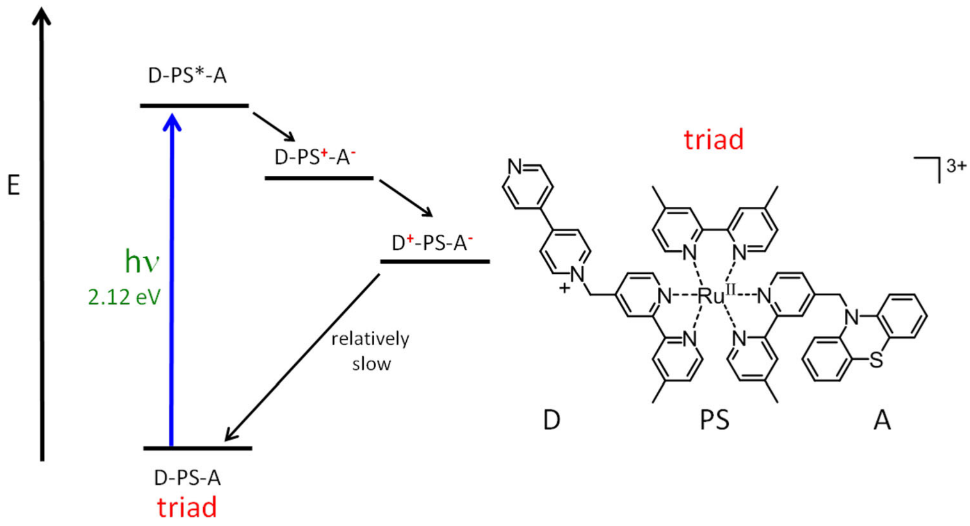


**Fig. 20** Photoinduced charge separation in a triad (Maxwell et al. 2000)

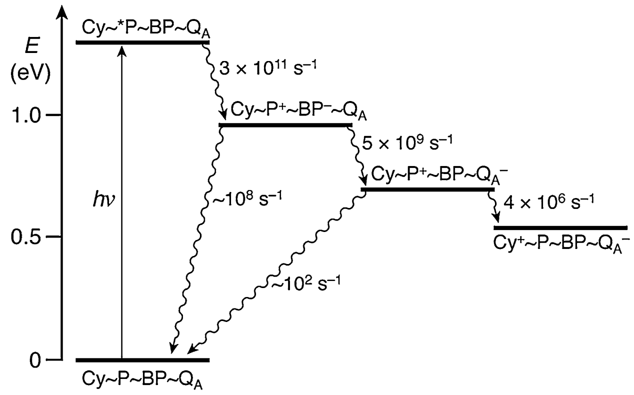


**Fig. 21** Energy-level diagram and rate constants of the electron transfer steps involved in the charge separation process of the reaction center of *Rhodopseudomonas viridis*. *Cy c*-type cytochrome, *P* bacteriochlorophyll "special pair", *BP* bacteriopheophytin, $Q_A$ quinone

concomitant formation of a hole in the valence band (Fig. 23). Electrons and holes can recombine (BET) or migrate to the surface of the semiconductor where charges can drive thermodynamically allowed reduction and oxidation reactions, such as those involved in water splitting.

To achieve efficient water splitting using a photoelectrochemical system based on a single semiconductor, very demanding properties are required to the selected material:

- The positions of the band edges need to straddle the redox levels for the water oxidation and water reduction to provide a driving force for the reaction.
- The band gap must be high enough to provide the needed overpotential, but still small enough to allow absorption of a large portion of the solar spectrum.
- The semiconductor surface must be able to play a catalytic role with respect to both oxidation and reduction of water, while remaining stable in water under illumination.
- The material should be engineered with a mechanism for separation of the photogenerated charge carriers, as well as for transport out of the electrolyte interface without recombination.

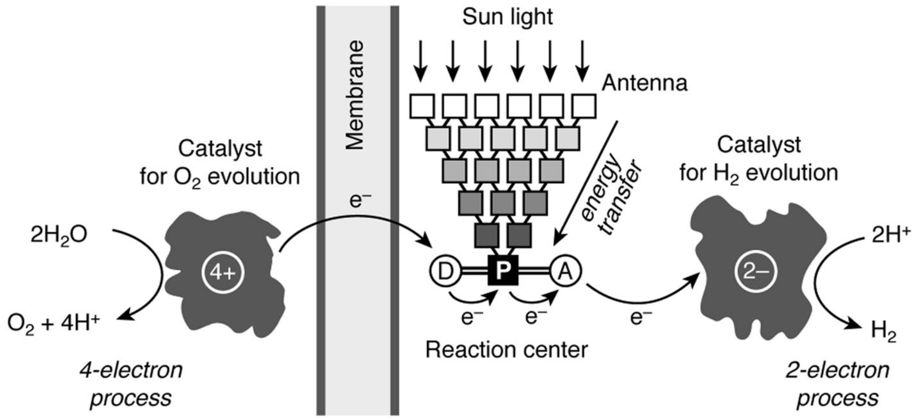


**Fig. 22** Schematic representation of the strategy for photochemical water splitting (artificial photosynthesis). Five fundamental components can be recognized: an antenna for light harvesting, a charge separation triad D–P–A, a catalyst for hydrogen evolution, a catalyst for oxygen evolution, and a membrane separating the reductive and the oxidative processes. Adapted from (Balzani et al. 2014)

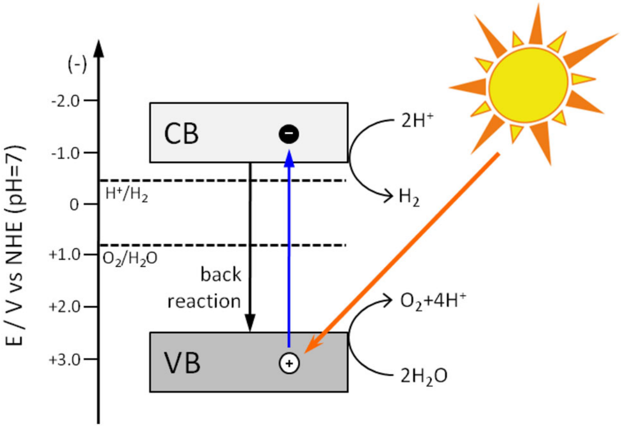


**Fig. 23** Fundamental steps for water splitting by solid-state photocatalysis. For simplicity, band bending is not shown. Adapted from (Balzani et al. 2015)

- For large-scale application, the material should be not toxic and based on inexpensive elements.

Given this set of requirements, it is not surprising that, in spite of over four decades of intense effort, no material performing well in all the fundamental steps has been found (Kisch 2013, 2015; Qu and Duan 2013; Li et al. 2015).

Therefore, more elaborated, multi-component systems have been proposed (Jacobsson et al. 2014; Nielander et al. 2015). A first attempt to create viable photoelectrochemical devices consists in separating the light absorption from the catalytic functions by depositing catalytic particles on the semiconductor (Fig. 24).

Taking inspiration from green plant photosynthesis, the so-called Z-scheme can be adopted (Bard 1979), which is based on two different semiconductors, one suitable for $H_2$ generation and the other one for $O_2$ generation (tandem cells) (Fig. 25). The two semiconductors can be connected directly (back contact), by solid material, by an electron mediator (as represented in Fig. 25).

The Z-scheme is important not only because it allows using narrow band gap semiconductors, but also because it involves the formation of separated reduction and oxidation sites in two different photocatalysts, thereby avoiding the occurrence of surface back reactions [see, e.g., the recent tutorial review (Hisatomi et al. 2014)].

A photoelectrochemical (PEC) system for water splitting can be photosensitized. An example of dye sensitized photoelectrochemical (DSPEC) cells is illustrated in Fig. 26 (Youngblood et al. 2009). The $TiO_2$ photoanode is covered by a Ru photosensitizer that carries an $IrO_2$ nanoparticle as oxygen evolving complex. In DSPEC cells light absorption and charge carrier transport are separated and can thus be optimized. In general, a major problem for PEC is the stability of the photoelectrode interface under illumination because of severe pH conditions and presence of free radicals. Geometries with spatially separated electrodes connected by wires are preferred because they enable investigation and optimization of the two half-reactions independently.

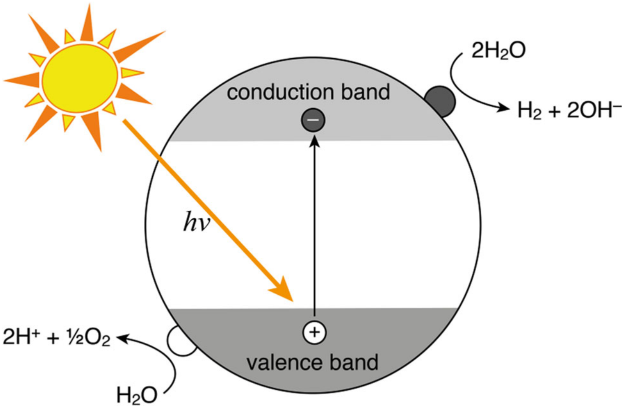


**Fig. 24** Schematic diagram showing a photoelectrochemical system based on a single semiconductor implemented with proper catalysts for water oxidation (*white circle*, *left*) and reduction (*grey circle*, *right*)

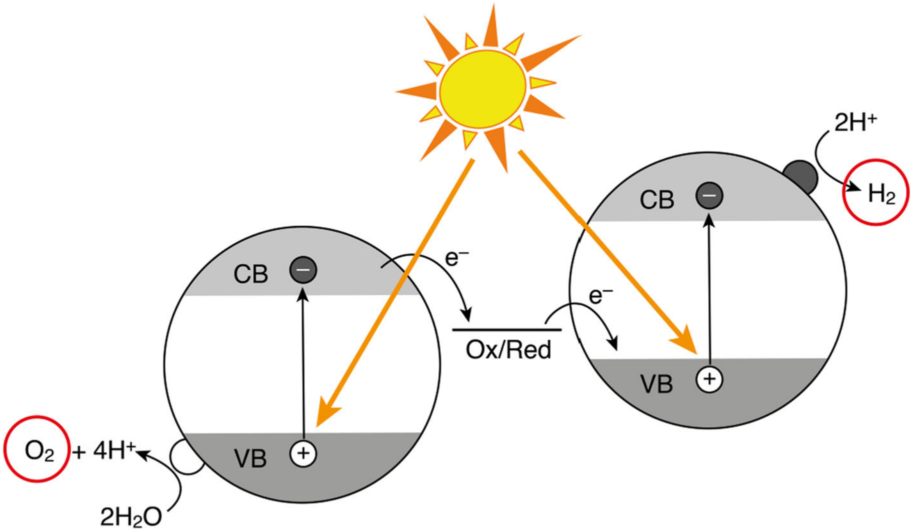
The removal of the photoelectrode from the electrolyte allows more flexibility, e.g., the use of photoelectrodes connected in series to satisfy the energy requirements of electrolysis. Solar-to-hydrogen efficiencies in the range 10–12 % have been obtained with solar cells of this type based on perovskite that, however, are not very stable (Luo et al. 2014). Constraints toward industrial application of PEC water splitting devices arise not so much from efficiency, but especially from stability and scalability.

### 9.3 PV electrolysis

At present, PV electrolysis, that is the generation of electric energy by photovoltaic panels followed by water electrolysis (Fig. 27), is the simplest and more efficient route towards sustainable hydrogen production.

It is indeed a mature technology because both PV panels and water electrolyzers have been commercially available since a long time. PV electrolysis can be carried out using PV electricity directly or through the grid, by appropriate converters. With current electricity price, the hydrogen production cost has been estimated to be about twice that of hydrogen produced by steam reforming of methane (Armaroli and Balzani 2016). Currently, however, it seems that renewable electricity can more efficiently be used to power electric cars through batteries rather than to generate hydrogen that should then be reconverted into electricity by fuel cells.

**Fig. 25** Schematic diagram showing a photoelectrochemical system based on the Z-scheme: two different semiconductors are used in conjunction with proper catalysts for water oxidation (*white circle*, *left*) and reduction (*grey circle*, *right*)



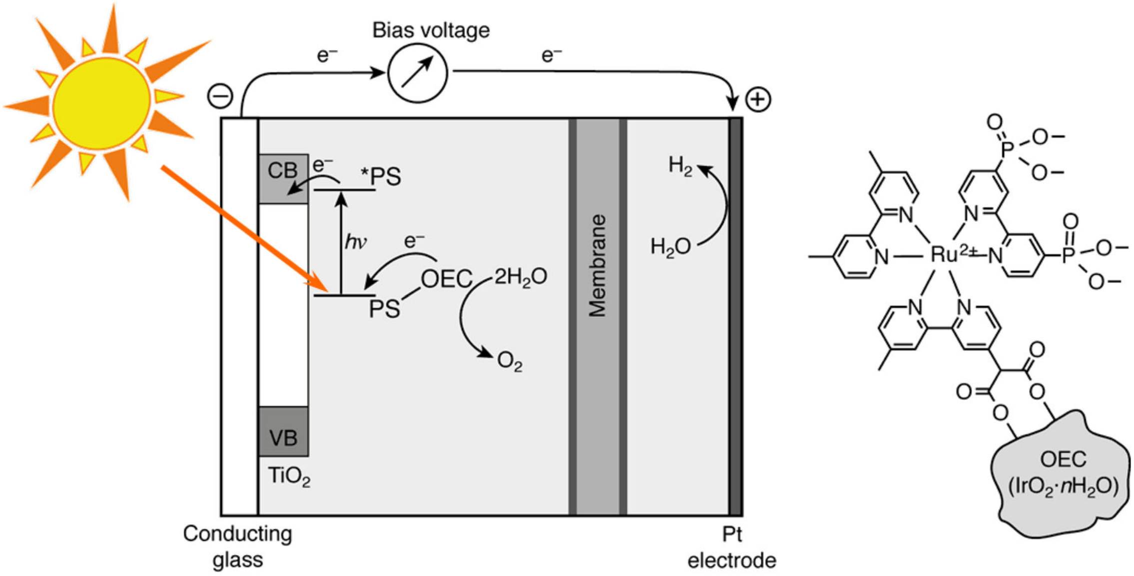
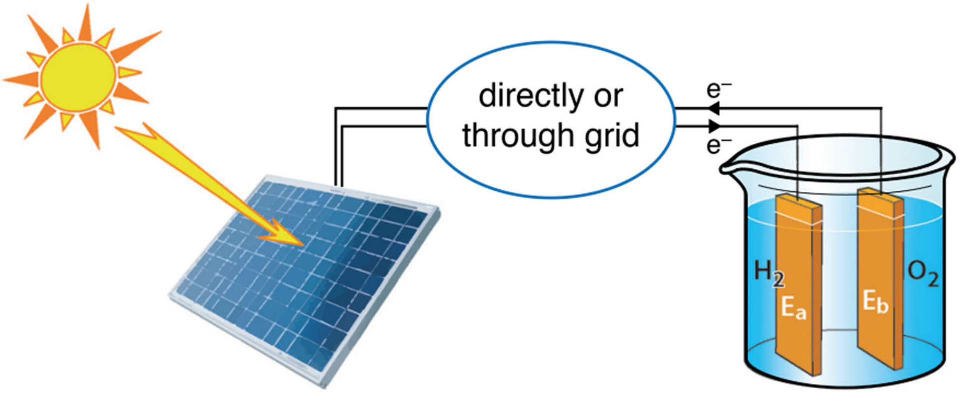


**Fig. 26** Water splitting, obtained with the help of a small potential electric bias, in a DSPEC in which a nanoparticulate $TiO_2$ photoanode is sensitized by a ruthenium polypyridine complex (*right*) (Youngblood et al. 2009). Adapted from (Balzani et al. 2015)

**Fig. 27** Schematic representation of a photovoltaic panel coupled, directly or through grid, to an electrolysis cell for water splitting



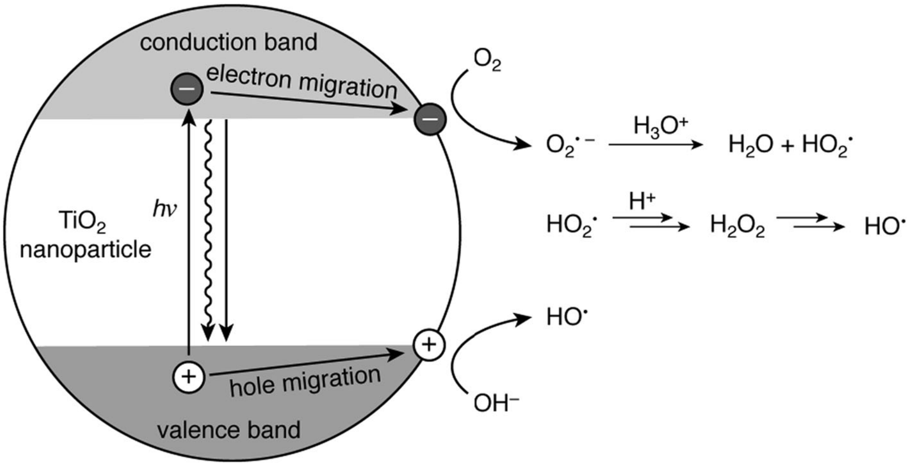


**Fig. 28** Interfacial electron transfer reactions with the solvent generated by light excitation of $TiO_2$

## 10 Photocatalysis for pollution remediation

From the practical viewpoint, this is probably the most important application of photocatalysis: recovery of waters from industrial, agricultural and domestic usages, as well as decontamination of the atmosphere and soil through the mineralization of the pollutants, or at least their transformation into non-toxic compounds. Since this topichas been thoroughly reviewed by several authors, (Stochel et al. 2009; Ravelli et al. 2009; Verbruggen 2015) we will only illustrate some basic concepts.

In semiconductors like $TiO_2$, light excitation promotes an electron from the valence to the conduction band, and the promoted electron and the hole travel to the semiconductor surface where they give rise to interfacial electron transfer reactions with the solvent or other adsorbed species (Fig. 28). Reaction of holes with solvent water molecules generates $HO^\bullet$ radicals, whereas 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. Oxidation and reduction of other species by the excited semiconductor can also occur, often leading again to formation of $HO^\bullet$, $HO_2^\bullet$, and $O_2^{\bullet -}$ (Ravelli et al. 2009; Kisch 2013, 2015).

Photocatalysis is more effective than traditional chemical oxidations, such as chlorination, and is often coupled with a biological treatment for optimal wastewater recovery. The mechanism for the photooxidative degradation of many organic pollutants over titanium dioxide has been studied in depth and extensively reviewed (Serpone and Pelizzetti 1989).

In the presence of fluorides, more free $HO^\bullet$ radicals are formed, presumably because fluoride substitutes hydroxyl groups on the catalyst surface. Platinization (at high Pt dispersion) has a synergic effect with fluorination (Pt nanoparticles act as an electron sink) and may lead to a very large increase of the activity (Hidalgo et al. 2008).

Studies on photooxidation of simple organics on well-defined single crystal surfaces of $TiO_2(110)$ have provided considerable insight into the mechanism of molecular fragmentation, the role of adsorbed oxygen in promoting photoreaction, and the nature of the substrate-mediated charge transfer processes leading to molecular adsorbate excitation (Wilson et al. 2012).

Air purification can also be obtained at an illuminated surface coated with a semiconductor and this principle has been implemented for a variety of commercial applications, both outdoor and indoor (Hashimoto et al. 2005; Gaya and Abdullah 2008) that destroy nitrogen oxides and organic pollutants. For its sterilizing, deodorizing and anti-fouling properties, $TiO_2$ is added to paints, cements, windows, tiles, or other products (Tryk et al. 2000; Skorb et al. 2008). A number of applications to surfaces that remain clean after being exposed for months to polluted urban air have been demonstrated, including automobile body, the glass cover of street lamps (even in tunnels), polymers (e.g., in tents) and textiles.

## 11 Conclusions

Catalysis is a very important field of chemistry. The purpose of catalysis is that of modifying (usually, increasing) the rate of chemical reactions. This goal is achieved by performing the reaction in the presence of an additional substance that offers the process a different path involving a smaller activation energy (Fig. 1).

Photochemistry is not a field, but a new dimension of chemistry (Fig. 2). Light absorption promotes a molecule from its ground state, which is the species involved in common chemical reactions, into an excited state. Because of the extra amount of energy compared with the ground state, the excited state is, generally speaking, “more reactive” than the ground state. Being characterized by a different electronic structure, the excited state is, indeed, a new chemical species with its own specific properties, including energy content, bond lengths, spatial structure, charge distribution, acid–base properties and oxidation and reduction potentials (see, e.g., Tables 1, 2). In several cases, light excitation causes bond breaking or other irreversible processes that lead to the decomposition of the molecule. In some cases, however, light excitation can simply increase the rate of a dark reaction. Although light is consumed and the intimate mechanism of the photochemical reaction is completely different from that of a catalyzed reaction (see, e.g., Fig. 7), in such cases we can say that, formally, light plays the role of a catalyst.

Catalysis and photochemistry are formally connected from another viewpoint. Sometimes molecules are not able to absorb light and thus they cannot exploit the peculiar reactivity of their electronically excited states. In such a case, it is still possible to take advantage of light excitation by using a photosensitizer, a species that is not consumed and allows the reaction to occur with a fast rate (e.g., Fig. 10). A photosensitizer could, in principle, also be viewed as a catalyst for photochemical reactions.

The fundamental difference between catalysis and photochemistry concerns chemical equilibria. A catalyst has no effect on a chemical equilibrium because it can only affect the energy of the transition state, whereas light can increase the free energy of the absorbing species (see, e.g., Fig. 4) and thus can displace a chemical equilibrium. In these systems, when light excitation is switched off, the system can either go back (often in a very short time) to the original equilibrium [e.g., reaction (iii) in Fig. 19], or it may be directed, sometimes by using catalysts, to other reaction paths leading to valuable products. The most important application of this strategy is the conversion of sunlight into chemical energy, as it happens in the photosensitized water splitting process in which catalysts play a very important role by mediating between the one-photon one-electron rule that govern photochemical processes and the multielectron nature of the water splitting reaction (Figs. 22, 23, 24, 25, 26).

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