

Photocatalysis. A multi-faceted concept for green chemistry

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Photocatalysis (by semiconductors, molecules and ions) is used in such diverse applications as water hydrolysis for producing hydrogen as fuel, organic synthesis and the recovery of polluted effluents. This *tutorial review* discusses the common principles of such applications and their role in green chemistry.

1. General

1.1 Historical and definition

The evolution of the term ‘photocatalysis’ illustrates the development of some key concepts of photochemistry. The turning point that allowed photochemistry to become a science on its own was recognizing the difference with thermal chemistry. In fact, up to the beginning of the 20th century many scientists felt that irradiation was one of the many ways available for catalyzing a reaction, that is making it faster, such as heating or treating with some chemicals. The first scientist who devoted a systematic effort to understand the

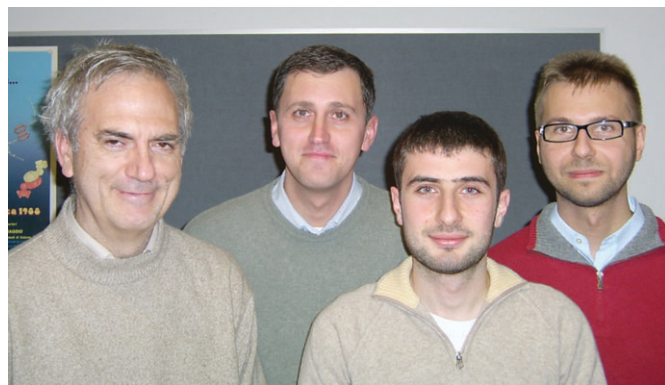
chemical effect of light, Giacomo Ciamician, took great pains in ascertaining whether ‘light and light alone’, and not, for instance, heat, caused the reactions he was discovering (1900–1920).¹ To these reactions the tag ‘photochemical’ was properly assigned, while the term ‘photocatalytic’ designated reactions accelerated by light, but maintaining the same course as the thermal reactions. A further step forward was recognizing that photochemical reactions involve electronically excited states, ‘electronic isomers’ of ground states that have a reactivity (and a thermodynamics) of their own. This was defined by Bodenstein in 1914, but became a common notion much later.

A further distinction that was also introduced at an early stage had to do with the overall thermochemistry of the process. Thus photosynthesis referred to reactions where part of the photon energy was incorporated in the products (that thus lay higher than the reagents on the potential surface,

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(Left to right) Angelo Albini, Maurizio Fagnoni, Davide Ravelli and Daniele Dondi

Davide Ravelli was born in 1984 and obtained his Master degree from the University of Pavia in 2008. He is currently a PhD student at the University of Pavia (Prof. Angelo Albini as the supervisor), and his research interests focus on decatungstate photocatalyzed reactions, aimed at the formation of the C–C bond.

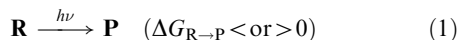
Daniele Dondi studied chemistry at the University of Pavia and obtained his BSc in 2000 and PhD in 2003 with a work on synthetic organic photochemistry under the supervision of Angelo Albini and Maurizio Fagnoni. After this period, he spent a year studying the photostability of sunscreens. He worked on the decatungstate photocatalysis in a project sponsored by the INCA consortium and actually he's working on mechanisms and effect of ionizing radiation on composite materials.

Maurizio Fagnoni graduated in Pavia in 1992 with a thesis on the synthetic applications of photo-SET reactions under the

guidance of Prof. Angelo Albini. He spent part of his PhD period at the University of Muenster (Germany) working on the photochemistry of cyclopropylketones (Prof. Jochen Mattay as the supervisor). He moved to the Istituto Ronzoni (Milan) where he worked on the synthesis of peptidomimetics and functionalized chitosans and in 1998 returned to the University of Pavia where in 2008 was appointed associate professor. His interests lie in the application of photochemistry to organic synthesis encompassing photocatalysis and phenyl cation chemistry.

Angelo Albini completed his studies in Chemistry in 1972, did postdoctoral work at the Max-Planck Institute for Radiation Chemistry in Muelheim, Germany (1973–74) and joined the Faculty at Pavia in 1975, where is currently Professor of Organic Chemistry, after a period at the University of Torino and stays at the Universities of Western Ontario (Canada 1976–77) and Odense (Denmark, 1983). He is active in the field of organic photochemistry, organic synthesis via radicals and ions, photoinitiated reactions, mild synthetic procedures in the frame of the increasing interest for sustainable/green chemistry, applied photochemistry.

$\Delta G_{R \rightarrow P} > 0$) and photocatalysis to the contrary case, see eqn (1):²



The sign of $\Delta G_{R \rightarrow P}$ is generally not given much consideration in thermal reactions (eqn (2)),



where added chemicals and conditions (temperature, solvent, *etc.*) are chosen so that the *overall* system evolves in the desired direction. In photochemical reactions that start from high-lying R^* it is conceivable that a high-lying product P is formed. However, this point is rarely commented upon and the term photocatalysis continues to be used as an (inappropriate) synonym of photoreaction, as is photolysis.

The large use of the term photocatalysis and the development of a discipline specifically designed by this name began in the 1970s, with reference to two different topics. First, the oil crisis gave a strong impulse to the research of alternative energy sources, and it was hoped that man could imitate nature by exploiting solar energy for the generation of a fuel, in particular of hydrogen by water splitting.^{3,4} Second, concern about pollution by chemicals increased and it was proposed that photocatalysis might clean up water and air avoiding the addition of further chemicals.⁵ The two topics grew up from different traditions (electrochemistry, inorganic chemistry, heterogeneous catalysis) and remained separated. Even more separated was a third application, *viz.* chemical synthesis, that began to develop later, although this was strongly connected by the fact that the same photocatalysts were used.⁶ Importantly, all of the three applications fit into the field of green – or sustainable – chemistry.

In the following, ‘photocatalysis’ refers to any reaction that requires the simultaneous presence of a catalyst and light (eqn (3)), with some limitations.⁵



Excluded are: (i) chain reactions *via* a photogenerated intermediate, *e.g.* the radical chain chlorination of alkanes, and *via* the photogeneration of a thermally active catalyst (both photoinitiated thermal reactions); and (ii) reactions involving the reagent excited states, even when another molecule absorbs light and transfers energy (*sensitized* photochemical reactions).

A photocatalyst C , differently from a thermal catalyst (compare Fig. 1A), is effective only in the excited state (C^*) and activates reagent R (with efficiency ≤ 1) through a *chemical* reaction, such as transfer of an atom or an electron, not through a *physical* step, such as energy transfer (compare Fig. 1C and 1B). An intermediate I is formed (a radical or radical ion), which in principle can be formed also through a thermal process. C^* reacts simultaneously and gives C' . If either C' or I react independently, a photochemical reaction occurs where C and R are consumed, a well known example being the photoreduction of a ketone by alcohols (eqn (4)):

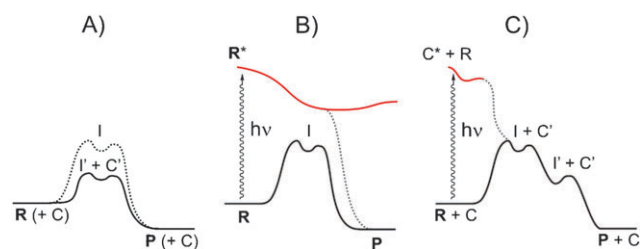
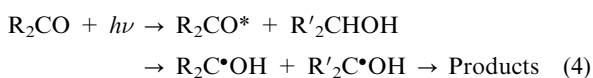
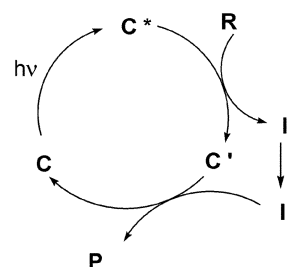


Fig. 1 Paths followed (A) in a thermal reaction ($R \rightarrow P$) catalyzed by C *via* intermediate I ; (B) in a photochemical reaction (the chemical reaction starts from the excited state surface of the reagent R^*); (C) in a photocatalyzed reaction (the catalyst C is active only in the excited state, but the chemical transformation of R occurs entirely on the ground state surface).



Scheme 1 C acts as a photocatalyst in the $R \rightarrow P$ reaction.

However, if intermediate I gives I' and this regenerates C , while giving end product P , the overall result is the transformation of R into P by absorbed light in the presence of *non-consumed* C^\ddagger (see Scheme 1). The entire *chemical* transformation $R \rightarrow P$ occurs on the *lowest potential energy surface* at any configuration, just as in thermal reactions, but contrary to photochemical reactions, where the chemical path in part occurs on an *excited surface* (from R^* , Fig. 1B). This is called photocatalysis since a new path on the *ground state* surface becomes accessible, just as in Fig. 1A.⁶

A condition is that the path leading to closing the cycle predominates over processes that consume or inactivate C (as expressed by the Turn Over Number, the moles of the reagent that a mole of catalyst can convert before becoming inactivated).

1.2 Photocatalysis and green chemistry

Photocatalysis occupies a central place in ecological equilibria. By far the main supply of energy on Earth is solar irradiation, a (to all practical purposes) perennial source that exceeds every conceivable need of mankind in the future (25 000–75 000 kWh per day and hectare). Human beings use directly only a small fraction of such energy (for getting warm, for generating vitamin D in the skin, in the vision process). Green plants use solar energy in the best photocatalytic process known, photosynthesis, a veritable chemical factory based on water splitting, where oxygen is liberated and reduced coenzymes are formed, which then reduce carbon dioxide to carbohydrates. The products serve both for building the plant structure (cellulose) and as an energy supply (starch). These have been

[†] Or only partially consumed; normally added in a concentration well below the stoichiometric.

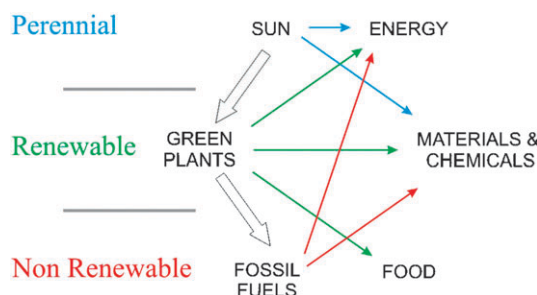


Fig. 2 Solar irradiation is the ultimate source of energy that is converted by green plants into chemical energy and, through their evolution, into fossil fuels (open arrow). Over the millennia, mankind has learned to exploit the renewable supply afforded by plants for obtaining food, materials and energy (green arrows). In the last two centuries man has learned to exploit a convenient, but non-renewable, source such as fossil fuels (red arrows). Will it be able to use solar irradiation directly for both energy and materials (blue arrows)?

the (renewable) source of food, energy and materials for mankind all along its history (see Fig. 2, green arrows), either directly or after further elaboration by other living beings (animals). Chemical transformations of the dead organisms over millions years produced oil, coal and natural gas. In the last two centuries, mankind has learned to use the (relatively) large supply of such fossil fuels by means of a new science, chemistry, and these are presently the main source of energy, materials and chemicals (red arrows). Agriculture remains the source of food, but is made more efficient by the use of fertilizers and thus indirectly again by fossil fuels.

This means that the present time welfare is built upon ‘fossil’ solar energy, a finite and non-renewable source that results from the irradiation of past eons. A rationale exploitation of green plants, *e.g.* obtaining energy and chemicals from agricultural waste or plants growing on non-cultivated grounds offers a renewable source, although in a limited amount. Obviously, learning to exploit *directly* solar energy (blue arrow in Fig. 2) would be a major breakthrough. An idea of the thermodynamics involved in these processes can be

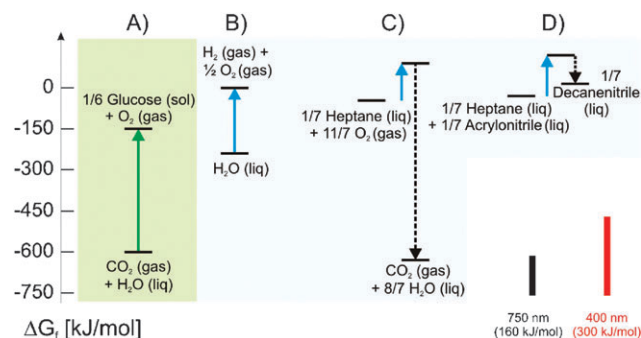
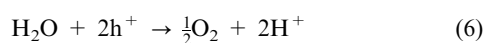


Fig. 3 Free energy of formation for some representative compounds. (A) Nature produces energy-rich glucose from CO_2 (green arrow) by using 8 photons (the energy of photons at the two limits of visible light is indicated). (B, eqns (5) and (6)) Artificial photocatalysis (blue arrow) may be used for accumulating energy carriers, *e.g.* H_2 from water, or alternatively for overcoming E_a and carrying out reactions under mild conditions, *e.g.* *via* radical intermediates, whether for the elimination of contaminants (C, eqn (8)) or for synthesis (D, eqn (7)).

obtained from Fig. 3, where the ΔG_f° of some relevant compounds is indicated and compared with the photon energy at the high- (400 nm) and low-energy (750 nm) borders of the visible-light range. Nature transforms solar into chemical energy by producing glucose from CO_2 and using (at least) 8 photons (Fig. 3A). After the organism’s death, natural substances evolve to fossil fuels (represented here by heptane), which lie even higher on the potential surface.

Actually, the three fields of ‘photocatalysis’ correspond to three basic *chemical* ways of exploiting *solar energy* by:

(i) Transforming *light* energy into the more easily stored and used *chemical* energy. The main effort is devoted to the production of a convenient fuel such as hydrogen from a largely available source such as water *via* electron/hole (e^-/h^+) exchange with excited **C** (eqns (5) and (6); Fig. 3B).

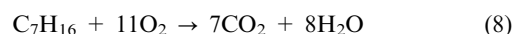


(ii) Using light for activating a chemical process; independently from the sign of $\Delta G_{R \rightarrow P}$, here excited **C** serves for overcoming the activation energy of the process. This is particularly useful when E_a is high and may allow energy sparing by using shorter synthetic sequences. An example is the generation of heptyl radicals directly from heptane (*via* hydrogen abstraction by the excited catalyst) and their trapping by acrylonitrile (eqn (7); Fig. 3D).



This leads to decanenitrile under mild conditions, skipping the otherwise required previous halogenation of the alkane and the use of a chain carrier such as a stannane.

(iii) Again using solar light for overcoming E_a , in this case for destroying undesired chemicals, *viz.* pollutants of industrial, urban or agricultural origin. This is a general method able to ‘burn’ (= oxidize) chemicals at room temperature by using molecular oxygen rather than chemical oxidants. With heptane, heptyl radicals would be formed and combine with oxygen, initiating a ‘cold combustion’ (eqn (8); Fig. 3C).



This is possible, but it is often more practical to oxidize water to OH^\bullet radicals – that then are the actual attacking species – rather than oxidizing the pollutants.

Many of the photocatalytic reactions reported below have been carried out by using lamps rather than solar light and thus do not fully exploit the ‘green’ potential of the method. Tests showed that at the ‘laboratory’ scale most photocatalytic reactions occur conveniently with solar light, although for industrial application the variable and intermittent character of this source is a stumbling block. In any case, it is important that absorption of the radiation is maximized,⁷ which is unsatisfactory in a cylindrical batch photoreactor, as normally used in exploratory studies. Light absorption is indeed receiving more attention in recent times, and more elaborate designs have been tested (whether in a fixed configuration, or with adjustable orientation, with or without concentration of the radiation). Clearly, such reactors are more expensive and whether the use of solar light is economically advantageous

depends on the reaction considered and on the insolation in the location chosen. For the moment, lamp-driven photocatalysis is the more practical choice, but it may be seen as a forerunner in view of arriving at exploiting solar light in the near future.‡

1.3 Photocatalysts: mode of action

Activation involves either atom or electron transfer.⁶ Convenient photocatalysts include both solid semiconductors, from powders to nanoparticles and colloids, and dissolved molecules or ions. The irradiation of a semiconductor promotes an electron from the valence band (VB) to the conduction band (CB). Electrons and holes (e^-/h^+) are thus available at the surface and the semiconductor behaves as a microscopic electrochemical cell. This is a short-lived phenomenon, but may affect substrates adsorbed on the catalyst surface causing electron transfer (ET) to occur both from a donor D to the VB and from the CB to an acceptor A (Fig. 4A). Due to the above mentioned kinetic limitation, the efficiency of such redox processes crucially depends on the adsorption equilibria.⁸

The most largely used semiconductor photocatalyst is titanium dioxide, often as the cheap white pigment Degussa P25. Although this performs reasonably well also under visible irradiation,⁷ physical forms of TiO_2 that give much better results have been reported. Indeed, a number of theoretical⁹ and experimental studies^{10,11} have been devoted to the relation of the efficiency with the crystal structure (anatase/rutile) and the size, form and mode of preparation of the crystals. As an example, using mixed phase nanocrystals prepared by sol-gel technique and calcination leads to a considerable advantage (see further Section 4.1).¹⁰

Photocatalysis may occur also in the homogeneous phase by using molecules as the catalysts, since molecular excited states are both stronger reductants (through the donation of the electron promoted in a vacant orbital) and stronger oxidants (by accepting an electron in the empty site in the HOMO) with respect to the ground state, leading again to an ET process (Fig. 4B). Alternatively, the structure of excited states may favor atom transfer. As an example, in the excited state of ketones (but also of soluble inorganic salts such as polyoxotungstates) the oxygen atoms acquire a radical character and hydrogen abstraction from an organic derivative R-H is facile (Fig. 4C).

The relevant redox potential for some photocatalysts **C** (left) and reagents **R** (right) are compared in Fig. 5. An excited photocatalyst (C^*) oxidizes a reagent when $E_{\text{ox}}(\text{R})$ is less positive (**R** blue line above that of C^*) and correspondingly reduces it when $E_{\text{red}}(\text{R})$ is more positive (**R** red line below that of C^*). The figure shows that excited TiO_2 is capable of causing water splitting, since the valence/conduction band gap is sufficiently large for encompassing the H_2O redox potentials (at least at low pH); thus both (multielectronic) processes (eqns (5) and (6)) are spontaneous. The drawback is that the large band gap corresponds to a high energy (UV) photon, a minor component in solar light (see below, however). The redox potential and absorption are similar to

‡ Furthermore, optimizing light absorption is an important issue also when using lamps, see Section 4.3.

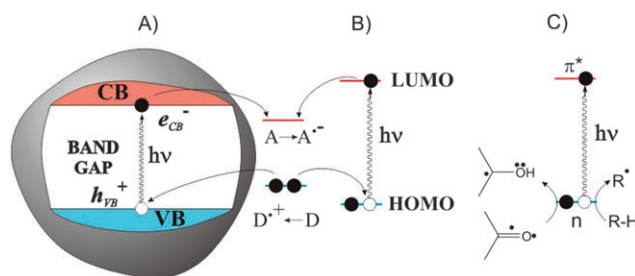


Fig. 4 Light excitation of either (A) semiconductor particles or (B) molecules leads to electron transfer or (C) to hydrogen abstraction.

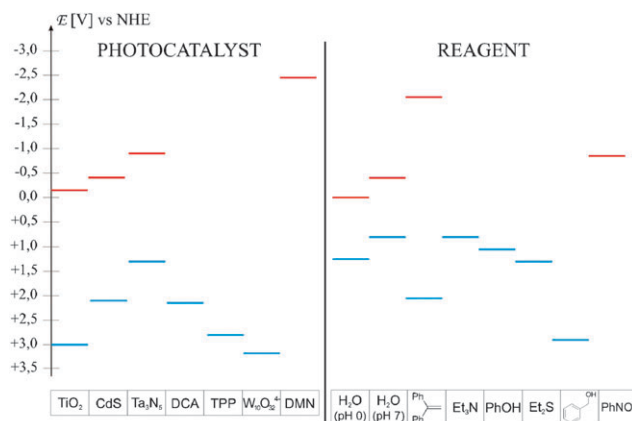


Fig. 5 Comparing the potential of the conduction (red) and valence (blue) bands of some semiconductors as well as the reduction potential (blue, DCA, 9,10-dicyanoanthracene; TPP, 2,4,6-triphenylpyrylium cation; $\text{W}_{10}\text{O}_{32}^{4-}$, decatungstate tetraanion) and oxidation potential (red, DMN, 1,4-dimethoxynaphthalene) of some excited photocatalysts (C^*), with the reduction (red) and oxidation (blue) potential of water and of some organic reagents (**R**).

those of polyoxotungstate anions (e.g. $\text{W}_{10}\text{O}_{32}^{4-}$ in the figure), which in this sense may be considered a homogeneous variation of TiO_2 . Cadmium sulfide absorbs at a longer wavelength. As for organic reagents, Fig. 5 evidences that donors (amines, sulfides, alkenes, aromatics) undergo mono-electronic oxidation with excited catalysts, while a moderate acceptor such as nitrobenzene is reduced by excited 1,4-dimethoxynaphthalene (DMN). The ET direction can be determined by choosing the appropriate photocatalyst, e.g. 1,1-diphenylethylene is oxidized by irradiated TiO_2 and 2,4,6-triphenylpyrylium salts (TPP), but reduced by DMN.

The applications of photocatalysis (see graphical abstract) are briefly surveyed in the following sections. These have in common with the natural version of photocatalysis – chlorophyll photosynthesis – two seemingly opposite characteristics, the mild conditions and the large chemical change caused. These reactions would thus occur thermally only under harsh conditions, whereas upon photocatalysis they are carried out under mild conditions, in accord with the paradigms of green chemistry.

2. Photocatalysis for producing hydrogen

The concern for the depletion of fossil fuels and the environmental problems accompanying their use fostered the

research for viable alternatives. Although the photocatalytic reduction of CO_2 is under investigation in several laboratories, most of the work has been devoted to the generation of hydrogen, potentially an excellent solution since this is the fuel with the highest energy capacity per unit mass as well as a clean energy carrier, because it produces neither CO_2 nor pollutants.

The obvious source of hydrogen is water, but splitting of this molecule requires temperatures in excess of 2000 °C, thus making its implementation problematic.⁴ Photocatalytic water splitting by solar irradiation is appealing and has been intensively studied in the last three decades.^{12–15}

Water splitting on an illuminated TiO_2 semiconductor surface has been first demonstrated by Fujishima and Honda in 1972.³ As shown in Fig. 4 and 5, absorption of a photon of energy equivalent to, or greater than, the semiconductor band gap promotes an electron to the CB, leaving a positive hole in the VB. A fraction of photogenerated e^-/h^+ avoid recombination and migrate to the surface, where these react with adsorbed molecules causing reduction and oxidation, respectively. Water reduction to H_2 and oxidation to O_2 require that the bottom of the conduction band lies at a more negative potential than $E_{\text{red}}(\text{H}^+/\text{H}_2)$, 0 V vs. NHE at pH 0, and the top of the valence band at a more positive value than $E_{\text{ox}}(\text{H}_2\text{O}/\text{O}_2)$, 1.23 V vs. NHE at pH 0; the two-electron process $\text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2} \text{O}_2$ is endoergonic, $\Delta G^\circ = 238 \text{ kJ/mol} = 2.46 \text{ eV}$, see Fig. 3. Thus, the minimum energy required to drive the reaction corresponds to that of two photons of 1.23 eV, corresponding to λ ca. 1000 nm, in the near infrared region. However, ET involves an activation barrier, and a photon energy greater than the above value is required for driving water splitting at a reasonable rate.

Suitable semiconductors are mostly based on transition-metal cations with d^0 (Ti^{4+} , Zr^{4+} , Nb^{5+} , Ta^{5+} and W^{6+}) or d^{10} electronic configurations (Ga^{3+} , In^{3+} , Ge^{4+} , Sn^{4+} , and Sb^{5+}). Other metal oxides with empty/filled d orbitals, such as V^{5+} , Mo^{6+} , and Zn^{2+} , are also expected to be active provided that the band position is suitable. For example, WO_3 cannot reduce H^+ to H_2 because the CB is at a more positive potential than that of water reduction, but functions as a robust photocatalyst for O_2 evolution in the presence of an appropriate electron acceptor. The top of the valence band is common for all the metal oxides [an O(2p) orbital located at ca. +3 eV].

Further requirements must be met, however. A second condition is stability under operative conditions. Thus, semiconductors based on Si, GaAs, InP and related materials, common in modern electronics and solar power engineering (photovoltaics), are not used in photocatalysis because, apart from their cost, they are unstable in aqueous solutions. Moreover, photogenerated holes may cause the oxidation of the semiconductor surface, resulting either in an isolating layer of oxide or in corrosion of the material. This is the case for CdS and CdSe, because the S^{2-} and Se^{2-} anions are more susceptible to oxidation than water, and are degraded.

Third, most of the above materials absorb in the UV region, corresponding to a few percent of solar emission, rather than in the visible (about a half). Various approaches for extending absorption and obtaining visible-light-driven water splitting,

considered one of the “Holy Grails” of chemistry, have been explored.^{12–14}

(i) Forming a donor level (DL) above the valence band by doping a conventional wide band-gap photocatalyst, such as TiO_2 , with traces of a different element. This reduces the band gap without affecting the CB level. The material becomes sensitive to visible light with an absorption coefficient dependent on the density of dopants. This method is largely employed, although the dopants also function as electron-hole recombination sites and, due to the discrete nature of the impurity levels created in the forbidden band, not necessarily favor the migration of photogenerated holes. Notice, however, that one may include in this category the addition of a large fraction of a different material as long as the crystal lattice remains unchanged, e.g. mixed Ti–M (M = V, Mo, Nb, W) metal oxides have been prepared and have shown activity under visible-light illumination.¹⁶ Notice, however, that the alternative view has been expressed that band-gap narrowing has a minimal role in the extended activity of such materials. This has rather been attributed to oxygen vacancies in the lattice that trap electrons and/or to F-type color centers.¹⁷

(ii) Using a different stoichiometric compound, such as (oxy)nitrides and oxysulfides, since its band structure arises from atomic orbitals [N(2p) and S(3p)] which lie at a lower (less positive) potential than that of the O(2p) orbitals (compare TiO_2 and Ta_3N_5 in Fig. 5). Accordingly, a new valence band is introduced in the place of that arising from pure O(2p) atomic orbitals, allowing hole migration at a potential <3 eV possible. This is important for the evolution of molecular oxygen that involves transfer of 4 electrons. Likewise, cations such as Pb^{2+} , Bi^{3+} , Ag^+ , or Sn^{2+} , which contain s electrons, enhance the top of the valence band and lead to visible-light activity.

(iii) Controlling the band structure by preparing a solid solution. The new levels must fit the potential for the reduction/oxidation of H_2O and have the suitable catalytic properties. As an example, a solid solution between Y_2WO_6 and Bi_2WO_6 formed BiYWO_6 (BYW) that acts as a photocatalyst for overall water splitting under visible light (with a cocatalyst, e.g. RuO_2). Bi(6s) and Y(4d) orbitals contribute to new VB and CB, respectively, and the band gap is 2.71 eV (BYW absorbs up to 470 nm and works satisfactorily upon 420 nm irradiation).¹⁸

A fourth point is the efficiency of the electron transfer process. This is the main stumbling block in the way towards a satisfactory system for water splitting. Actually the overall energy conversion efficiency never exceeds 0.1%, which stays in marked contrast with the conversion of solar light into electrical energy in photovoltaic cells, as well as in photoelectrochemical cells. In these cells such a limitation is overcome through the application of a small potential leading to a greater efficiency (e.g. 18%).¹⁹ Looking for a solution, cocatalysts such as Pt and NiO have been loaded on the surface for introducing active sites for hydrogen evolution. The Pt– TiO_2 system can be understood as a photoelectrochemical cell, where a TiO_2 semiconductor electrode and a platinum-metal counterelectrode are brought into contact. Well-dispersed metal particles act as mini-photocathodes, trapping electrons that reduce water to hydrogen.

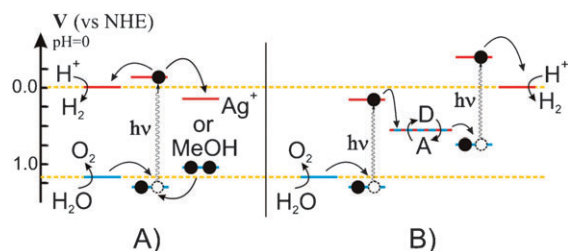


Fig. 6 Photocatalytic water splitting: (A) in the presence of sacrificial reagents, and (B) via a two-photon mechanism.

A different approach is using ‘sacrificial’ reagents that substitute water in one of the two processes involved in photohydrolysis, either the reducing or the oxidative one. Thus, a donor such as methanol is oxidized at the VB in preference to water (Fig. 6A) and this facilitates water reduction at the CB. Correspondingly, silver cations are reduced at the CB and this promotes water oxidation by VB holes.

In this case, photocatalysis actually transfers chemical energy from one compound to another one, rather than converting solar into chemical energy. However, a sacrificial reagent makes e^-/h^+ transfer much faster, controls the recombination process and causes an efficiency increase by a factor of 100 or more. This has been taken as an indication that catalytic systems for water splitting as presently evolved would perform adequately if back-electron transfer is controlled, a condition that can be obtained by imposing the proper spatial arrangement and chemical environment, analogously to natural photosystems. Indeed, in complex assemblies imposing the vectorial movement of charges, recombination is minimized.^{19,20}

Another approach is using two-photon systems, mimicking the characteristic Z-scheme of photosynthesis.²¹ Thus, an electron donor/acceptor (D/A) shuttle is added to two photocatalytic sites (see Fig. 6B). On the H_2 evolution photocatalyst site, D is oxidized to A by h^+ and this is reduced back to D at the O_2 evolution site, while holes oxidize water to O_2 . However, at the H_2 evolution photocatalyst, reduction of H^+ to H_2 and oxidation of D to A may cease when the concentration of A becomes high enough that reduction of A to D (a thermodynamically favored reaction) competes. Likewise, the rate of O_2 evolution over the other photocatalyst may decrease when backward oxidation of D to A becomes competitive. A thoughtful choice of the photocatalytic components and a fine tuning of conditions are required.

Suitable shuttles are the iodate/iodide (IO_3^-/I^-) and ferric/ferrous (Fe^{3+}/Fe^{2+}) redox pairs. Good results have been obtained by using Pt-ATaO₂N (A = Ca, Ba) and Pt-WO₃ for H_2 and O_2 evolution, respectively, and the iodate/iodide electron shuttle, with a spectral sensitivity extended to 660 nm (with Ba).^{21,22}

Finally, a convenient water splitting device requires that H_2 and O_2 are separated. Interestingly, a two-compartment Plexiglas cell has been developed where the two gases are separately produced. The device worked at the same rate for more than 30 runs (*ca.* 180 h of work),²³ although only under UV irradiation (efficiency = 2.1%; $\lambda > 300$ nm).

3. Photocatalysis in synthesis

As hinted above (see Fig. 3), the high energy of the electronically excited catalyst C^* comes useful also in (green) synthesis, in this case for overcoming a high activation energy under mild conditions. The ‘cold’ activation of reagent **R** allows a better control of the intermediates generated and thus in principle better yield and better selectivity. Thus, this method has been mostly applied to the activation of unreactive compounds, where a high E_a would otherwise demand harsh conditions. Typical examples are bringing to reaction stable compounds such as alkanes or carrying out oxidation processes by using molecular oxygen. A few examples below give an idea of the applications.

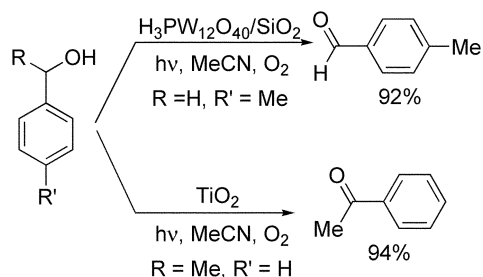
3.1 Photooxidation and oxygenation reactions

Upon photocatalysis, benzylic and allylic alcohols give carbonyl derivatives by using O_2 rather than inorganic oxidants based on noxious metals, improving both economic and environmental aspects. TiO_2 (anatase) was found suitable for the oxidation of 1-phenylethanol in dry acetonitrile (Scheme 2, lower part) under a slow stream of oxygen.²⁴ The rate-determining step involves the combination of radical ions $ROH^{\bullet+}$ and $O_2^{\bullet-}$ on the catalyst surface.

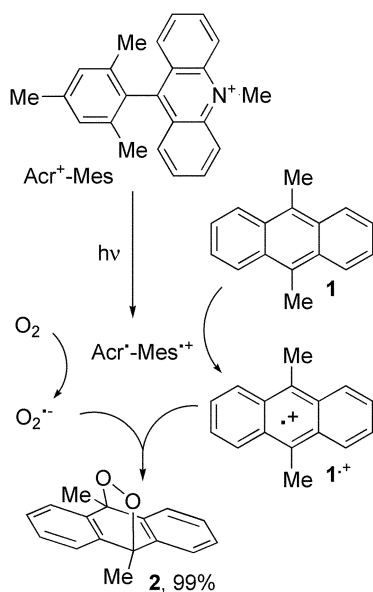
A similar selective procedure for primary and secondary benzylic alcohols has been reported by using polyoxometalates (POMs). Silica-encapsulated $H_3PW_{12}O_{40}$ was adopted as a recyclable heterogeneous photocatalyst (Scheme 2, upper part).²⁵ The activation involved hydrogen abstraction by the excited catalyst that was re-oxidized by oxygen and was recycled and reused with no decrease of the activity after several runs.

Photocatalyzed oxygenations by addition of superoxide to the reagent radical cation have been reported, as in the synthesis of the endoperoxides of polycyclic aromatics under visible light with bichromophoric 9-mesityl-10-methyl-acridinium ion (Acr^+-Mes , 10 mol%) as the photocatalyst in O_2 -saturated MeCN (see Scheme 3). The photocatalyst mimics the charge separation of semiconductors since photoexcitation causes intramolecular ET to $Acr^+-Mes^{\bullet+}$ that in turn undergoes two intermolecular ET reactions involving the 9,10-dimethylantracene (**1**)/ $Mes^{\bullet+}$ and the O_2/Acr^{\bullet} moieties. Finally, dimethylepidioxanthracene (**2**) is formed in a quantitative yield by coupling radical cation $1^{\bullet+}$ with superoxide.²⁶

Another application is the mild oxidation of sulfides to sulfoxides that, apart from the synthetic significance, is relevant for the desulfurization of fossil fuels, a demanding



Scheme 2 Photocatalyzed oxidation of benzylic alcohols.

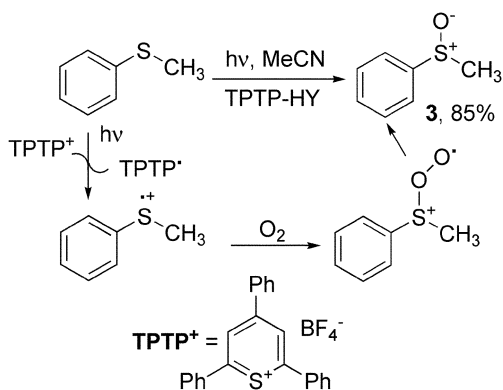


Scheme 3 Photocatalyzed formation of a peroxide by using oxygen.

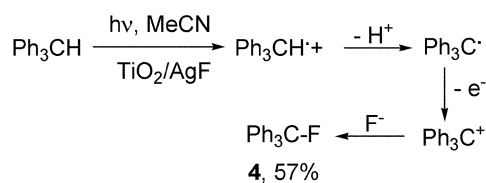
technological problem. Alkylaryl and diaryl sulfides were cleanly oxidized by using as the photocatalyst 2,4,6-triphenylthiopyrylium salt (TPTP) encapsulated within a HY zeolite through a ship-in-the-bottle synthesis.²⁷ As an example, Scheme 4 reports the oxidation of thioanisole to sulfoxide (**3**) in 85% yield upon irradiation by blue light (as a model for solar light). The catalyst TPTP-HY is not significantly degraded and is easily recovered by filtration, allowing reuse with no loss of activity, contrary to what happens with soluble TPTP. Organic catalysts encapsulated, or at any rate tethered, to a solid support are quite convenient and maintain the versatility of organic molecules, while eliminating the photolability of most of such compounds. Materials as robust as semiconductor photocatalysts are obtained.

3.2 Further oxidative functionalizations leading to C–X and C–N bonds

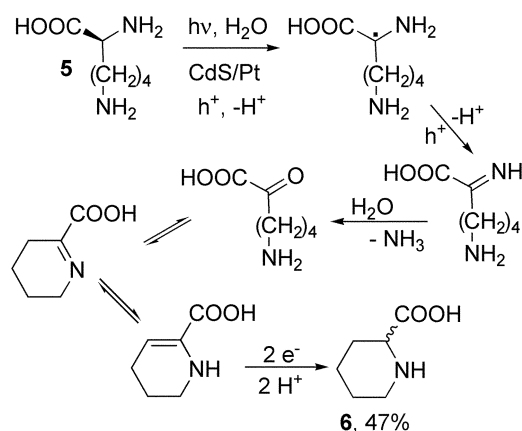
Titanium dioxide is a powerful oxidation photocatalyst, capable of oxidizing even hydrocarbons. This feature has been exploited for substituting a C–F for a C–H bond at benzylic positions by irradiation under argon in the presence of AgF as the fluorinating agent at room temperature. The photocatalytic



Scheme 4 TPTP-HY photocatalyzed oxidation of thioanisole.



Scheme 5 Fluorination of triphenylmethane.



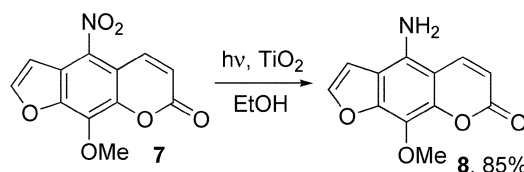
Scheme 6 Oxidative cyclization of L-lysine.

method employs safe, easy-to-handle reagents and avoids the use of elemental fluorine or of highly reactive derivatives usually required.²⁸ Oxidation to the radical cation and deprotonation give the benzyl radical that, after further oxidation to the cation, adds fluoride. Product **4** is formed in 57% yield from triphenylmethane (see Scheme 5).

CdS photocatalysis of L-lysine (**5**) gave a low yield of piperidine-2-carboxylic acid (**6**) via a photocatalyzed deamino-*N*-cyclization (Scheme 6), along with extensive racemization of the starting compound.²⁹ Loading the catalyst with a small amount (<0.3 wt%) of Pt or PtO₂, however, increased the conversion by about 2.5 times, while maintaining the stereochemistry of the unreacted amino acid. The metal induced a spatial separation of the surface sites for oxidation (CdS) and reduction (Pt).

3.3 Photoreduction

The photoinduced reduction of organic compounds on semiconductor particles is less common and only a few reactions of this type have been reported. The reduction of aromatic and aliphatic nitro compounds to the corresponding amines is one of the best examples. Thus, when a suspension of titanium dioxide (anatase, 5.0 g/L) in ethanol containing 5-nitro-8-methoxypsoralen (**7**) is irradiated under nitrogen, 5-amino-8-methoxypsoralen (**8**) is formed in 85% yield (see Scheme 7).³⁰



Scheme 7 Photocatalyzed reduction of a nitromethoxypsoralen.

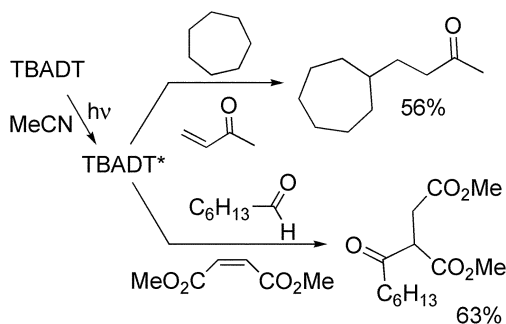
The nitro derivative undergoes overall six-electron reduction through a series of ET, protonation, and dehydration steps, with concomitant formation of acetaldehyde (from EtOH oxidation). The photocatalyst could be recovered by filtration and reused with no loss of efficiency. Since the nitro compounds absorb light competitively with the catalyst, the reduction yields increase when the concentration of the nitro compound decreases. Furthermore, the selective reduction of polynitro derivatives was achieved by exploiting the different E_{red} of the nitro compounds involved. Accordingly, 1,4-dinitrobenzene (-0.17 eV) is quantitatively reduced to *p*-nitroaniline (-0.35 eV) avoiding a further reduction step.

3.4 Formation of C–C bonds

Alkyl and acyl radicals are usually generated starting from alkyl halides or, respectively, acyl selenides. Such reactions mostly utilize as chain carriers tin derivatives (*e.g.* Bu_3SnH), which are toxic and not easily removed from the end products. Photocatalysis makes possible the direct (and selective) activation of C–H bonds. Indeed, it has been demonstrated that the simplest organic molecule, methane, can be activated by silica, alumina, and silica-alumina photocatalysis under UV irradiation and converted to higher alkanes (with the last catalyst 60% ethane formed up to 5.9% conversion).³¹

Photocatalysis gives preparatively useful results in the alkylation of electrophilic alkenes by activating R–H and RCO–H bonds under mild conditions, thus skipping the preliminary conversion into the more reactive derivatives R–X and RCO–X and the use of a chain transfer agent that are required in the corresponding thermal processes. Thus, polyoxotungstate salts (*e.g.* tetrabutylammonium decatungstate, TBADT, 2×10^{-3} M) have been used as photocatalysts in the radical conjugate addition of electron-poor olefins (0.1 M) by cycloalkanes (Scheme 8, upper part).^{32,33} TBADT was active for at least 50 cycles and was easily separated.

Thus, 4-cycloheptyl-2-butanone was prepared in 56% yield from 3-buten-2-one and cycloheptane.³² Hydrogen abstraction from aldehydes likewise smoothly occurred and the acylation of α,β -unsaturated nitriles, ketones and esters was again successful. Noteworthy, equimolar amounts of aldehyde and olefin were used, in contrast to thermal methods where a large excess of aldehyde is required (see Scheme 8, lower part). Moreover, the reaction could be carried out at a low temperature (*e.g.* < -50 °C), thus preventing the decarbonylation of the intermediate acyl radicals that competes or predominates in



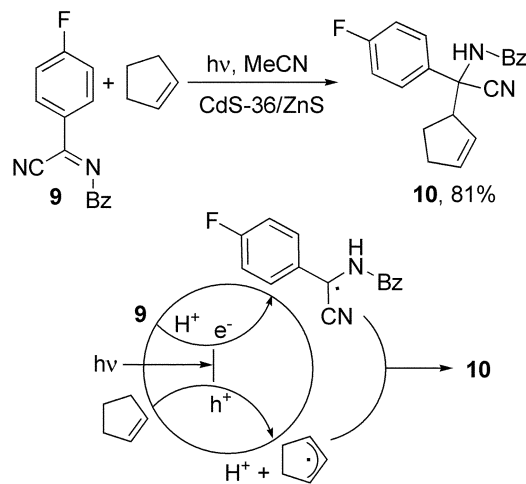
Scheme 8 Alkylation and acylation of electrophilic alkenes.

thermal reactions. This made acylation successful also with α -substituted aldehydes.³³

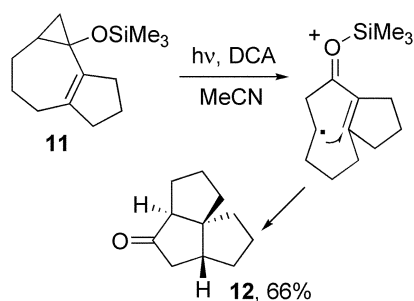
The benzylation of electron-poor olefins was likewise reported under TiO_2 photocatalysis. In this case, a benzyl silane $\text{ArCH}_2\text{SiMe}_3$ acts as a fragmentable donor whereas the olefin (*e.g.* maleic anhydride) has the double role of electron acceptor and radical trap. Oxidation of the silane at the semiconductor surface and desilylation generates benzyl radicals that are trapped by the olefin.⁶ The reaction was conveniently carried out under solar light irradiation on the gram scale (*ca.* 3 g of isolated product per batch, 10 h exposure, 0.2 m^2 exposed surface) in Almeria, Spain.³⁴ This synthesis satisfies the green chemistry criteria since both solvent and semiconductor were easily recovered and reused, and negligible amounts of by-products were formed.

A different strategy for the formation of a C–C bond by photocatalysis is the coupling of radicals.⁶ A chemoselective heterocoupling of radicals is the photocatalyzed alkylation of some phenylcyano-*N*-benzoylimines (*e.g.* **9**) by using cycloalkenes and CdS supported on ZnS (Scheme 9).³⁵ This addition involves the concomitant reduction of the imine and oxidation of the cycloalkene at the catalyst surface, proton exchange and coupling to give adduct **10** (81%). Notice that when silica-supported CdS was used, a dark reaction occurred causing the hydrocyanation of the imine, a thermal reaction eliminated by supporting on ZnS.

As seen above, semiconductors also play a predominant role in synthetic photocatalysis. However, dissolved organic molecules can be a good choice. Cyanoarenes are robust photocatalysts, strong oxidants and are used in many photoinduced electron transfer (PET) syntheses due to their high reduction potential in the (singlet) excited state, although the short lifetime of such states requires a large reagent concentration.⁶ Thus, some cyclic cyclopropyl silyl ethers bearing an olefinic or acetylenic side chain give polycyclic (bis- to tetra-cyclic) products.³⁶ The initial oxidation gives a β -carbonyl radical cation that undergoes nucleophile-assisted desilylation. Polycyclic compounds are formed *via* cyclopropane ring opening and radical addition with well defined stereochemistry at the ring juncture. An example is shown in Scheme 10, with the dicyanoanthracene (DCA) photocatalyzed



Scheme 9 Coupling between imines and alkenes.



Scheme 10 Formation of tricyclic ketone **12**.

reaction of 2-trimethylsilyloxy-tricyclo[6.3.0.0^{2,4}]undec-1(8)-ene (**11**) in MeCN to form the tricyclic ketone **12** (66% yield).

The final step of the reaction is either hydrogen transfer from the solvent (acetonitrile) or a stepwise electron transfer/protonation reaction involving traces of moisture present in solution. The experimentally determined stereoselectivity of the products was compared with the predictions from quantum chemical calculations.³⁶

Another appealing application of PET in synthesis is the extension of the Diels–Alder reaction to diene/dienophile pairs having similar HOMO and LUMO energies.⁶ The reaction relies on the Umpolung of either the diene or the dienophile when oxidized to the corresponding radical cations; these intermediates act as the electron-poor educts in the usual 4 + 2 cycloaddition.

4. Photocatalytic depollution

A further main application of photocatalysis, and the one to which this name is most often referred, is the recovery of water of industrial, agricultural or civil origin, as well as the decontamination of atmosphere and soil,³⁷ through the mineralization of the pollutants, or at least their transformation into non-toxic compounds. Here the ecological advantage is apparent since remediation does not make recourse to the stoichiometric addition of chemicals, potentially themselves polluting, but is obtained by irradiation (solar irradiation is a possible choice)⁷ in the presence of oxygen. Degradation is carried out both under homogeneous and heterogeneous³⁷ conditions (see Fig. 4), but solid semiconductors are more extensively used, because they are cheaper, more robust and easily recovered and reused than soluble photocatalysts.

4.1 Heterogeneous photocatalysis

In this application, titanium dioxide and its modifications with extended activity spectrum are used.

The fast recombination of the photogenerated electron-hole pairs limits redox processes to compounds that are adsorbed on the photocatalyst surface. In a dilute, air-equilibrated aqueous solution, the main processes thus involve water and oxygen, respectively. Scavenging of photogenerated holes (see Fig. 7, path *a*) gives hydroxyl radicals, the most active species in the photodegradation process, and that of photogenerated electrons gives the superoxide anion (path *b*). Protonation yields the hydroperoxide radical (*c*) that is further reduced to hydroperoxide anion (*d*) and hydrogen peroxide (*e*). Pollutants strongly adsorbed on the catalyst surface may

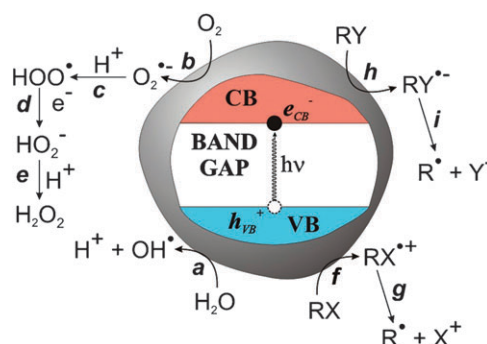


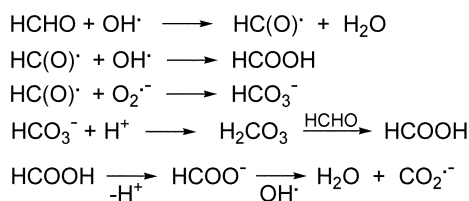
Fig. 7 Photocatalysis for pollutants elimination: chemical paths.

undergo ET, either oxidation to give a radical cation (*f*) or reduction to a radical anion (*h*), according to their redox potential, and fragmentation processes may ensue (*g*, *i*).

The largest part of the OH• radicals formed do not migrate in the bulk of the solution and react with the close-lying molecules. The active species are thus often indicated as $\{>Ti^{IV}OH^{\bullet+}\}$ and $\{>Ti^{III}OH\}$, the surface-trapped VB hole and CB electrons, respectively, which react as the free species.³⁸ Notice that the density of such centers depends on the crystal parameters. An example is a study where pure and mixed phase TiO₂ samples were prepared by sol-gel techniques under systematically varied conditions and characterized for the morphology, shape and dimensions of the crystals. It resulted that charged centers were present in a greater number in rutile crystalline rods *ca.* 15 × 100 nm than in crystals with different morphology, dimension or shape and it was possible to correlate the structure with the observed activity.¹¹

In this application, photocatalysis is regarded as one of the advanced oxidation treatments (AOTs), along with other methods likewise based on the generation of OH• radicals, such as H₂O₂/hν and O₃/hν. Several groups of organic compounds are not liable to biological treatment. Physical methods are often adopted in such a case, *viz.* adsorption on active charcoal or, for volatile organic compounds (VOCs), air stripping. Such methods simply transfer pollutants from one phase to another, in contrast to photocatalytic mineralization (compare the oxidation of heptane to CO₂ and H₂O in Fig. 3, although the actual mechanism with TiO₂ is different, see Fig. 7). Photocatalysis is more effective than traditional chemical oxidations, such as chlorination, and is often coupled with a biological treatment for optimal wastewater recovery. The general application of photocatalysis is due to the uniformly high (mostly 10⁶ to 10⁹ mol⁻¹ s⁻¹) rate of reaction of OH• radicals with organic materials.

Since most of the chemistry occurs on the surface, the removal rate of a given compound under photocatalyzed conditions depends on the coverage of the semiconductor surface (which can be evaluated in dark experiments), resulting initially in an apparent first-order law for the degradation when the contaminant starting concentration is low ($\ll 1 \times 10^{-3}$ M) and in an apparent zero order when this is higher ($> 5 \times 10^{-3}$ M). The initial degradation rate law is rarely valid up to complete degradation, due to the stepwise nature of the process and to the variety of intermediates subsequently involved.



Scheme 11 Chemical paths in the photodegradation of formaldehyde.

The many classes of organic compounds to which photocatalysis has been applied are listed in several reviews^{37,39} and the mechanism for the photooxidative degradation of many organic pollutants over titanium dioxide has been studied in depth and extensively reviewed.³⁹ Although the end result may be mineralization, the reaction involves several subsequent intermediates. The structure of such intermediates has been investigated for several systems although the support supplied for the attribution is often limited. The identification of these intermediates is important because some of them may be more persistent and possibly toxic themselves. A few examples will give an idea of the chemistry occurring. The photogenerated hydroxyl radical abstracts H from aliphatic compounds, adds to the ring with aromatic compounds, or undergoes ET from oxidizable moieties, such as the carboxylate anion. Thus, H abstraction is the key step with formaldehyde (see Scheme 11, notice that in contrast direct UV irradiation of CH₂O produces toxic CO).⁴⁰

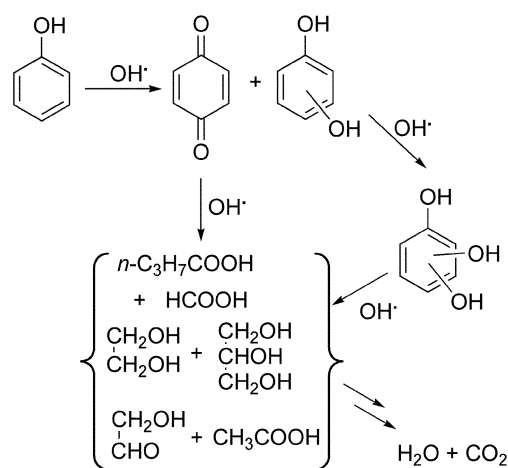
With aliphatic acids both H-abstraction from the chain and hole transfer to the carboxylate group occur initially, the latter causing decarboxylation; the thus formed radicals further react with the photocatalyst, other intermediates and oxygen.⁴¹ The degradation of benzenepolycarboxylic acids proceeds up to complete mineralization *via* oxidative decarboxylation and ring hydroxylation.⁴²

An example of the titania-assisted photodegradation of aromatics is the mineralization of phenol with *p*-benzoquinone, hydroxylated aromatic compounds and aliphatic compounds as intermediates (Scheme 12).⁴³ Hydroquinone and catechol accumulate, consistent with initial *ortho-para* attack by OH[•] radicals. Indeed, the photodegradation rate for *o*-substituted phenols correlates with the stability of the σ adducts with the OH[•] radical.

In other cases a reductive path is followed, as in the case of polyhalogenated derivatives, where electron transfer leads to dehalogenation, as apparent from the experiments in the absence of oxygen (see Scheme 13).⁴⁴ These compounds can be degraded by using visible-light in the presence of a ruthenium complex that sensitizes TiO₂.⁴⁵

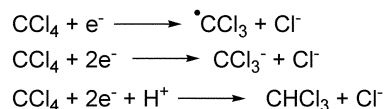
The case of herbicide fenitrothion is shown in Scheme 14. Different reactive moieties are present and participate to the reaction, with initial oxidative desulfurization and cleavage of the thiophosphate moiety and stepwise degradation of the thus formed nitrophenol down to mineralization.⁴⁶

As mentioned, TiO₂ photocatalysis has a broad application. However, the rate of reaction varies over a large span and a few compounds, in particular highly-stabilized, electron-poor heteroaromatics, *e.g.* cyanuric acid, are persistent under these conditions. A general relation between structure and overall

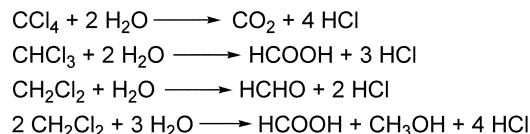


Scheme 12 Photocatalytic degradation of phenol.

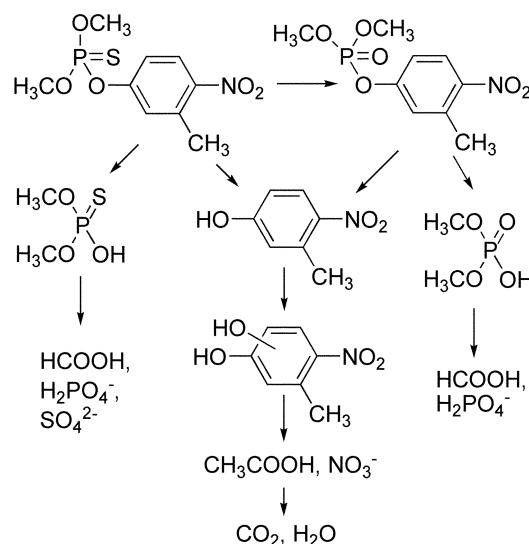
in the absence of oxygen



overall process



Scheme 13 Photodegradation of chloromethanes.



Scheme 14 Photodegradation of fenitrothion.

rate of degradation is difficult to establish, because the compound structure affects not only the chemical reaction rate, but also other phenomena, *e.g.* the adsorption on the photocatalyst surface that, contrary to chemical reactivity, is generally increased by electron withdrawing groups. A further effect involves temperature, an increase of which enhances the recombination rate of charge carriers as well as the

desorption processes, both effects resulting in a decrease of photocatalytic activity.³⁷

Various modifications that enhance the photodegradation efficiency have been devised. Thus, in the presence of fluorides more free OH• radicals are formed, reasonably because fluoride substitutes hydroxyl groups on the catalyst surface,⁴⁷ so that the efficiency increases and even cyanuric acid is decomposed. Platinization has a synergic effect with fluorination (Pt nanoparticles act as an electron sink) and may lead to a very large increase of the activity, particularly when adopting a sulfated pre-treatment during the sol-gel preparation of the catalyst (a higher Pt dispersion is produced).⁴⁸ Likewise, electron acceptors such as hydrogen peroxide, bromate and persulfate both increase formation of OH• radicals and inhibit (e⁻/h⁺) recombination.⁴⁹ The use of TiO₂-SiO₂ binary oxides has a great potential in the removal of VOCs and the activity depends on the structure, proposed to result from an increase of charge recombination caused by crystallite defects.⁵⁰

The application has been extended to other phases. Thus, some organic pollutants remain on the soil surface and the possibility of their photodegradation by adding a heterogeneous photocatalyst has been tested. In fact, solar irradiation in the presence of TiO₂, in some cases modified, leads to the degradation of recalcitrant pesticides such as Diuron, DDT and γ -hexachlorocyclohexane⁵¹ as well as spent motor oil.

As for the gas phase, heterogeneous photocatalysis has shown to be effective for the elimination of pollutants. As an example, nanosized nitrogen-containing TiO₂-based materials with anatase-type structure gave interesting results for the degradation of alkenes as models of the VOCs present in urban atmospheres.⁵² In the absence of moisture, the photocatalytic degradation of some chemicals (e.g. toluene, formaldehyde) is seriously retarded and the total mineralization to CO₂ does not take place. However, too large an amount of water vapor on the catalyst surface causes a decrease of the reaction rate since water molecules displace the low concentration VOCs from the active sites.⁵³

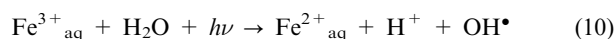
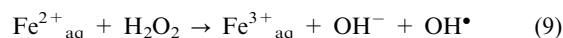
4.2 Homogeneous photocatalysis

Despite the advantages of heterogeneous photocatalysis, homogeneous systems should not be underestimated and it is possible that in the future organic dyes may play a greater role.⁵⁴ Dyes show intensive bands not only in the UVA but also in the visible range. However, their use is not free from limitations, such as their difficult recovery after the reaction, their photolability and their possible toxicity. Probably for these reasons, homogeneous catalysis is now in the preliminary stage of application, although explorative and mechanistic studies have been carried out. For practical applications, a logic step forward is heterogenization by adsorbing the dye onto a solid support, as indicated above.

Apart from generating singlet oxygen (*via* a physical sensitization, falling outside the scope of the present discussion), dyes oxidize pollutants *via* ET. An example is TPP (compare Section 1) that absorbs efficiently up to 450 nm and acts as a strong oxidant in the excited state. The thus

generated pyranil radical is re-oxidized to TPP (on a relatively slow time-scale) in the presence of oxygen, which is the ultimate electron sink. Pyrylium salts have been tested in the homogeneous phase as solar photocatalysts and found to be rather promising, *e.g.* several phenolic pollutants have been eliminated under these conditions.⁵⁴

Another important (and inexpensive) method is the photo-Fenton reaction (H₂O₂/Fe salts/*h* ν)⁵⁵ that generates effectively OH• radicals. The actual mechanism is more complex than that indicated by the minimal scheme of eqns (9) and (10). Various complexes (ligands are OH⁻, H₂O, HO₂⁻, carboxylates, *etc.*) and hydroxides of iron ions are involved in the cyclic process.



The Fe³⁺ complexes exhibit quite intensive ligand-to-metal charge transfer bands that extend into the visible region (up to 580 nm), making this method well suited for solar irradiation and more effective than the TiO₂/UV and H₂O₂/UV systems. Upscaling the experiment gave results even more satisfactory, due to more efficient light absorption. Furthermore, tests based on the photo-Fenton reaction and solar irradiation have been carried out at different latitudes, with different reactor types and waste waters of different origin and gave satisfactory results even with highly polluted water. This method will probably find increasing application, provided that some points are improved, such as avoiding the need for separating the iron cations after the treatment (*e.g.* adopting immobilization) and extending the useful pH range towards neutrality, since the reaction presently occurs under acidic conditions.⁵⁵

4.3 Practical applications

Photocatalysis has progressed from explorative research to commercial exploitation. A look to the recent literature reveals a steadily flux of more than 1300 international patents per year in this field for various applications from 2000 on (compared to a few tenths before 1990), most of which were concerned with pollution control and were based on the use of TiO₂.

With regard to water recovery, both semiconductor-based and homogeneous (photo-Fenton) photocatalytic methods have shown great promise, as mentioned above. However, the actual use in large scale water purification plants requires that several critical issues are confronted and overcome. These include the stability of the photocatalytic system, the possibility of recovering and reusing the catalyst⁵⁶ and the appropriate reactor design. The last issue is obviously determining for arriving at an economically acceptable scale up. The efficient illumination of the photocatalyst surface and an efficient mass transfer within the reactor have been the subject of experimental studies and simulations.⁵⁷ These suggested indeed that an elaborated design of the photoreactor is required. Using a slurry of photocatalyst, as usually done in explorative studies, is not the best choice for large scale application, because separation after the treatment is technically difficult and expensive and furthermore this makes it difficult to obtain a uniform illumination, although the latter

limitation can be overcome by an appropriate reactor design. Thus, both fluidized bed reactors where the catalyst is supported on beads that are circulated in the solution and the use of immobilized catalysts have been considered, obtaining an important advancement in the efficiency, but the problem remains of having a convenient and inexpensive light source. A pilot plant experiment has shown that the use of solar light is a viable possibility (by using either P25 titania and an oxidant or the photo-Fenton reaction), although the limitation due to the variable flux seems difficult to overcome.⁵⁵

More advanced is the application to the removal of gas phase pollutants. In view of the limited amount of pollutants involved, photocatalysis appears to be well suited in this case, and is capable of obtaining effective air purification at room temperature. Air pollutants mainly include nitrogen oxides (NO_x), carbon oxides (CO and CO₂), VOCs, such as aromatics, aldehydes, halocarbons, and particulates, and are often present at a higher concentration indoors, due to the release from cooking stoves, electrical appliances and other sources.⁵³ Given the toxicity of such compounds, a method for their degradation is important. Air-cleaning reactors are available for industrial and household application and photocatalytic filter elements, usually containing activated carbon for trapping pollutants that are then mineralized by photooxidation.

Air purification can also be obtained, at least up to a certain extent, at an illuminated surface coated with a semiconductor and this principle has been implemented for a variety of commercial applications, both indoor and outdoor. Probably everybody is familiar with self-cleaning surfaces, such as external walls or windows that are largely advertised.⁵⁸ Thus, coatings, cementitious materials, paints and tiles have been developed and commercialized that destroy atmospheric pollutants such as nitrogen oxides (NO_x) and organic pollutants.⁵⁹ The dirt-repellent effect arises from two actions by the photocatalysis, destroying small amounts of pollutants and making the surface exposed to the environmental agents hydrophilic, so that water forms a thin layer rather than droplets and contaminants are more easily washed away. A number of applications to surfaces that remain clean after being exposed for months to polluted urban air has been demonstrated, including automobile body, the glass cover of street lamps (even in tunnels), polymers (e.g. in tents) and textiles.

Once again the physical state of the titania used is determining and the use of nanoparticles has been shown to be advantageous. Composite materials have been devised for multifunctional action, e.g. covering titania with an apatite layer favors adsorption of contaminants on that inert material and thus allows a prolonged action of the photocatalyst.⁶⁰ The porosity of the titania layer greatly affects the penetration of the chemicals and can be modified by the addition of different materials, e.g. calcium carbonate.⁵⁹

Photooxidation also brings about effective bactericidal and anti-fungal action. This principle has been applied to disinfection of bacteria-contaminated water⁶¹ as well as to self-sterilizing materials, e.g. for operating rooms. Photoactive tiles covering walls, ceiling and floor are able to kill bacteria and viruses.⁶²

Applications of photocatalysis are not limited to organic molecules and are indeed extended to inorganic compounds, e.g. for the recovery of metals and the synthesis of metal nanoparticles.⁶³

5. Conclusions and outlook

The variety of reactions reported above, a limited choice from a very large number, are all based on the generation by light of a highly reactive species C* (see Scheme 1), such as a molecular excited state or charge pair in a semiconductor. In turn, these species are able to activate a reagent by some chemical process that occurs under mild conditions, which would otherwise require a harsh procedure. The following course of the process regenerates C, which thus is a non-consumed catalyst. The large amount of energy of the absorbed photon (see Fig. 3) makes C* able to catalyze unusual paths and to generate high energy intermediates. This principle lends itself nicely to such different targets as converting solar energy into storable chemical energy and catalyzing chemical reactions in synthesis and eliminating pollution. Considering the different fields, one notices that the extremely important photocatalytic water splitting has encountered serious problems that have been only partially overcome and, at the moment, does not compete with photovoltaics or photoelectrochemistry as a means for exploiting solar energy. Synthetic applications are limited at the moment, but some classes of useful reactions are emerging. The photodegradation of pollutants has been more largely developed and its practical significance demonstrated.

In all of these applications, photocatalysis can be considered as one of the most innovative methods in green chemistry. Although the research towards the different targets has developed separately and has reached different levels, the understanding of the common base of these processes should help further development by sharing the knowledge acquired under different conditions.

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