We are IntechOpen,
the world's leading publisher of
Open Access books
Built by scientists, for scientists

4,800

Open access books available

122,000

International authors and editors

135M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities

CLARIVATE ANALYTICS

BOOK CITATION INDEX

INDEXED

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

Semiconductors in Organic Photosynthesis

Cristian Gambarotti, Lucio Melone
and Carlo Punta
*Department of Chemistry, Materials and Chemical Engineering "Giulio Natta",
Politecnico di Milano
Italy*

1. Introduction

It is commonly accepted that "Organic Synthesis" was born in 1828, when the german chemist Friedrich Wöhler succeeded to make urea from simple materials (Friedrich, 1828). After only few years, Becquerel reported the first example of photo-induced electrochemical reaction (Becquerel 1839). In his work, he found that a voltage and an electric current were obtained by illuminating a silver chloride electrode immersed in an electrolyte solution and connected to a counter electrode. But the world had to wait until 1955, when Brattain and Garret, working on germanium semiconductor electrodes, well understood the origin of that strange photovoltaic phenomenon (Brattain & Garret, 1955). The modern "Photo-electrochemistry" era was born.

However, the year was 1900 when it appeared the first article onto the use of light to promote an organic reaction (Albini & Fagnoni, 2008; Ciamician & Silber 1900). Ciamician and his colleague Silber carried out the first systematic studies on the behaviour of organic substances in the presence of sunlight, thus, nowadays they are regarded as the fathers of modern Organic Photochemistry.

Nowadays, if we open SciFinder Scholar client and we write the word "Synthesis" in the "Research topic" field, almost 10 millions of references will be shown. This means that in the last two centuries more than 50000 papers per year onto the argument have been published. Moreover, we are considering only an average value, whereas it is well known that the number of publications has known an exponential-type growth in the last decades. However, only 70000 references are reported for "Photocatalysis", indicating how relatively young is this research field, although the first paper was published more than a century ago.

The question is: why in the last two-three decades the use of light in chemistry has aroused a such worldwide attention? The answer could be summarized mainly in one word: environment.

A great impetus to the development of photocatalysis is derived from the growing demand to reduce the environmental pollution (air and ground). This has led to the development of several photo-induced protocols for the oxidative degradation of organic pollutants, in which semiconductors play a key role in the reaction mechanism, focusing the attention onto the photodegradation of water and air pollutants.

2. Semiconductors

It was 1782 when Alessandro Volta used for the first time the term "semiconducting". One century later, in 1883, Michael Faraday documented the first observation of a semiconductor effect. Faraday noted that the electrical resistance of silver sulphide decreased with increasing temperature, showing a behaviour opposite to that of metals (Łukasiak & Jakubowski, 2010).

Nowadays, everywhere we look, we can certainly see articles that contain semiconductors. The modern microelectronics applications are based on semiconductor technologies. Moreover, building materials, health care products, materials for special applications and much more, often employ semiconductors due to their chemical and physical properties. It is sufficient to write "semiconductor applications" into any internet search engine to get many tens of millions of responses.

2.1 Electrical behavior of semiconductors

By definition, a semiconductor is characterized by the absence of a continuum between the states (as for metals) but shows a band structure. The filled levels, called "valence band" (VB), are an energetically closely spaced array of orbitals composed by the valence electrons of the material. A similar, higher energetic, spaced array is formed by the unoccupied orbitals and it is called "conduction band" (CB). The gap existing between the top edge of VB (E_c) and the lower edge of CB (E_c) is called "band-gap" (Chattopadhyay & Rakshit, 2010).

2.1.1 Intrinsic semiconductors

Pristine semiconductors are generally called "intrinsic semiconductors". In an intrinsic semiconductor (IS) the Fermi-level (E_F), which can be the highest occupied energy level at T = 0 K, lies near the middle of the band-gap and the corresponding Fermi-Dirac distribution $f(E)$ is plotted in Fig. 1. At T = 0 K the probability of an electron to occupy a state in the CB is zero and the VB is totally full (see the thick black line). At room temperature (blue sigmoid curve) some electrons can jump into the CB and fill the states closed to the bottom of the CB. In this case the tail of $f(E)$ is extended into the CB, thus, there is a probability to have electrons there. In this condition an equal number of holes exists close to the top of VB. E_F is now the energy level at which the probability of occupancy is half and it lies near the middle of the band-gap.

2.1.2 Extrinsic semiconductors

The *ad hoc* introduction (doping) of impurities into the semiconductor lattice allow to modulate its electrical properties: these doped semiconductors are generally called "extrinsic semiconductors". Extrinsic semiconductors with a larger electron concentration than hole concentration are known as "*n*-type" semiconductors, whereas those with a larger hole concentration than electron concentration are known as "*p*-type" semiconductors. The energy band diagrams for *n*-type and *p*-type semiconductors are given in Fig. 1. In the figure, E_A and E_D represent respectively the energy level of the acceptor and the donor specie. Assuming a complete ionization of the donor atom at a given temperature, we see that the free electrons coming from the donor atoms fill the state close to the bottom of the CB. Thus, it is more difficult for the electrons in the VB to cross the band-gap only by thermal agitation. Therefore, the number of holes in the VB decreases. This means that, if we

consider E_F as the energy for which the occupancy probability is 0.5, E_F must move closer to the CB for a *n*-type semiconductor (Fig. 1 scheme on the right). Similarly, E_F must move closer to the VB for a *p*-type semiconductor (Fig. 1 scheme on the left). In the extreme cases, in which the doping level is very high, the Fermi levels move into the CB for *n*-type semiconductor and into the VB for *p*-type semiconductor.
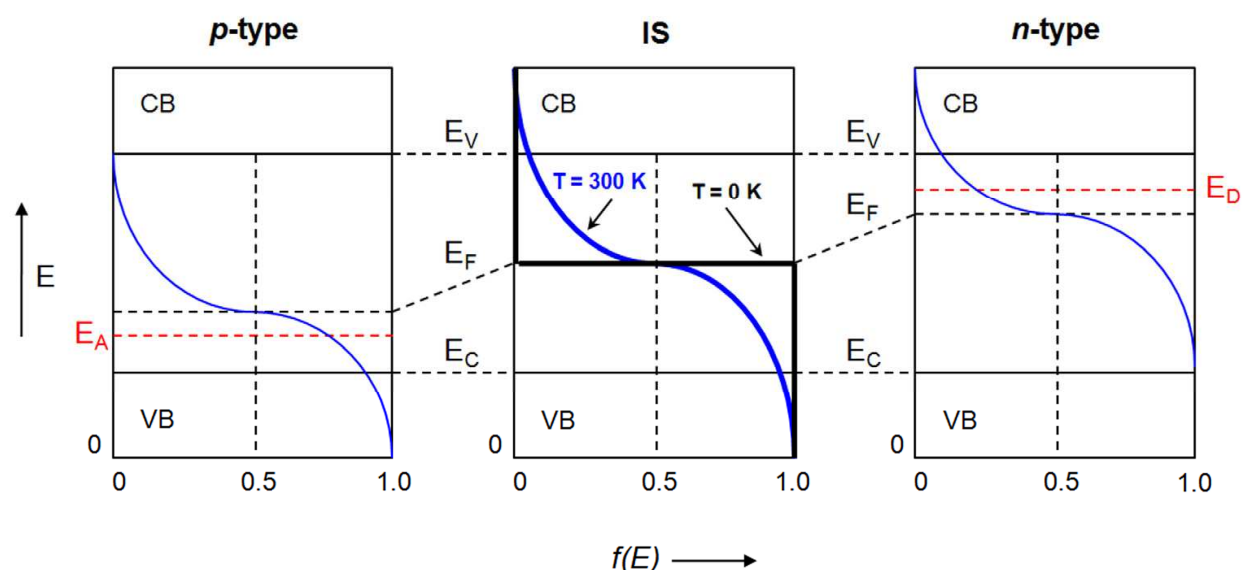

Fig. 1. Energy diagram and Fermi distribution function *f(E)* for semiconductors

2.2 Electrical properties of illuminated *n*-type semiconductors

The application of several *n*-type semiconductors on photocatalysis has experienced an exponential growth in the last 20 years (Fox & Dulay, 1993; Hashimoto et al., 2005; Hoffmann et al., 1995; Maldotti et al., 2002a). Let we consider now the influence of photo-irradiation onto *n*-type semiconductor properties (Fox, 2001).

When a semiconductor surface is brought into contact with an electrolyte containing a redox couple, interfacial electron transfer can transpire, to equilibrate the solution phase potential and the energy levels of the bulk semiconductor. As electron exchange takes place across the interface, equilibration with the solution occurs and the bulk E_F moves to the solution-phase equilibrium potential, whereas the band-edge positions at the surface remain fixed at their original values (Fig. 2). Thus, in moving inward from the semiconductor-electrolyte
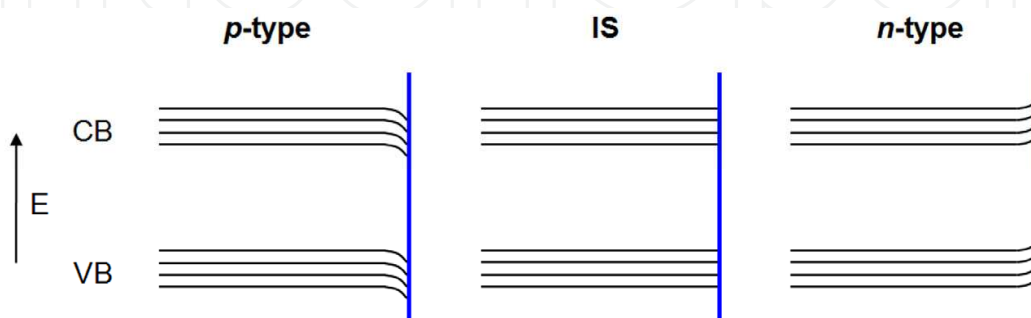

Fig. 2. Band bending into *n*-type and *p*-type semiconductors. The vertical lines represent semiconductor / solution interface.

interface, the bands bend. Charge injection in this region of bent bands forces electrons to move in the opposite direction from holes: in a *n*-type semiconductor, electrons move away from the surface and toward the bulk of the semiconductor while the holes move toward the surface. Thus, band bending assists in improving the efficiency of photoinduced charge separation. As a result of band bending, the surface of an irradiated *n*-type semiconductor becomes electron-deficient and acts as a photoanode toward an oxidizable adsorbate.

2.3 Redox reactions onto irradiated *n*-type semiconductors

When a semiconductor surface is irradiated by light of an energy higher than the band-gap, a band to band transition takes place. An electron (e⁻) moves from the filled VB to the empty CB, leaving an electron hole (h⁺) in the VB (Fig. 3).
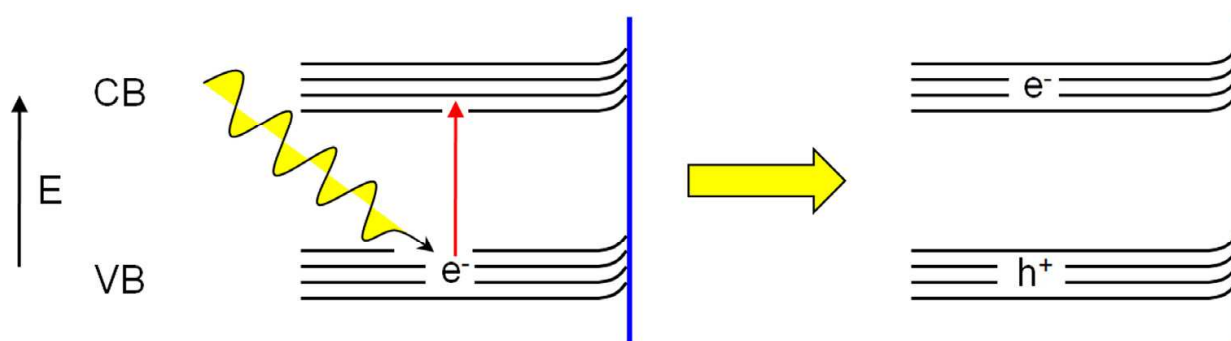

Fig. 3. Photo-irradiation of a semiconductor particle

Depending on their own band-gap, for each semiconductor exists a minimum light frequency to promote the electron jump. Thus, the absorption of a photon induces a charge separation, generating a highly energetic electron and creating a lower-energy vacancy in the valence band. This intermediate species is called "electron-hole pair". In this excited state, the recombination of the electron-hole pair, due to back electron transfer, is of course strongly thermodynamically favored. But, because of the absence of states in the semiconductor band-gap, quantum restrictions slow recombination by back electron transfer and the lifetime of the photogenerated electron-hole pair is sufficiently long to allow charge trapping. Thus, the life time of VB hole, in principle, can be enough long to act as an anode, whereas, similarly, the CB can act as cathode. As a consequence, the excited semiconductor is able to promote redox reactions on substrates that may be present on its surface or in solution. In *n*-type semiconductors, the surface becomes electron-deficient and acts as an oxidative site toward oxidizable organic substrates. If an adsorbed substrate has an appropriate redox potential, it can trap one of the charge carriers faster than the electron-hole recombination and photoinduced chemistry will be observed. As represented in Fig. 4, the e⁻ promoted in the CB is transferred to the adsorbed acceptor (A) and the VB hole is filled by an e⁻ coming from the adsorbed donor species (D). The rate of the electron-transfer processes compete with spontaneous back electron transfer of the electron-hole pair.

If the trapping of both VB hole and CB e⁻ are faster than the spontaneous back electron transfer, singly oxidized and reduced intermediates are formed on the photocatalyst surface. Because these adsorbed species are free to move along the surface, novel chemistry is likely to ensue. This is a unique characteristic of photochemical catalysts, that are able to promote oxidations and reductions on the same surface.
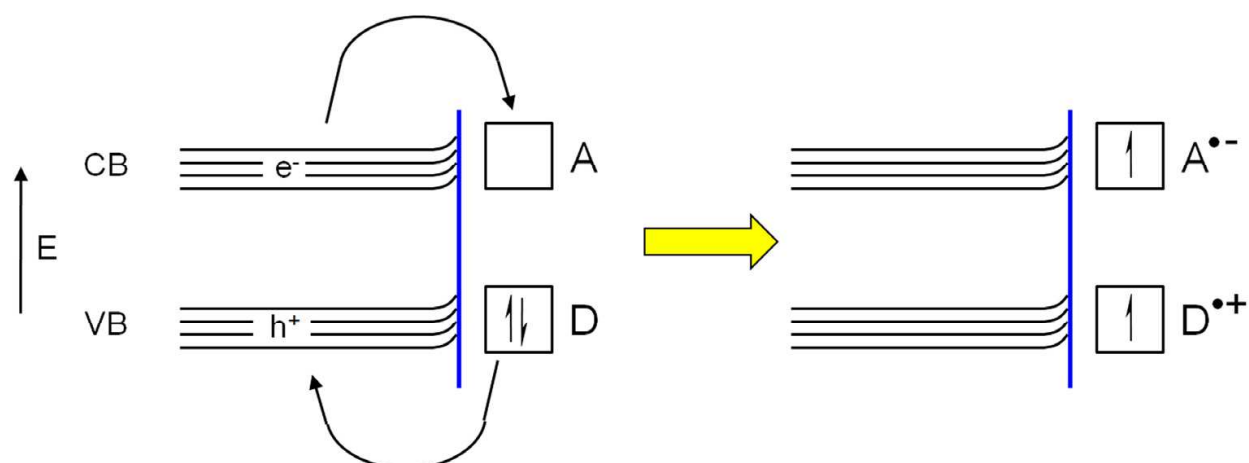
Fig. 4. Interfacial electron transfer on semiconductor surface

For practical applications, because the simultaneous presence of cathodic and anodic site onto the same particle, the semiconductor photocatalyst can be considered as a "short circuit" electrochemical cell, when prepared by deposition island of an inert metal onto its surface (Fig. 5) (Bard, 1979).
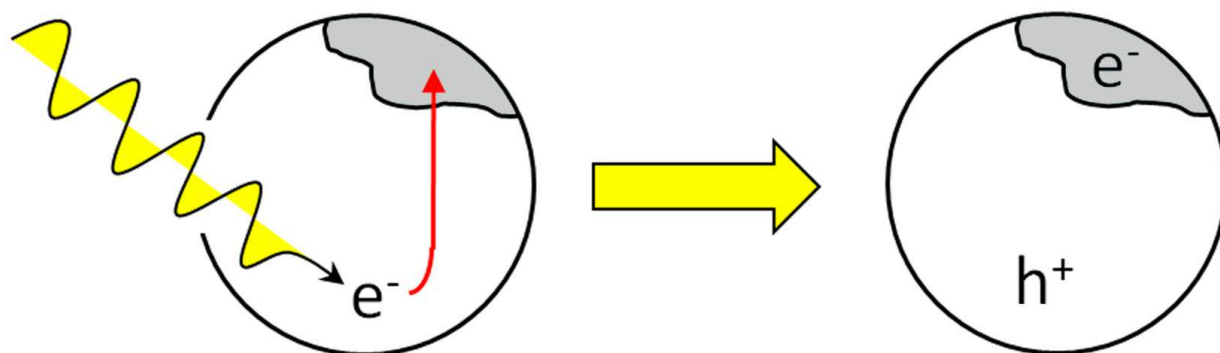

Fig. 5. Irradiation of metalized semiconductor particle

These metalized particles bear regions for both photoactivated oxidation of organic substrates adsorbed at the semiconductor-electrolyte interface and collection of the photogenerated electrons on the metal island. Thus, as in a electrochemical cell, these metalized powders include sites for photoinduced oxidation and reduction, analogous to the working anode and cathode. On platinized TiO_2 powders, however, no external current flow accompanies these transformations.

Anyway, even pristine wide band-gap semiconductors often show photoactivity if the two redox sites can be separated; metalized semiconductors are essential to promote some redox processes, such as selective hydrogenations of alkenes and alkynes (Fox, 2001).

3. Applications of *n*-type semiconductors

In the last decades photocatalytic processes induced by semiconductors have attracted the great interest, due to their low environmental impact. Nowadays, many *n*-type semiconductors are studied and applied in several application fields, such as energy production, smart-materials technology, environment depollution, chemical synthesis,

whereas *p*-type semiconductors are rarely used because of their limited presence in nature and their usually too small band-gap (Palmisano et al., 2007a; Mills & Lee, 2002; Mills & Le Hunte, 1997). Certainly, the most studied and widely used is the titanium dioxide (TiO_2), which can be considered the "king" of the photocatalysts.

3.1 TiO$_2$: King of the photocatalysts

Between the various semiconductors applied in photocatalysis, certainly TiO_2 is the most used. The reasons for its widespread are due to its high environmental tolerance, large commercially availability and low price.

Its history began just in the late 60th dacades when Fujishima and Honda began to study the photoelectrolysis of water. The first paper, published in 1972, brought the world aware of its photo-catalytic potential (Fujishima & Honda, 1972). This important observation promoted extensive works focused on the solar energy conversion for the production of hydrogen from water. Moreover, it soon became apparent that novel redox reactions of organic and inorganic substrates could also be induced by band-gap irradiation of a variety of semiconductor particles, of sizes ranging from clusters and colloids to powders and large single crystals.

TiO_2 is present in the three common allotropic forms: anatase, rutile and brookite: anatase and rutile belong to thetragonal crystal system, while brookite belongs to orthorhombic system (Linsebigler et al., 1995). Anatase and rutile are the two principal catalytic forms. Commercially available anatase is typically less than 50nm in size. These particles have a band-gap of 3.2 eV, corresponding to a UV wavelength of 385 nm. The adsorptive affinity of anatase for organic compounds is higher than that of rutile, and anatase exhibits lower rates of recombination in comparison to rutile due to its 10-fold greater rate of hole trapping. In contrast, though some exceptions exist, the thermodynamically stable rutile phase generally exists as particles larger than 200 nm. Rutile has a smaller band-gap of 3.0 eV with excitation wavelengths that extend into the visible at 410 nm. Nevertheless, anatase is generally regarded as the more photochemically active phase of titania, presumably due to the combined effect of lower rates of recombination and higher surface adsorptive capacity.

In the last decade, Gray and co-workers reported the enhanced photoactivity in the mixed-phase (anatase and rutile) Degussa P25 TiO_2 (Deanna et al., 2003). This fact is explained by the presence of small rutile crystallites, which creates a structure where rapid electron transfer from rutile to lower energy anatase lattice trapping sites under visible illumination, leads to a more stable charge separation. Transfer of the photogenerated electron to anatase lattice trapping sites allows holes that would have been lost to recombination to reach the surface. Subsequent electron-transfer moves the electron from anatase trapping sites to surface trapping sites, further separating the electron/hole pair. By competing with recombination, the stabilization of charge separation activates the catalyst and the rutile-originating hole can participate in oxidative chemistry. Three main factors are employed in this increase in the photoactivity: (1) the smaller band-gap of rutile extends the useful range of photoactivity into the visible region; (2) the stabilization of charge separation by electron transfer from rutile to anatase slows recombination; (3) the small size of the rutile crystallites facilitates this transfer, making catalytic hot spots at the rutile/anatase interface. This process depends critically on the interface between the TiO_2 phases and particle size. The atypically small size of the rutile particles in this formulation, and the intimate contact with anatase that the comparable size allows, are crucial to enhancing the catalyst activity.

3.2 Applications of TiO₂

Nowadays, due to its most photoactivity, highest stability, low cost and non-toxicity, TiO_2 is most probably the only photocatalyst suitable for heavy industrial applications (Hashimoto et al., 2005; Ravelli et al., 2011). In the last 30 years various research groups have developed several photocatalityc processes in which it plays a key role as catalyst. Generally those applications regard the photo-induced redox reactions of adsorbed substances, the photo-induced hydrophilic and/or hydrophobic behaviour of TiO_2 itself and the use as white pigment from ancient times (Anpo & Kamat, 2010; Ohama & Gemert, 2011).

3.2.1 Water splitting

Water reduction to H_2 and oxidation to O_2 requires that the bottom of the conduction band lies at a more negative potential than $E°_{red}(H^+/H_2)$, 0 V, and the top of the valence band at a more positive value than $E°_{ox}$ (H_2O/O_2), 1.23 V. The two-electron process from one mol of H_2O to give one mol of H_2 and half mol of O_2 is termodinamically unfavored, $DG° = 237$ kJ/mol = 2.46 eV. Thus, the minimum energy required to drive the reaction corresponds to that of two photons of 1.23 eV, corresponding to l ca. 1000 nm, in the near infrared region. However, to overpass the activation barrier, higher photon energy is required in order to promote water splitting at a reasonable rate. Water splitting for hydrogen production aroused a great interest during the second oil crisis, in the 1970s. In this period Fujishima and Honda reported the possibility to easily obtain H_2 and O_2 using sunlight as energy source (Fig. 6) (Hashimoto et al., 2005).
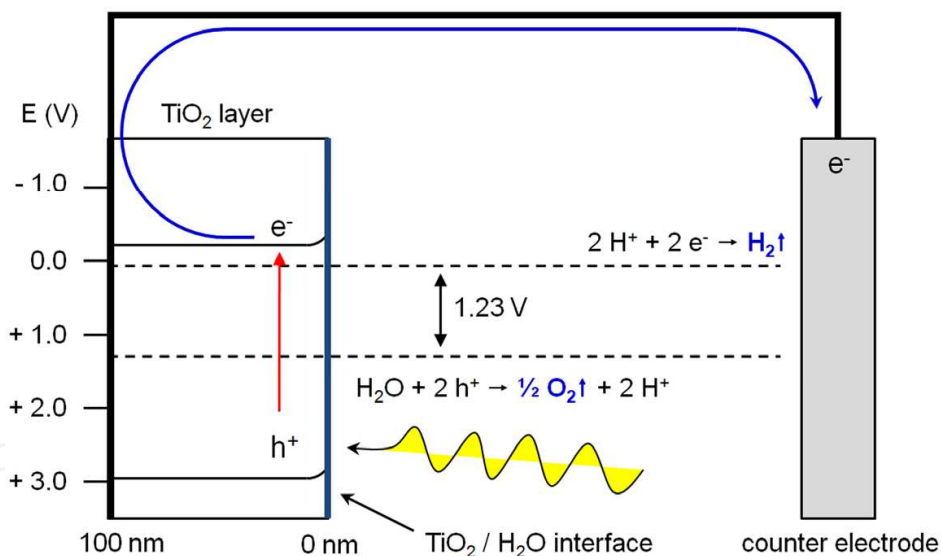

Fig. 6. Schematic representation of water splitting process at pH = 1

Then, photocatalysis drew the attention of many researchers as one of the promising methods for hydrogen production. However, despite the high reaction efficiency, TiO_2 can adsorb only the UV light present in a solar spectrum. This means that only about 3% of solar light was effective on the reaction and, in few years, from the productive technological point view, TiO_2 photocatalysis lost its initial actractive. Thus, in the last 20 years, many efforts have been made in order to improve the photocatalytic performance of TiO_2 by different approaches, such as doping/mixing with several other metals and semiconductors, like Pt, Cr, Ce, Ag, CdS, CdSe, use of zeolites and nanostructured TiO_2 nano-arrays, and more (Balzani et al., 2008; Esswein & Nocera, 2007; Li et al., 2010; Maeda & Domen, 2007; Zhang et al., 2010).

3.2.2 Photodegradation of pollutants

During the same period, Frank and Bard applied TiO_2 photocatalysis in the destruction of pollutants (Frank & Bard, 1997). Their preliminary studies on the oxidation of cyanide to cyanate, by using four different forms of TiO_2 under xenon lamp, opened the way for the photodegradation of environmental pollutants.

In the last three decades, TiO_2 powders have known wide applications into the recovery of water of industrial, agricultural or civil origin, as well as the decontamination of atmosphere and soil, through the mineralization of the pollutants, or at least their transformation into non-toxic compounds (Fox & Dulay, 1993; Gaya & Abdullaha, 2008; Hoffmann et al., 1995; Ravelli et al., 2011). Of course, the great advantage of these photocatalytic systems depends on the fact that they do not need the use of stoichiometric quantities of chemicals, potentially themselves polluting, but they act under light (often sunlight represents the best choice) in the presence of oxygen (Malato et al., 2007).

Moreover, the high band-gap value of TiO_2 allow to oxidize various organic substrates, such as hydrocarbons and their derivatives to lower molecular weight ozidized species and CO_2, volatile organic compounds (VOCs) and nitrogen oxides (NO_x) present in urban atmosphere (Carp et al., 2004).

3.2.3 Anti-bacterial materials

Photocatalytic decomposition reactions can be applied to the destruction of bacteria. Escherichia coli (*E. Coli*) cells are completely destroyed in one week under 1 mW/cm^2 UV irradiation on TiO_2 (Evans & Sheel, 2007; Fu et al., 2005; Liu et al., 2008; Sunada et al., 1998). Usually, an analogous anti-bacteria effect can be achieved in nearly 1 h under outdoor UV light intensity. However, the typical indoor UV light intensity is in the order of mW/cm^2, thus the photocatalytic disinfection under indoor conditions require too long time to be considered useful from the practical point of view. The antibacterial function of TiO_2 is strongly enhanced, even with weak UV intensity, using a fluorescent lamp assisted by the presence of Ag or Cu (Sunada et al., 2003). TiO_2 photoactivity reaction assists the intrusion of the copper ions into the cell, which is probably the cause of the destruction of the *E. Coli* colonies even under very weak UV light.

Actually several nanostructured TiO_2 derivatives are studied and applied as germicidal species, especially on the treatment of water contaminated with pathogenic micro-organisms presenting a potential hazard to animals and human beings (Mccullagh et al., 2007; Skorb et al., 2008).

3.2.4 Wettability of TiO_2 and self-cleaning materials

During '90s, Fujishima and Heller independently reported the potential utilization of TiO_2 in the development of self-cleaning ceramic materials (Heller, 1995; Watanabe et al., 1992). In these works, thin films of organic contaminants were photocatalytically oxidized on TiO_2-coated surfaces. The typical oxidation-rate, evaluated in 1-5 picometers per day was sufficient to maintain clean the surface then in the case of low flux of contaminants. Typically several hundred mW/cm^2 of UV light are available in the day-time and from the outdoor shade, which corresponds to about 1000 photons/cm^2 per second. This is, of course, a very small quantity of energy, but very high if compared to the number of molecules adsorbed on the surface. This suggested the potential applications in the self-cleaning material technology. One of the first commercially applications was the self-cleaning glass-cover for tunnel light. The largely used high pressure sodium lamps show an UV emission of about 3 mW/cm^2, enough to keep efficient the photo-oxidative self-cleaning process.

Nowadays, various self-cleaning materials are used in commercial applications and intense researches are aimed to improve these materials (Parkin & Palgrave, 2005).

During the studies on the self-cleaning surfaces, it was found a marked change in the water wettability of the TiO_2 surface before and after UV light irradiation (Wuang et al., 1997). During the UV light exposition the contact angle of TiO_2 coated surface showed a strong decrease from typically initial several tens of degrees (depending on the surface roughness) to nearly 0° (Sakai et al., 2003; White et al., 2003; Zubkov et al., 2005). This discover widened the commercial applications of TiO_2 coated materials. The limitations of the self-cleaning efficiency, due to the low quantity of UV-light present in sunlight spectrum and outdoor shade, were resolved. The stains adsorbed onto TiO_2 surface can be easily washed only by using water, because water is adsorbed between stain and the highly hydrophilic TiO_2 surface. Moreover, even if the quantity of light is too low to decompose the stains, the surface is maintained clean by supplying water. Thus, outdoor coated surfaces can be kept clean by rainwater. Such called "Photocatalytic Building Materials" have found use in outdoor application, for example, an exterior glass of 20000 m^2 was installed in the terminal of Chubu International Airport in 2005.

The same UV-induced high hydrophilic behaviour of TiO_2 coated surface has been applied in the development of anti-fogging treatment (Gan et al., 2007; Tricoli et al., 2009). Drops are formed when there is low affinity between water and the surface; on a highly hydrophilic surface, no water drops are formed but a uniform liquid thin film.

3.3 Applications of other semiconductors

Despite the widespread use TiO_2 in many applications, the relatively high cost of the photoactive anatase has proved to be uneconomical for large-scale water treatment operations. Thus, several other ways for the photocatalytic degradation of pollutants have been explored (Chatterjee & Dasgupta, 2005; Mills & Le Hunte, 1997).

Because of their narrower band-gaps, metal calcogenides, such as CdS, ZnO and CdSe, show good sensitivities toward incident light in the visible spectrum. However, these narrower band-gap, make the semiconductor suitable of the photo-corrosion process, which can be partly suppressed by the addition of sulfide and sulfite to the contacting solution.

Because of its similar band-gap (3.2 eV), ZnO photocatalytic capacity should be comparable to that of TiO_2. Due to its high light absorption in the region between 300 and 400 nm, ZnO is found to be as reactive as TiO_2 toward the degradation of phenol (Dindar & Içli, 2001). However, as previously reported, photo-corrosion phenomenon can occurs under UV light, and this is one of the main reasons for the decrease of ZnO photocatalytic activity in aqueous solutions. Recently, ZnO nanoparticles have been reported as better photocatalysts in degrading common organic contaminants as compared to bulk ZnO and commercial TiO_2 Degussa P25 (Hariharan, 2006).

Similarly to ZnO, nanostructured ZnS particles show good catalytic activity and are used in the removal of organic pollutants and toxic water pollutants (Hu, 2005).

Enhanced photocatalytic activities may result from doping semiconductors by transition metals. These techniques generally influence the optical and electronic properties of the semiconductors, and can induce a shift of the optical absorption toward the visible region (Pouretedal et al., 2009; Ullah & Dutta, 2008).

Water splitting is another important field of application of semiconductor-sensitized systems. In this area, as already reported for TiO_2, many efforts are aimed to the

development of efficient photoelectrochemical devices, in which illuminated semiconductors are the process promoter (Mills & Le Hunte, 1997).

Often, platinum group metal, deposited on the surface of the semiconductor, are used to facilitate the reduction of water by the photogenerated electrons and platinum group metal oxides are often used to mediate the oxidation of water by the photogenerated holes. Of course, in the presence of a large band-gap semiconductors (TiO_2 as example), with band-gap potential much higher than the oxygen one, there is a sufficiently large over-potential for the reaction to proceed readily without an oxygen redox catalyst.
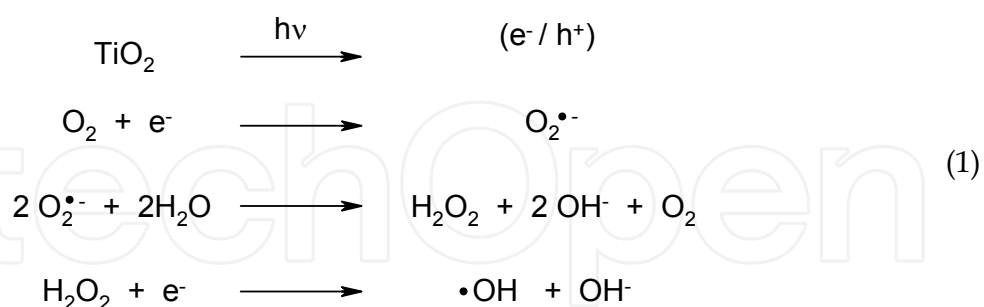
4. Photo-induced organic synthesis

Photocatalysis in organic synthesis concerns the use of light to induce chemical transformations onto organic substrates which are transparent in the wavelength range employed. Radiation is absorbed by a photocatalyst whose electronically excited states induce electron- or energy-transfer reactions able to trigger the chemical reactions of interest. Significant examples of photocatalytic processes employed for synthetic purposes are oxidation and reduction processes, isomerization reactions, C-H bond activations, and C-C and C-N bond-forming reactions. The use of solar light as a reagent in oxidative catalysis is particularly relevant to realize innovative and economically advantageous processes for the conversion of hydrocarbons into oxygenates compounds and, at the same time, to move toward a "sustainable chemistry" that has a minimal environmental impact. The main reasons are because the sunlight represents a totally renewable source of energy; the photochemical excitation requires milder conditions than thermal activation and allows one to conceive shorter reaction sequences and to minimize undesirable side reactions. Generally, an important role in the photocatalyzed processes is played by O_2. It is important to underline that the search for new catalysts capable of inducing the oxofunctionalization of hydrocarbons with this environmentally friendly and cheap reagent represents a major target from the synthetic and industrial points of view. On the basis of pure thermodynamic considerations, most organic compounds are not stable with respect to oxidation by O_2. There are, however, kinetic limitations in this process mainly imposed by the triplet ground state of the O_2 molecule, which is not consistent with the singlet states of many organic substrates. Activation of both O_2 and the organic substrate may be achieved by photochemical excitation with light of the visible or of the near-ultraviolet regions (> 300 nm). The use of heterogeneous and organized systems is a suitable way to control efficiency and selectivity of catalytic processes through the control of the microscopic environment surrounding the catalytic centre. In particular, the nature of the reaction environment may affect numerous physical and chemical functionalities of the photocatalytic system, such as the absorption of light, the generation of elementary redox intermediates, the rate of competitive chemical steps, and the adsorption-desorption equilibria of substrates, intermediates, and final products. Moreover, another fundamental role of a solid support is to make the photocatalyst more easily handled and recycled.
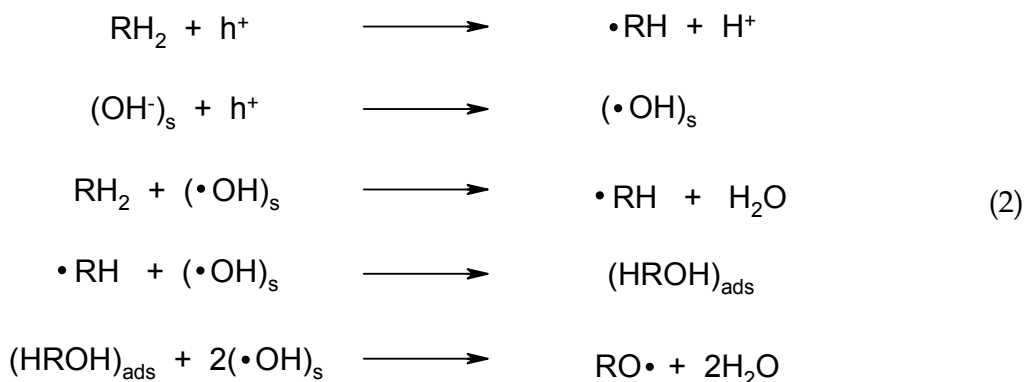
4.1 Role of O_2

In dispersed semiconductor photocatalytic processes oxygen acts as electron acceptor. On illuminated TiO_2 surfaces, in the presence of air (O_2), hydrogen peroxide and reactive

oxygen-centred radical species are formed via oxygen reduction (Karraway, 1994 & Kormann, 1988). The first step of O_2 action consists in the capture of the electron promoted in the CB by light irradiation of semiconductor surface (Eq. 1).
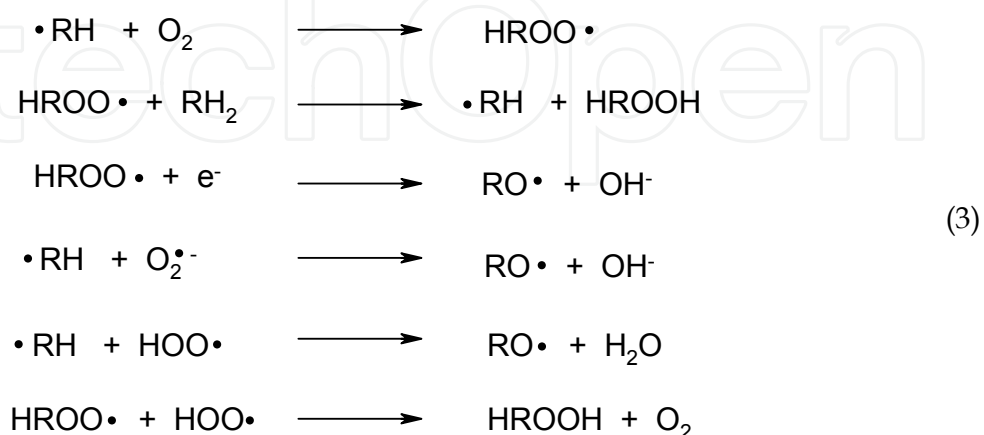
$$TiO_2 \xrightarrow{h\nu} (e^- / h^+)$$

$$O_2 + e^- \longrightarrow O_2^{\bullet -}$$

$$2\,O_2^{\bullet -} + 2H_2O \longrightarrow H_2O_2 + 2\,OH^- + O_2 \tag{1}$$

$$H_2O_2 + e^- \longrightarrow {}^{\bullet}OH + OH^-$$

The role of O_2 is not just that of scavenging the photogenerated electrons: it produces the so-called active oxygen species while the simultaneous oxidation of an organic substrate yields radical intermediates (Eq. 2).

$$RH_2 + h^+ \longrightarrow {}^{\bullet}RH + H^+$$

$$(OH^-)_s + h^+ \longrightarrow ({}^{\bullet}OH)_s$$

$$RH_2 + ({}^{\bullet}OH)_s \longrightarrow {}^{\bullet}RH + H_2O \tag{2}$$

$${}^{\bullet}RH + ({}^{\bullet}OH)_s \longrightarrow (HROH)_{ads}$$

$$(HROH)_{ads} + 2({}^{\bullet}OH)_s \longrightarrow RO^{\bullet} + 2H_2O$$

(s = surface, ads = adsorbed)

Therefore, through a Kisch type B photocatalysis mechanism, coupling reactions of oxidation and reduction intermediates lead to products of partial or total oxidation, depending on experimental conditions (Eq. 3) (Macyk & Kisch, 2001).

$${}^{\bullet}RH + O_2 \longrightarrow HROO^{\bullet}$$

$$HROO^{\bullet} + RH_2 \longrightarrow {}^{\bullet}RH + HROOH$$

$$HROO^{\bullet} + e^- \longrightarrow RO^{\bullet} + OH^-$$

$${}^{\bullet}RH + O_2^{\bullet -} \longrightarrow RO^{\bullet} + OH^- \tag{3}$$

$${}^{\bullet}RH + HOO^{\bullet} \longrightarrow RO^{\bullet} + H_2O$$

$$HROO^{\bullet} + HOO^{\bullet} \longrightarrow HROOH + O_2$$

As shown above, oxygen represents the source of highly reactive radical intermediates, which are the "engine" of the photocatalyzed reaction mechanisms.

4.2 Redox potentials of semiconductors

The relevant redox potential for some photocatalysts and H_2O are compared in Fig. 7 (Kisch, 2001; Ravelli et al., 2011). An excited photocatalyst (C*) oxidizes a substrate (S) when E(C*) is more positive than the E(S), whereas there is reduction when E(C*) is lower than E(S). For example as shown in Fig. 6, excited TiO_2, as previously reported, 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 values) (Montalti, 2006). Single crystal catalysts in aqueous systems usually shift cathodically with higher pH value by approximately 0.06 V per pH unit as reported for TiO_2 (Ward, 1983), CdS (White & Bard, 1985), and ZnS (Fan et al., 1983). In addition to this pH dependence, surface impurities, adsorbed compounds and the change to organic solvents may induce strong shift in the redox potential. In the case of CdS, the removal of traces of elemental sulphur and cadmium from the surface induces a cathodic shift of even almost 1 V! (Meissner & Memming, 1988).
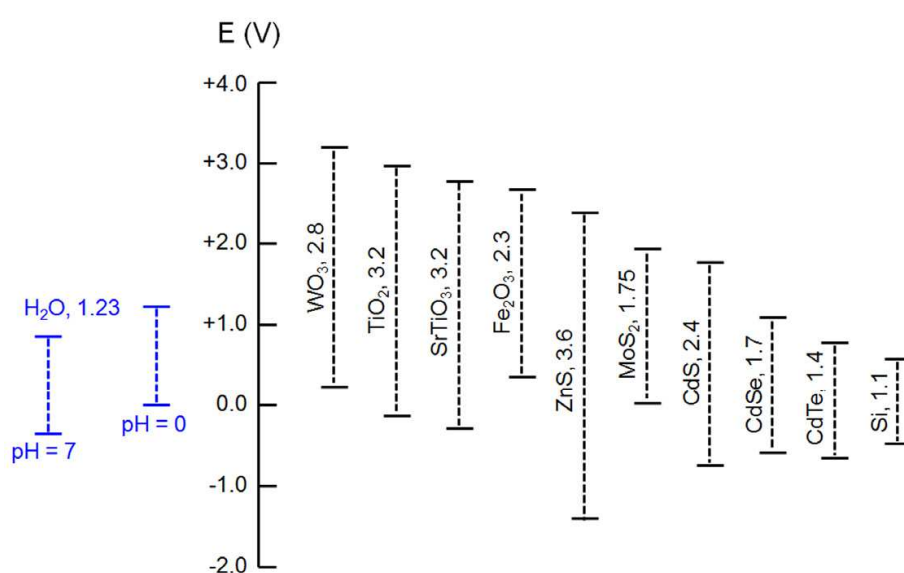
Fig. 7. Band-gap and redox potentials (*vs*. NHE) at pH = 1 vs H_2O at pH = 0 and 7

4.3 Influence of catalyst shape on photoactivity

The rate of products formation is influenced by the specific surface area of the catalyst. Typically, two opposite effects play a key role: the rate of electron-hole recombination and the concentration of adsorbed substrates (Heller et al., 1987). The recombination rate increases linearly with surface area, and accordingly the reaction rate should decrease. On the contrary, there is a linear increase on the redox process rate due to increasing concentration of adsorbed substrates, which should also increase the product formation rate. Moreover, it is expected that, depending on the nature of semiconductor and substrates, the reaction rate may increase, decrease or remain constant with increasing surface area. For example, Reber founds that in the photoreduction of H_2O, only CdS with very large (>> l00 m^2/g) or very low (< 6.7 m^2/g) specific surface areas produce hydrogen at a significant rate (Reber & Rusek, 1986).

The chemoselectivity may also depend on the surface area, usually related to the particle size. Maira and co-workers have studied the effect of particle size in the gas-phase photooxidation of toluene over TiO_2. Particles from 6 to 20 nm have show to influence the

activity and selectivity of the photocatalyst; in particular, selectivity toward benzaldehyde production increases as the particle size increases (Maira et al., 2001). These results can be explained considering that smaller particles are characterized by a larger surface area and also by a larger proportion of edges and corners which increases as size decreases. Edges and corners are expected to exhibit different catalytic and adsorption properties compared with the more planar surface sites. The involvement of $Ti^{4+}-O^-$ radicals could be the reason of the increase of selectivity to benzaldehyde as the particle size of the TiO_2 samples increases from 6 to 20 nm.

Matra has found that size can affect the acid-base properties of surface hydroxyl groups (Martra, 2000). In the Merk TiO_2 these groups are electron acceptor centres, while in Degussa P25 they present a nucleophilic character. These differences can explain the different selectivity toward benzaldehyde formation in the gas-phase photocatalytic oxidation of toluene, in particular, the lower selectivity observed with P25 is ascribed to a stronger adsorption of the aldehyde.

5. Organic synthesis in the presence of illuminated semiconductors

Although semiconductor materials like as TiO_2 have been extensively applied in the environmental field in order to mineralize organic pollutants, their application as tool for the organic synthesis has been also investigated. Recently, some reviews on this field have been published (Gambarotti, 2010; Pastori, 2009; Shiraishi, 2008; Anpo & Kamat, 2010). Herein we report some examples taken from the literature which can be used to take a view on the recent state of the art.

5.1 TiO₂ in organic photosynthesis

The selective oxidation of hydrocarbons under mild conditions is an important industrial and scientific challenge because relatively cheap feedstocks are converted into highly value-added products.

5.1.1 Synthesis of phenol derivatives

Phenol is an highly important chemical intermediate because it is used in a large number of different sectors including the production of phenolic resins, caprolactam, aniline, alkylphenols, diphenols, and salicylic acid (Weber et al., 2005). It is produced from benzene mainly through the cumene process (Hock process). Currently, in the USA and Western Europe, about 20 % of the total benzene production is consumed for the synthesis of phenol (Weissermel & Arpe, 1997). In the last years interests have aroused for the direct production of phenol from benzene, despite these proposed processes are still not effective and competitive if compared with the classic procedures (Bal et al., 2006; Guo et al., 2009; Tani et al., 2005; Tlili et al., 2009). Among them, photocatalytic processes, in particular based on the use of semiconductors, gained attention both in industriy and academy as an economically and environmentally favourable approach (Chen et al., 2009). Recently, Molinari and co-workers reported the direct benzene conversion to phenol in a hybrid photocatalytic membrane reactor (Molinari et al., 2009a). The authors used TiO_2 Degussa P25 as catalyst to promote the oxidation of benzene to phenol in water under UV irradiation (λ = 366 nm, power = 6.0 mW cm^{-2}). The particularity was the adoption of a membrane reactor having two compartments, one containing the aqueous phase, in which TiO_2 and benzene were

dispersed, and the other one containing the organic phase, consisting on benzene, whose role was to remove phenol, produced during the photocatalysis, from the aqueous phase. The membrane was a hydrophobic polypropylene porous flat sheet. The authors claimed that the system allowed the production of the phenol and its separation, although the formation of intermediate oxidation by-products, like benzoquinone, hydroquinone and other oxidized molecules was observed.

Recently Zhang et al. (Zhang et al., 2011) reported the selective photocatalytic conversion of benzene to phenol by using titanium oxide nanoparticles incorporated in hydrophobically modified mesocellular siliceous foams (MCF) as shown in Fig. 8.
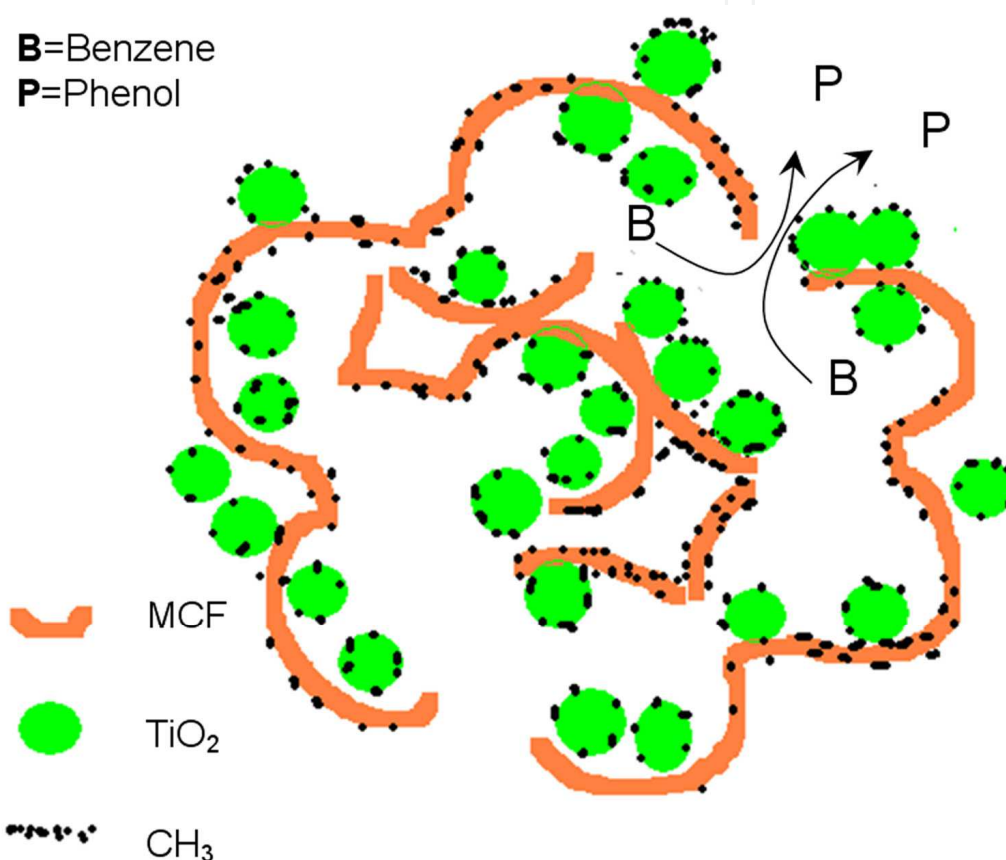
Fig. 8. Titanium oxide entrapped in the cagelike mesopores of hydrophobically modified MCF for the hydroxylation of benzene

Generally, the hydroxyl radicals generated during the photo-illumination of the TiO_2 crystals are highly reactive and unselective causing a large formation of secondary by-products. The main characteristic of this method is based on the hydrophobicity of the MCF, for that benzene is preferentially attracted into the hydrophobic mesopores while the more hydrophilic phenol is rapidly release from the cavity before it undergoes further oxidation. In this way an increase in the selectivity is obtained. In particular, the authors compared the catalytic activity of three materials (TiO_2@MCF, TiO_2@MCF/CH_3, TiO_2@MCF/CH_3/UV) with the corresponding

activity of TiO_2 in the anatase form performing the oxidation of benzene in water under 300 W Xe-arc lamp irradiation for 24 h. The catalyst indicated with $TiO_2@MCF$ consists of TiO_2 crystals incorporated in the MCF structure. Such crystals had a size of 9 nm, lower than the corresponding ones of the simply TiO_2 (16 nm). The surface area (S_{BET}) of $TiO_2@MCF$ (29.5 wt % of TiO_2) was 637 m^2g^{-1}. In order to increase the hydrophobicity of the catalyst, $TiO_2@MCF$ was treated with triethoxymethylsilane (TMS) getting the material $TiO_2@MCF/CH_3$ (TiO_2 wt %: 21.7, S_{BET}: 450 m^2g^{-1}). Finally, the methylsilyl groups grafted on the TiO_2 surface were selectively removed by post UV-irradiation treatment obtaining the catalyst $TiO_2@MCF/CH_3/UV$ (TiO_2 wt %: 23.3, S_{BET}: 491 m^2g^{-1}). The authors found that $TiO_2@MCF$ had better performances than TiO_2 with regard to both the phenol yield (Y_P, mmol phenol / g TiO_2) and the phenol selectivity (S_P, %). In particular Y_P increased from about 10 mmol/g TiO_2 for TiO_2 to about 35 mmol/g TiO_2 for $TiO_2@MCF$. Similarly an increase of S_P was observed (from 15.8 to 22.2 %). Upon silylating $TiO_2@MCF$, a reduction of the catalytic performance is experienced (Y_P is lower than the correspond value of TiO_2, while S_P remains practically similar to the value of $TiO_2@MCF$, essentially because the active TiO_2 surface sites were blocked by the methylsilyl groups in $TiO_2@MCF/CH_3$. The removal of such groups by UV irradiation allows to recover the catalytic properties. In fact $TiO_2@MCF/CH_3/UV$ gave a Y_P above 50 mmol/g TiO_2 while S_P is about 35 %.
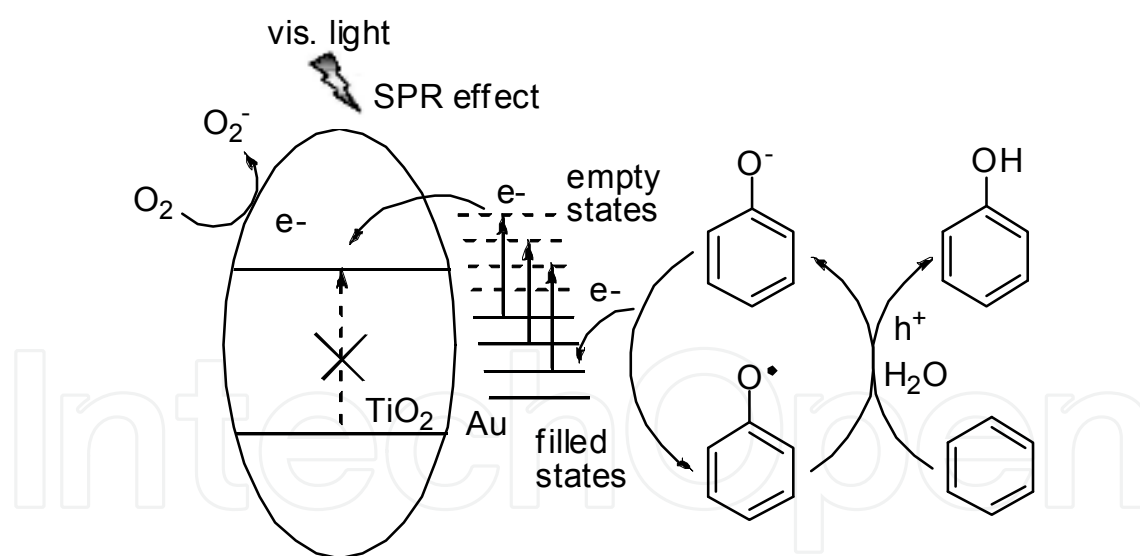

Fig. 9. Proposed mechanism for the photooxidation of benzene

The photocatalytic activity of TiO_2 can be modified by depositing noble metal nanoparticles on the particles surface. This is the case of the work of Zheng et al (Zheng et al., 2011). The authors developed a noble-metal plasmonic photocatalyst effective for the oxidation of benzene to give phenol under visible light irradiation. Three different noble metal were used: Pt, Au and Ag. Between them Au@TiO_2 microsphere having 2 wt % of Au showed the best catalytic

performance (Au > Pt >> Ag) giving high yield (above 60 %) and selectivity (about 90 %). Such results were obtained irradiating the reacting mixture (phenol (0.06 g) dissolved in 50 mL of deionized water (50 mL) with benzene (0.07 mL) and the catalyst (50 mg)) with a 300 W Xe arc lamp for a variable time (up to 5 h). No reaction was observed when metal-free TiO_2-microspheres were used because the visible light ($\lambda \geq 400$ nm) cannot excite TiO_2 (band-gap 3.2 eV). In Fig. 9 it is shown the mechanism proposed by the authors to explain the photooxidation of benzene into phenol in the presence of an initial amount of phenol under visible light irradiation. An initial concentration of phenol is of paramount importance and the higher is the concentration, the higher are the yield and the selectivity. The O_2 involved in the mechanism is the oxygen already dissolved in the reacting mixture because this was not purged with nitrogen. The visible light excites the electrons in the Au nanoparticles to move fast toward the conduction band minimum of the TiO_2 where they are withdrawn by the O_2 so reducing it. The phenoxy ions are oxidized to phenoxy free radicals through the release of electrons to the electron-depleted Au nanoparticles. The phenoxy radicals are finally involved in the oxidation of the benzene to phenol becoming phenoxy ions again. The importance of this work relies on the possibility of a modulation of the catalytic properties of the TiO_2 by depositing different noble metals on the base of the different spectral characteristic of the light and with regard to a wider class of organic substrates.
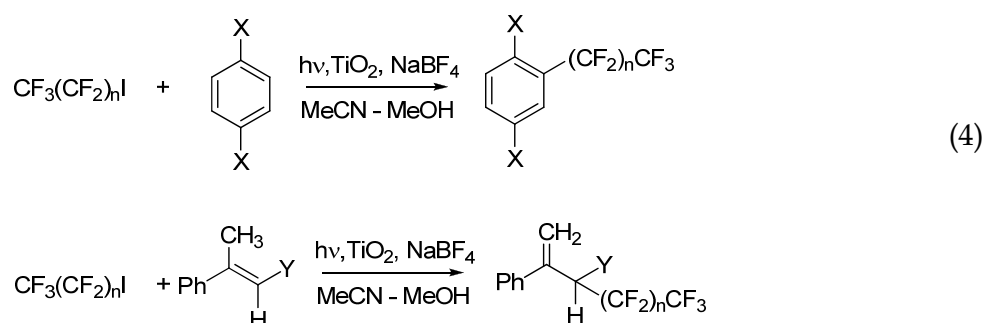
Toluene is another aromatic hydrocarbon having relevancy in the industry. It is mainly converted to benzene by catalytic dealkylation and sometimes it is used for production of xylenes by transalkylation and disproportionation (Weber et al., 2005). The oxidation of toluene with O_2 to produce benzaldehyde throughout TiO_2 photocatalytic reactions has been investigated by different authors in the last years. Recently Ouidri and Khalaf (Ouidri & Khalaf, 2009) reported the oxidation of toluene by using TiO_2-pillared montmorillonite in acetonitrile or water or mixture of them and irradiating the reaction mixture by a 125 W Hg lamp for 1 h. The authors found that reactions performed in water gave the higher yield of benzaldehyde. Furthermore, the catalyst prepared according to this protocol showed a superior catalytic activity than the Degussa P25. The authors explained this experimental evidence with the higher capacity of the TiO_2-pillared montmorillonite to adsorb toluene compared with the Degussa P25. The presence of the catalyst is mandatory for the effectiveness of the process.

A further method is described by Cao et al. (Cao et al., 2011) who prepared TiO_2 hollow spheres by the hydrothermal reaction between TiF_4 and H_2O. Such material was used in the photocatalytic oxidation of toluene to give benzaldehyde in water under irradiation with a light of 310 nm. The TiO_2 spheres had a diameter of about 1 μm as shown by the FESEM and TEM images. The S_{BET} was in the range of 6.6 – 19 m^2g^{-1} while the anatase crystals size was in the range of 31 – 56 nm depending on the reaction time adopted for the synthesis (hydrothermal time). Such crystals covered the surface of the hollow spheres exposing the {001} face. The authors found that the conversion of toluene gradually increased from 9.0 % to 21 %, when the hydrothermal time was increased from 20 min to 6 h while the selectivity was about 90 %. In particular the catalytic activity was in the following order: TiO_2-20 min < TiO_2-40 min << TiO_2-6 h < TiO_2-12 h < TiO_2-72 h. The TiO_2-72 h microspheres showed activity two times higher than the commercial Degussa P25. As this last one has a S_{BET} of 45 m^2g^{-1} (higher than 6.6 m^2g^{-1} associated to the TiO_2-72h) and the {101} facets are more developed than that of TiO_2-72 h, the difference in the reactivity could be ascribed to the wider {001} facets in TiO_2-72h. The superior catalytic activity of the {001} facets has been already documented for different reactions in particular with regard to the degradation processes of water pollutants

(Liu et al., 2010). Indeed, it has been reported that water molecules undergo spontaneous dissociative adsorption on clean anatase {001} forming hydrogen peroxide and peroxyl radicals which are then involved in the degradative process (Selloni, 2008).

### 5.1.2 Other hydrocarbon functionalizations

More complex functionalizations of aromatic hydrocarbons have also been promoted by TiO_2. For example the perfluoroalkylation of arenes and α-methylstyrene derivatives in acetonitrile using titanium oxide as photocatalyst and in presence of alcohols and $NaBF_4$ has been reported (Eq. 4, Iizuka & Yoshida, 2009). The electrons in the conduction band of TiO_2 can reduce the perfluoroalkyl iodide forming a perfluoroalkyl radical and iodide ion. The resulting radical reacts with the arene forming an arenium radical, which is successively oxidized to the corresponding arenium cation by the action of the holes providing at the end the product. Different alcohols were considered. The best performances were obtained with methanol and ethanol while 2-propanol gave lower conversions and selectivities in the desidered products. Both alcohol and $NaBF_4$ may act as modulators of the red-ox network in particular reducing the hole-electron recombination process.

$$CF_3(CF_2)_nI \ + \quad \begin{array}{c} X \\ \bigcirc \\ X \end{array} \quad \xrightarrow[\text{MeCN - MeOH}]{h\nu, TiO_2, NaBF_4} \quad \begin{array}{c} X \\ \bigcirc (CF_2)_nCF_3 \\ X \end{array} \qquad (4)$$

$$CF_3(CF_2)_nI \ + Ph \underset{H}{\overset{CH_3}{\diagup}} Y \quad \xrightarrow[\text{MeCN - MeOH}]{h\nu, TiO_2, NaBF_4} \quad Ph \underset{H}{\overset{CH_2}{\diagup}} \underset{(CF_2)_nCF_3}{Y}$$

Heterocyclic compounds have also been synthesized through the use of TiO_2. Shiraishi and co-workers investigated a one-pot synthesis of benzimidazoles by simultaneous photocatalytic and catalytic reactions on Pt@TiO$_2$ nanoparticles (Shiraishi et al., 2010). A number of *ortho*-arylenediamines were converted to their corresponding benzimidazoles by Pt@TiO$_2$ catalyzed reaction with different alcohols at 303 K for 30 min under UV irradiation (xenon lamp, 2 kW; light intensity, 18.2 Wm^{-2} at 300 – 400 nm) using, in some cases, MeCN as co-solvent. A comparison between Pt@TiO$_2$ and a commercial TiO$_2$ similar to Degussa P25 (JRC-TIO-4 TiO$_2$ from the Catalyst Society of Japan with a anatase/rutile = 8:2) was reported, showing a significant improvement in both conversions (> 99%) and yields (generally above 80 % with different cases where the yield was above 95 %) after using Pt@TiO$_2$ (Eq. 5). The UV-light excite TiO$_2$ creating e$^-$/h$^+$ pairs. The hole pairs oxidize the alcohol to the corresponding aldehyde on the surface of the TiO$_2$. The aldehyde spontaneously condense with the arylenediamine forming an imine intermediate, which undergoes cyclization furnishing a benzimidazoline. This last one is finally fast oxidized to the product by the catalytic action of Pt. In this way Pt@TiO$_2$ has a double role: it works as *photocatalyst* in the oxidation of the alcohol and works as *catalyst* (due the presence of Pt) in the conversion of the benzimidazoline to the benzimidazole. Indeed, if Pt were not present the fast step from **5** to **2** (Eq. 6) would not be possible, allowing the shifting of the equilibrium **4**-**5** toward **4**. So, a further aldehyde molecule would condense giving the diimine **3** which finally furnishes the by-product **6**.

$$\text{(5)}$$

$$\text{(6)}$$
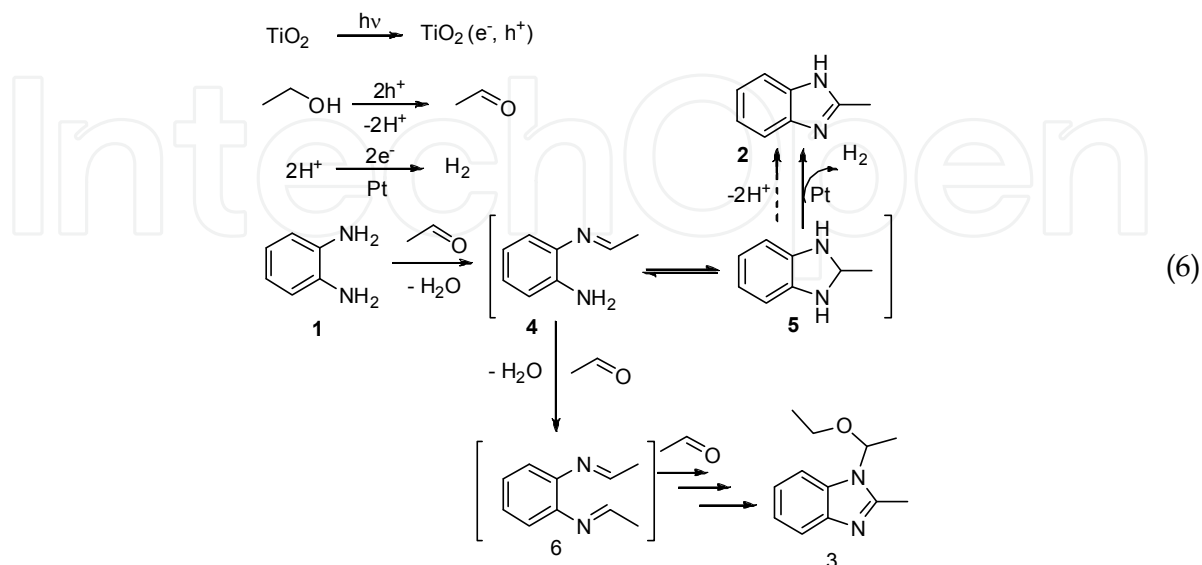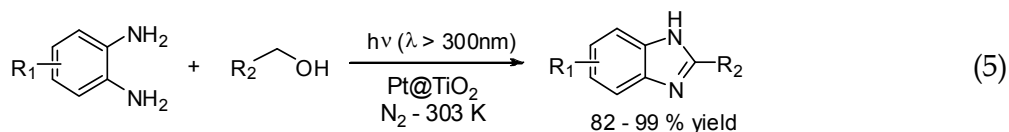
A similar approach for the synthesis of benzimidazoles and indazole has been reported (Selvam & Swaminathan, 2010). The authors found that 2-nitrophenyl azide, in the presence of different alcohols, undergoes a combined redox reaction and condensation after irradiation in the presence of TiO$_2$, giving 2-alkylbenzimidazoles as the main product, whereas, using 2-nitrobenzyl azide, the reduced amine does not react with aldehyde but undergoes cyclization to form indazole. The photoactivity was significantly enhanced by doping TiO$_2$ with Ag or Pt especially under solar light irradiation. In this case, for example, the yield of 2-methylbenzimidazole increased from 85 % by using Degussa P25 to 98 % with both Ag-TiO$_2$ and Pt-TiO$_2$ (Eq. 7)
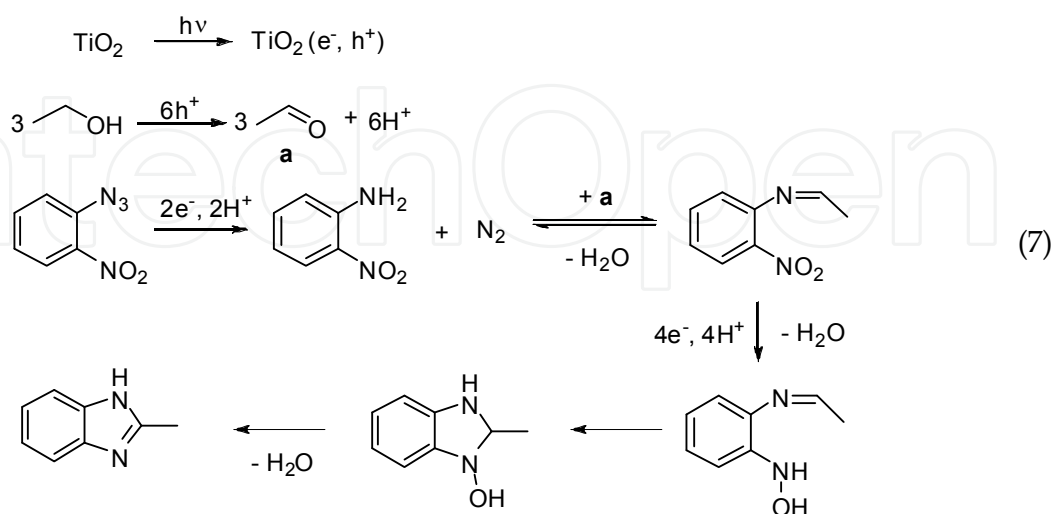
$$\text{(7)}$$

The substitution of protonated heteroaromatic bases by nucleophilic carbon-centered radicals, commonly reported as "Minisci Reaction" (Minisci et al., 1986), is one of the main general reactions of this class of aromatic compounds as a result of the large variety of

successful radical sources, the high regio- and chemoselectivity and the simple experimental conditions. The well known Friedel–Crafts aromatic substitutions are unfavored when carried out on aromatic substrates bearing electron withdrawing groups. 6-Membered mono and poli *N*-heteroaromatic bases behave as electron poor substrates toward "classic" ionic electrophylic substitutions and only carbon atoms in b-position to nitrogen are suitable of substitution. However the reaction rate is much lower than the one carried out on benzene-systems. Otherwise C-centered radicals show nuchleophilic character and easily react with deactivated bases reproducing most of the Friedel–Crafts aromatic substitutions, but with opposite reactivity and selectivity. One of the main goal of the free-radical nucleophilic substitution is represented by the almost total absence of by-product formation during the reaction. In fact only catalytic amount of catalysts or initiators, depending on the reaction types, are needed to promote the reactions, whereas the classic Friedel–Crafts protocol needs stoichiometric quantity of Lewis acids. TiO_2 photocatalysis offers an alternative to the free-radical functionalization of heteroaromatic bases in the presence of classic metal-peroxide system (Gambarotti et al., 2010; Augugliaro et al., 2010). Caronna and co-workers reported the carboxyamidation of bases in the presence of H_2O_2 or air under sunlight (Eq. 8 a) (Caronna et al., 2003; Caronna et al., 2007a). A similar protocol has been successfully applied to the etherification of bases, affording, in the case of 1,3,5-trioxane and 1,3-dioxolane, a green-route to heteroaromatic aldehydes (Eq. 8 b) (Caronna et al., 2005). Moreover, in the presence of aliphatic aldehydes the bases are both acylated and alkylated (Caronna et al., 2007b). Particularly, it is interesting the fact that under the reaction conditions, the decarbonylation rate of the acyl radical intermediate is extraordinarily high, and good conversion to the corresponding alkyl derivatives are obtained also with primary aldehydes (Eq. 8 c).


$$(8)$$
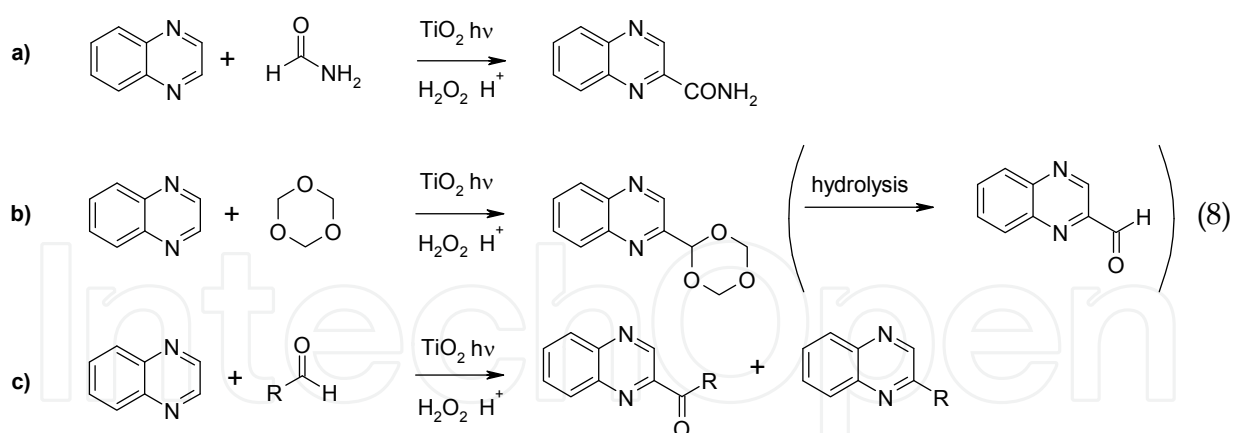
Recently Selvam reported the synthesis of quinaldines from photocatalytic conversion of aniline and its derivatives in ethanol under mild conditions in the presence TiO_2 or Au-TiO_2 (Eq. 9) (Selvam & Swaminathan, 2010). The authors found that Au-TiO_2 has superior catalytic properties compared to TiO_2. Using Au-TiO_2, after only 4 hours of photo-irradiation at 365 nm the yield of quinaldine was about 75 % with a 10 % yield of 2,3-dimethylindole and 5% yield of other by-products, whereas, with TiO_2 the yield of quinaldine was about 50 % after 6h with 15 % of 2,3-dimethylindole. The presence of water reduces drastically the yield of quinaldine (5 % yield with a 96/4 ethanol-water ratio).

$$ \text{(9)} $$
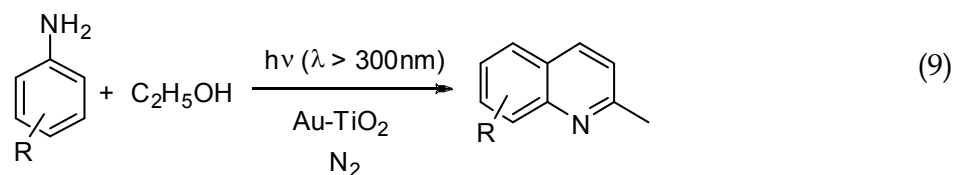
The partial oxidation of alcohols for the production of fine and specialty chemicals represents a further field of investigation having high scientific and industrial impact. The use of TiO_2 to promote the oxidation of alcohols to the corresponding aldehydes has been investigated by different authors in the last years. Pillai and Sahle–Demessie described the oxidation of various primary and secondary alcohols to aldehydes in a gas-phase photochemical reactor with immobilized TiO_2 (Pillai & Sahle–Demessie, 2002). Enache reported the solvent-free oxidation of primary alcohols to aldehydes using Au-Pd/ TiO_2 catalysts without light irradiation (Enache et al., 2006).

Molinari investigated the photooxidation of geraniol to citral (Eq. 10), which is used in perfumes, flavourings and in the manufacture of other chemicals (Molinari et al, 2009b).

$$ \text{(10)} $$
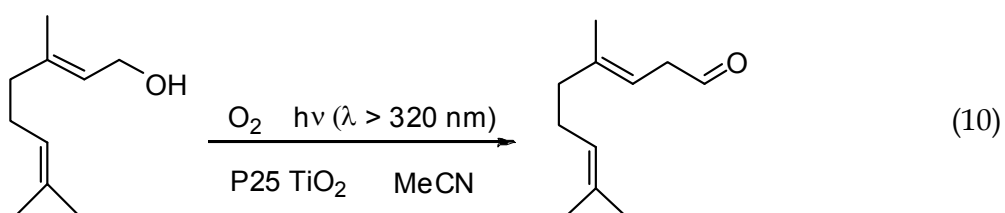
In this work, dispersions of Degussa P25 TiO_2 in CH_3CN containing geraniol (0.01 M) were irradiated by UV-light ($\lambda > 320$ nm), at room temperature and under 760 Torr of O_2 for different times (up to 140 min). The formation of citral occurs as consequence of the adsorption of the geraniol on the surface of the TiO_2 forming an alkoxide ion, RCH_2O^-. This latter is then oxidized to its corresponding alkoxide radical $RCH_2O\cdot$ and finally to the aldehyde $RCHO$ by the direct electron transfer to the positive holes. Hence, the mechanism proposed by the authors is not based on the intervention of the hydroxyl radicals and it is supported by some ESR experiments. Furthermore, the experiments showed that water has negative effect on the oxidation of the -OH group of geraniol. In fact, water reduces the adsorption of the alcohol on the TiO_2 photoactive surface both due to the increase of the polarity which keep the geraniol preferentially in the solution and also due the competitive adsorption of water on the TiO_2. Finally, this inhibits the direct electron transfer from geraniol to the electron holes of TiO_2 reducing its catalytic effect. In order to investigate the effect of the nature of alcohol, the authors compared the reactivity of geraniol with that of trans-2-penten-1-ol, an allylic alcohol similar to geraniol but with a shorter chain of carbon atoms. As expected, trans-2-penten-1-ol is adsorbed on TiO_2 much better than geraniol and hence higher amount of aldehyde is obtained. Furthermore, if primary aliphatic alcohol with chains of the same lengths are considered like as citronellol (as corresponding of geraniol) and 1-pentanol (as corresponding of trans-2-penten-1-ol), it is observed that each primary alcohol is always better adsorbed than the corresponding allylic alcohol getting an increase of the yield of aldehyde.

The conversion of p-anisyl alcohol to p-anisaldehyde, an important intermediate for pharmaceutical industry, through the use of N-doped mesoporous titania (meso-$TiO_{2-x}N_x$) under sunlight as well as UV-lamp irradiation has been reported (Sivaranjani & Gopinath, 2011). The catalyst was prepared by a SCM technique introducing an aqueous solution of

titanyl nitrate and urea into a muffle furnace at 400 °C. The fast evaporation of water was followed by a smouldered combustion of the titanyl nitrate (acting as precursor of Ti) in ammonia atmosphere (acting as fuel) obtained by the decomposition of the urea to NH_3 and CO_2. Different N-doped solid catalysts were prepared changing the precursor/fuel ratio. The oxidations were performed in aqueous solutions and without bubbling oxygen, obtaining yields of *p*-anisaldehyde of 25 % under sunlight and 30 % under laboratory light source in 7 hours. Despite the absence of oxygen, these results are comparable to that reported by Palmisano, who used a home-prepared TiO_2 as well as TiO_2 Merck (100 % anatase) and Degussa P25 (Palmisano et al., 2007b). In this work, 10 % yields of *p*-anisaldehyde was obtained in the presence of TiO_2 Merck or Degussa P25 and 30 - 40 % yields in the presence of home-made catalyst (depending on its amount, phase constitution and morphology).

More recently Chen described the photo-catalytic acetylation of 2-phenylethanol by acetic anhydride in the presence of TiO_2 nanoparticles (Chen, 2011). The synthesis was performed by suspending TiO_2 nanoparticles (32 nm grade) in H_2O_2 (30 % wt) for 30 min. under UV light (254 nm, 15 W) and then concentrating it in order to photoactivate the TiO_2 surface (Eq. 11). The solid was suspended in a solution of 2-phenylethanol in CH_2Cl_2 and irradiated for 10 h. The authors investigated the effects of the oxidant (O_2, *t*-butyl hydroperoxide, H_2O_2) finding that hydrogen peroxide was the most effective (99 % conversion) despite, even in absence of oxidant, a 88 % conversion was obtained. Moreover, different solvents were used finding that CH_2Cl_2 was the best one (> 99% conversion after 10 h) while reactions performed in toluene, hexane, ether, THF, acetone, ethyl acetate and CH_3CN gave lower or null conversions also during longer times. A screening of different TiO_2 catalyst (anatase, rutile) having different morphological parameters as well as other oxides like as Y_2O_3, WO_3, ZrO_2, was also carried out, finding that 32 nm TiO_2 (anatase/rutile = 4/1) was the optimal photo-catalyst both with regard the yield (> 99%) and the reaction time (10 h).


$$\text{(11)}$$
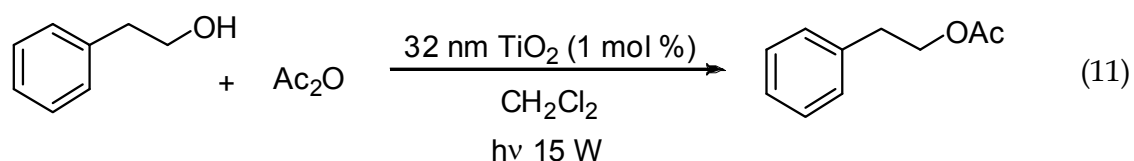
5.2 Other semiconductors in organic photosynthesis

As described before, TiO_2 is undoubtedly the most commonly used catalyst in organic photosynthesis. It is often metal-doped, in order to increase the wavelength radiation adsorption, and supported over inert materials (silica or zeolites), with the unique scope of increasing the surface area and consequently enhancing the reaction rate.

In the last decades, several other inorganic semiconductors have been investigated for the development of innovative organic photosynthetic strategies, including metal sulfides (ZnS and CdS) (Kisch, 2001), metal oxides (ZrO_2, ZnO, V_2O_5, SnO_2, Sb_2O_4, CeO_2, WO_3 and Sn/Sb mixed oxides) (Maldotti et al., 2002a), and polyoxometalates.

One of the reasons, which often make TiO_2 the photocatalyst of choice, is the higher protocol efficiency usually observed, in terms of both conversion and selectivity, when it is compared with other semiconductors. This is, for example, the case for the selective photoactivated radical addition of tertiary amines to electron deficient alkenes such as α,β-unsaturated lactones (Marinković & Hoffmann, 2001, 2003), conducted in the presence of TiO_2, ZnS or SiC. When reacting the *N*-methylpyrrolidine, the best results were achieved with TiO_2 (Eq.

12 a), while the reaction of *N*-methylpiperidine led to a different product distribution (Eq. 12 b). In particular, TiO_2 favoured the selective formation of product **A**, deriving from a classical Michael addition, while ZnS promoted the formation of product **B** in poor yields, probably because of its less oxidative properties.

$$(12)$$
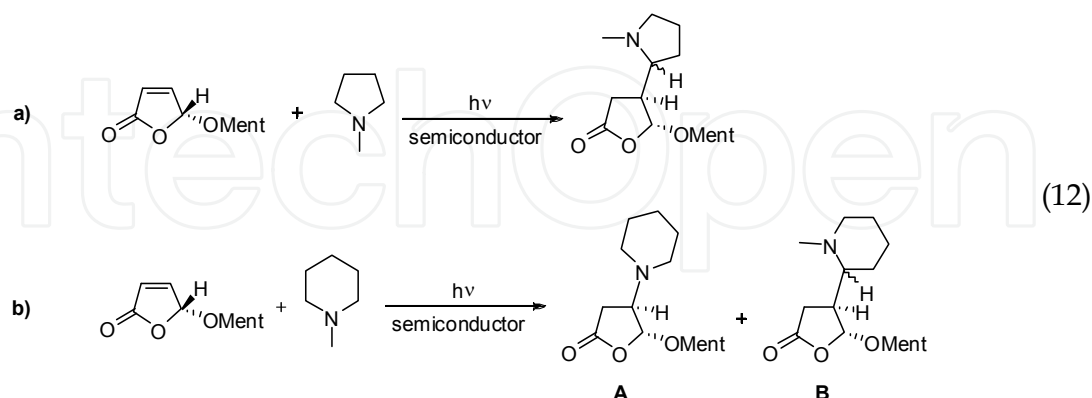
Another significative example is furnished by the selective synthesis of 2-methylpiperazine from *N*-(β-hydroxtpropyl)-ethylenediamine by means of semiconductor-zeolite composite photocatalysts (Subba Rao & Subrahmanyam, 2002). Also in this case, zeolites modified with semiconductors ZnO and CdS were not very effective, while TiO_2-zeolites composites considerably facilitated the intramolecular cyclization (Eq. 13).

$$(13)$$
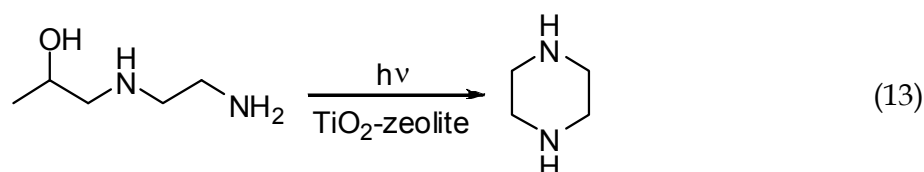
Nevertheless, in many cases inorganic semiconductors different from TiO_2 have recently allowed to afford new and intriguing photosynthetic approaches. In this section we aim to show a few very recent examples of the application of these photocatalysts for selective oxidation, reduction and C-C bond forming reactions.

5.2.1 Oxidation reactions

One of the main drawbacks in semiconductor catalyzed photoxidations in the presence of O_2 is the low selectivity in the desired product. In fact, in many cases the photomineralization of the substrate occurs, leading to the formation of CO_2.
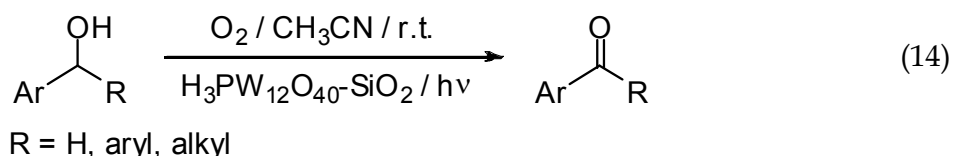
A successful route to overcome this limitation is to employ the semiconductor, usually in the form of metal oxide, fixed or dispersed on a suitable inorganic support. Additional advantages in the use of semiconductors in their heterogenized form are the availability of wide range of supports and the easy recovery and recycle of the catalyst. Once again, TiO_2 is often the first choice, but in many cases other metal oxides provide better results.

Highly dispersed ($Me^{n+}O$)-Si binary oxides, prepared by both conventional impregnation and sol-gel procedures, have been widely employed under irradiation for the aerobic oxidation of alkanes and alkenes (Maldotti, 2002a). Propylene was converted to different oxidized species, varying the final product on the basis of the photocatalyst of choice: the corresponding epoxide in the presence of ZnO-SiO_2 (Yoshida et al., 1999), acetaldehyde with V_2O_5-SiO_2 (Tanaka et al., 1986), a mixture of both by means of CrO_x-SiO_2 (Murata et al., 2001).

Alkanes too were shown to undergo partial oxidation, when illuminated in the presence of silica-supported vanadium oxide, affording the corresponding carbonylic products in good yields with only traces of CO_x (Tanaka et al., 2000).

Supported polyoxometalates based on tungsten afforded high photocatalytic activity in the oxidation of different substrates. $(n\text{-Bu}_4N)_4W_{10}O_{32}$ (TBADT), supported on silica by impregnation procedure, was successfully employed at room temperature and atmospheric pressure to promote by irradiation ($\lambda > 300$ nm) the aerobic oxidation of cyclohexane to a 1:1 mixture of cyclohexanol and cyclohexanone (Molinari et al., 1999), while under analogous conditions cyclohexene was converted to the corresponding cyclohexenyl hydroperoxide with 90 % of selectivity (Molinari et al., 2000). This decatungstate was also immobilized on a mesoporous MCM-41-type material, which allows to obtain a better dispersion of the semiconductor, and the new material was tested in the oxidation of the cyclohexane for comparison with the silica supported material (Maldotti et al., 2002b). These studies showed the key role of the solid matrix in controlling the ketone/alcohol ratio of the products. In fact, the higher surface area of the mesoporous material favored the conversion of cyclohexanol to the corresponding cyclohexanone, affording a higher final ratio ketone/alcohol (2.4).

Another tungsten-based heteropolyoxometalate supported on amorphous silica ($H_3PW_{12}O_{40}/SiO_2$) was successfully used for the selective aerobic photocatalytic oxidation of benzylic alcohols to the corresponding aldehydes and ketones, with yields up to 97 % (Farhadi et al., 2005). Even more interesting, in spite of the higher reactivity of carbonylic derivatives, no overoxidation was observed, and no traces of carboxylic acids were found in the final products (Eq. 14).

$$
\underset{Ar}{\overset{OH}{\diagup}}R \xrightarrow[\text{$H_3PW_{12}O_{40}$-SiO_2 / $h\nu$}]{\text{O_2 / CH_3CN / r.t.}} \underset{Ar}{\overset{O}{\diagup}}R \tag{14}
$$

R = H, aryl, alkyl

5.2.2 Reduction reactions

If we exclude the conversion of CO_2 into more useful hydrogenated chemicals, which is however characterized by low energy conversion efficiencies, the main application of the photoinduced reduction reaction is the transformation of nitro-aromatic derivatives.

Being the most powerful reducing semiconductor, CdS usually provides highest yield and selectivity by converting nitro-benzenes into corresponding anilines, if compared with the common TiO_2 (Maldotti et al., 2000). Nevertheless, it requires UV light to be activated, this limiting the range of applications.

Very recently, Pfitzner and coworkers (Füldner et al., 2011) have reported that the blue light irradiation of $PbBiO_2X$ ($X = Cl$ or Br), in the presence of triethanolamine (TEOA) as an electron donor, provides the selective and complete reduction of nitrobenzene derivatives to their corresponding anilines (Eq. 15). By replacing bismuth with antimony in the oxide halide no conversion was observed. The same unreactivity resulted by operating in the presence of $PbBiO_2I$. The authors suggest that the different catalytic activity should be ascribed to multiple factors, including the crystal structures and their optical and redox properties. Photocatalyst recycling experiments showed that sonication of $PbBiO_2X$ before reuse was essential to retain its activity up to five catalytic cycles.

$$\text{NO}_2 \quad \xrightarrow[\lambda = 440 \text{ nm} / 20 \text{ h}]{\text{PbBiO}_2X / \text{TEOA}} \quad \text{NH}_2 \qquad (15)$$

$$> 99 \%$$
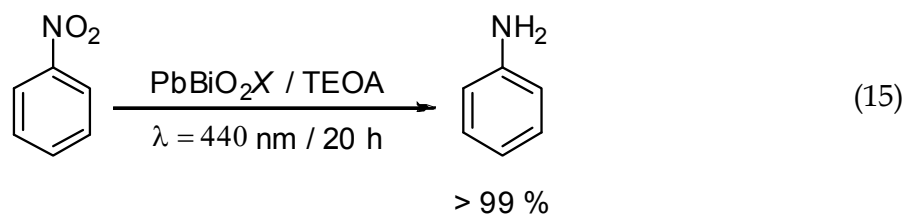
Anilines can be also obtained in 50 % yields and complete selectivity by photoreduction of aryl azides catalyzed by CdS or CdSe nanoparticles (Warrier et al., 2004). The reaction, which occurs under very mild conditions (room temperature, atmospheric pressure, neutral pH and aqueous medium), requires the presence of sodium formate as sacrificial electron donor (Eq. 16).

$$\text{N}_3 \xrightarrow[\quad h\nu \quad]{\text{CdS}} \text{NH}_2 \qquad (16)$$

$$\text{HCO}_2\text{Na} \qquad \qquad \text{CO}_2$$
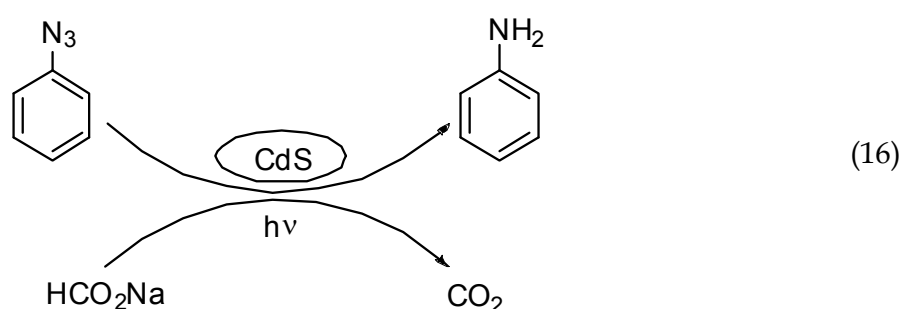
The high efficiency of this photocatalyzed reduction is attributed to the large driving force for electron transfer to the azide, which in turn arises from the much more negative potential of excited CdS nanoparticles electrons relative to the azide reduction potential.

More recently, the same photocatalytic approach was successfully applied to the reduction of aryl azide-terminated, self-assembled monolayers on gold to the corresponding arylamine species (Radhakrisham et al., 2006).
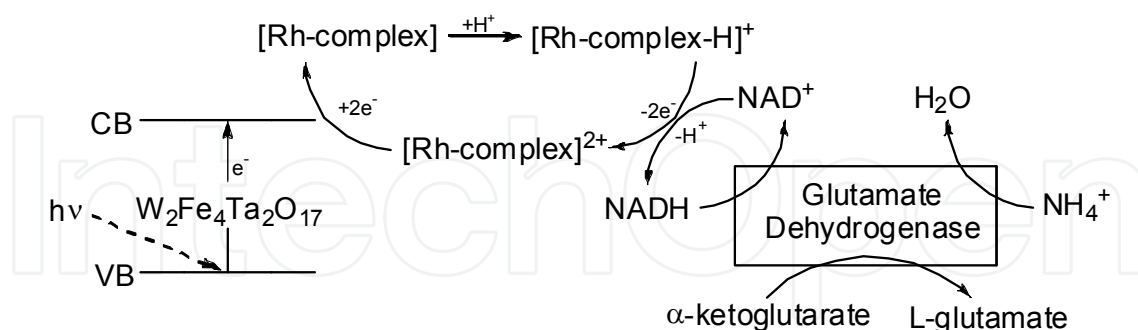
Fig. 10. Schematic diagram of photocatalyst $W_2Fe_4Ta_2O_{17}$ mediated bioreactor for the enzymatic synthesis of L-glutamate.

Photoreduction has been also applied to the design of a novel photobioreactor capable to couple a redox enzyme biocatalysis (Glutamate Dehydrogenase) with the new visible-light active heterogeneous photocatalyst $W_2Fe_4Ta_2O_{17}$ for the production of L-glutamate (Park et al., 2008). The idea arises from the necessity to develop an efficient and industrially feasible

method for the in situ regeneration of nicotinamide (NAD) co-factor, on which depend the activity of many enzymes. In fact, the high cost of NAD often limits the industrialization potentials of many promising enzymatic processes. The overall schematic mechanism, which regulates this photobioreactor, is reported in Fig. 10. In the photocatalytic cycle, the $W_2Fe_4Ta_2O_{17}$ upon band-gap excitation by visible light ($\lambda > 420$ nm) promotes electrons to the conduction band, which are in turn easily transferred to an organometallic Rh complex. The latter, after undergoing hydrogen abstraction from the aqueous medium, transfers electrons and hydride to NAD^+, forming NADH.

5.2.3 C-C bond forming reactions

Among semiconductor photocatalysts, Ru(II)polypyridine complexes are attracting increasing interest because of their stability at room temperature and enhanced photoredox properties (Narayanam & Stephenson, 2011). In particular, Ru(bpy)$_3$Cl$_2$ has been widely employed, as its irradiation with visible light leads to the excited species Ru(bpy)$_3^{2+*}$, which in turn can be employed as strong single electron oxidant and reductant, depending upon reaction conditions. Besides classical oxidative reactions introducing oxygen atoms and reductive hydrogenations, Ru(bpy)$_3$Cl$_2$ has found large use in the photocatalytic promotion of C-C bond formation.

Irradiation of aryl enones, in the presence of a mixture of Ru(bpy)$_3$Cl$_2$, i-Pr$_2$NEt and LiBF$_4$ in acetonitrile, allowed to develop a highly diasteroselective intramolecular [2 + 2] cycloaddition reaction, which, in all the examples reported, led to the formation of the corresponding *cis*-cyclobutanes (Eq. 17) (Ischay & al., 2008). In the reaction mechanism, i-Pr$_2$NEt has the role to reduces the excited species Ru(bpy)$_3^{2+*}$ to Ru(bpy)$_3^+$, which seems to be the real initiator of the process, while LiBF$_4$, being a Lewis acid, favours the solubility of Ru complex in acetonitrile.

The same system was applied to promote the intermolecular homo-dimerization of aryl enones (Eq. 18) and the crossed intermolecular cyloaddition (Eq. 19) (Du & Yoon, 2009).


$$\text{(17)}$$

$$\text{(18)}$$

$$\text{(19)}$$
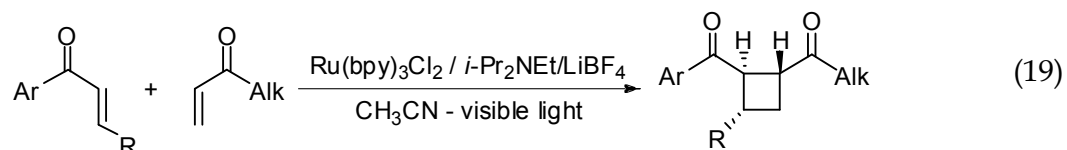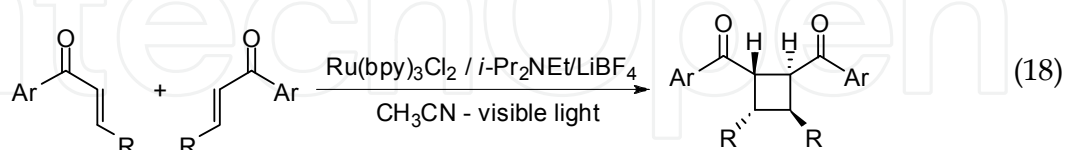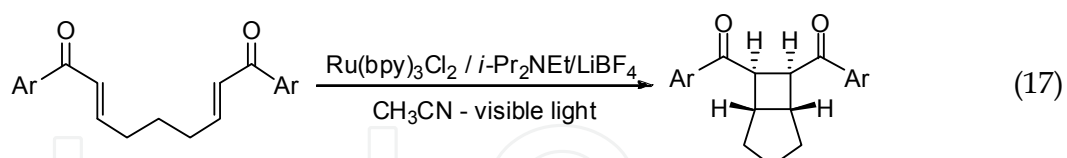
More recently, a photoredox strategy based on Ru(bpy)$_3$Cl$_2$ photocatalyst was successfully employed both for the selective α-trifluoromethylation upon in situ or pre-generated enolsilanes and silylketenes (Eq. 20) (Pham et al., 2011) and to promote an oxidation/[3 + 2] cycloaddition/aromatization cascade reaction (Zou et al., 2011), the latter leading to the

formation of pyrrolo[2,1-α]isoquinolines from ethyl 2-(3,4-dihydroisoquinolin-2(1*H*-yl) acetate (Eq. 21)

$$(20)$$

$$(21)$$
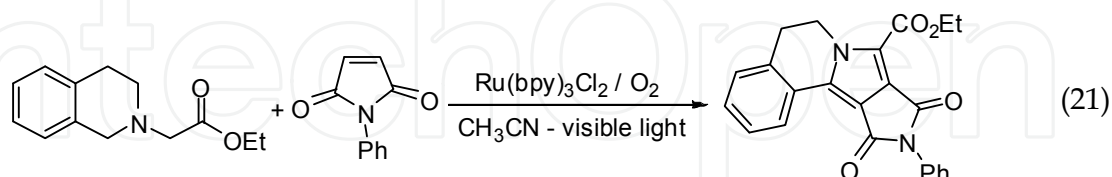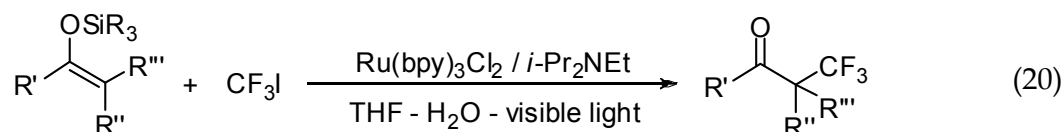
We have already reported the photocatalytic activity of tetrabutylammonium decatungstate salt ((n-Bu$_4$N)$_4$W$_{10}$O$_{32}$) in selective photoxidations. TBADT has been also used by Albini and coworkers to promote the photocatalytic radical conjugate addition of electron-poor olefins by cycloakanes (Eq. 22) (Dondi et al., 2006) and the acylation of α,β-unsaturated nitriles, ketones and esters (Eq. 23) (Esposti et al., 2007), affording the desired products in good yields.

$$(22)$$

$$(23)$$
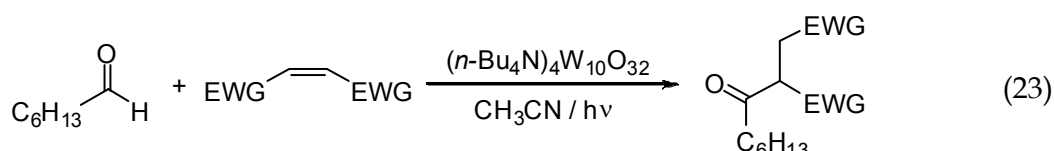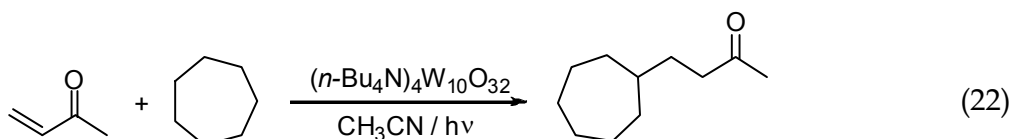
The same group has recently shown that irradiated TBADT can also effectively catalyze the alkylation at position 2 of 1,3-benzodioxoles, making this moiety more biological active and enzyme-specific (Eq. 24) (Ravelli et al., 2011).

$$(24)$$
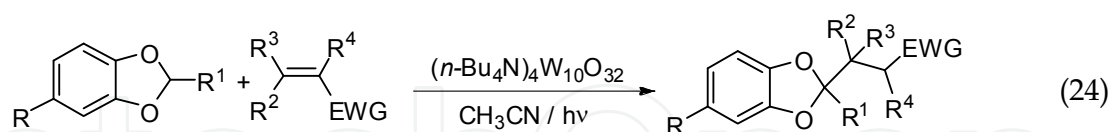
Another significative example of potentials of semiconductor photocatalysis is represented by the artificial photosynthesis design, that is the fixation of CO$_2$ molecules to afford higher organic compounds (Hoffmann et al., 2011).

For example, many studies have concentrated on the fixation of CO$_2$ in carboxylic acids to produce intermediates in key cellular processes. Recently Guzman and Martin have reported that a glyoxylate can be methylated to produce the corresponding lactate, directly involved in the reductive tricarboxylic acid cycle, by photocatalytic fixation of CO$_2$ mediated by ZnS (Guzman & Martin, 2010).

Nevertheless, it has been recently outlined (Yang et al., 2010) that many results reported in the literature and related to these studies could be influenced by the presence of carbon residues left over from the synthesis of metal oxide semiconductors. In other words, there could be experimental artefacts affecting reports and final conclusions, so that more investigations in the field of artificial photosynthesis is still mandatory.

6. Conclusions

In the last decades a growing interest has been devoted to the development of photocatalytic processes both in the homogeneous and in the heterogeneous phase. Particularly, concerning the heterogeneous systems, great interest has aroused the use of photosensitive semiconductors as catalysts for organic processes, due to their ease to use, recycle and low environmental impact. Although most of the actual applications are restricted to the decomposition of organic pollutants, semiconductors are becoming more and more important for the development of new photocatalyzed organic protocols, as an alternative to the conventional metal-catalyzed thermal processes. Generally, TiO_2 has a dominant role in all the semiconductor-phtocatalyzed applications, including the organic synthesis, however, in the last decades many others transition metals photocatalysts, have been developed. Actually, in the scientific landscape, big challenges are represented by the reduction of energy consumption and environmental impact, and photocatalysis could be one of the winning answers in the chemistry field.

7. References

Albini, A., & Fagnoni, M. (2008). 1908: Giacomo Ciamician and the Concept of Green Chemistry, *ChemSusChem*, vol. 1, pp. 63–66, ISSN 1864-564X

Anpo, M., & Kamat, P.V. (Eds.). (2010) *Environmentally Benign Photocatalysts*, Springer, ISBN 978-0-387-48441-9, Dordrecht Heidelberg London New York

Augugliaro, V., Caronna, Di Paola, A., Marcì, G., Pagliaro, M., Palmisano, G., & Palmisano, L. (2010). TiO_2-Based Photocatalysis for Organic Synthesis. In: *Environmentally Benign Photocatalysts*, Anpo, M., & Kamat, P.V. (Eds.), pp. 623-645, Springer, ISBN 978-0-387-48441-9, Dordrecht Heidelberg London New York

Bal, R., Tada, M., Sasaki, T., & Iwasawa, Y. (2006). Direct Phenol Synthesis by Selective Oxidation of Benzene with Molecular Oxygen on an Interstitial-N/Re Cluster/Zeolite Catalyst, *Angewandte Chemie International Edition*, Vol. 45, pp. 448–452, ISSN: 1521-3773

Balzani,V., Credi, A., & Venturi, M. (2008*). Photochemical Conversion of Solar Energy. *ChemSusChem*, Vol. 1, pp. 26-58, ISSN 1864-564X

Bard, A.J. (1979). Photoelectrochemistry and heterogeneous photocatalysis at semiconductors. *Journal of Photochemistry*, Vol. 10, pp. 59-75, ISSN 1010-6030

Becquerel, C R. (1839). Mémoire sur les effets électriques produits sous l'influence des rayons solaires. *Comptes Rendus de l'Académie des Sciences*, Vol. 9, pp. 561-567

Brattain, W.H., Garret, C.G.B. (1955). *Bell System Technical Journal*, Vol. 34, p. 129

Cao, F.L., Wang, J-G., Lv, F-J., Zhang, D-Q., Huo, Y-N., Li, G-S., Li, H-X., & Zhu, J. (2011). Photocatalytic oxidation of toluene to benzaldehyde over anatase TiO_2 hollow spheres with exposed {001} facets, *Catalysis Communications*, Vol. 12, pp. 946–950, ISSN 1566-7367

Caronna, T., Gambarotti, C., Palmisano, L., Punta, C., & Recupero, F. (2003). Sunlight induced functionalisation of some heterocyclic bases in the presence of polycrystalline TiO_2, *Chemical Communications*, Vol. 18, pp. 2350-2351, ISSN 1364-548X

Caronna, T., Gambarotti, C., Palmisano, L., Punta, C., & Recupero, F. (2005) Sunlight-induced reactions of some heterocyclic bases with ethers in the presence of TiO_2 - A green route for the synthesis of heterocyclic aldehydes, *Journal of Photochemistry And Photobiology A: Chemistry*, Vol. 171, pp. 237-242, ISSN 1010-6030

Caronna, T., Gambarotti, C., Mele, A., Pierini, M., Punta, C., & Recupero, F. (2007a). A green approach to the amidation of heterocyclic bases: the use of sunlight and air, *Research on Chemical Intermediates*, Vol. 33, pp. 311-317, ISSN 1568-5675

Caronna, T., Gambarotti, C., Palmisano, L., Punta, C., Pierini, M., & Recupero, F. (2007b). Sunlight-induced functionalisation reactions of heteroaromatic bases with aldehydes in the presence of TiO_2: A hypothesis on the mechanism, *Journal of Photochemistry And Photobiology A: Chemistry*, Vol. 189, pp. 322-328, ISSN 1010-6030

Carp, O., Huisman, C.L., & Reller, A. (2004). Photoinduced reactivity of titanium dioxide. *Progress in Solid State Chemistry*, Vol. 32, pp. 33-177, ISSN 0079-6786

Chatterjee, D., & Dasgupta, S. (2005). Visible light induced photocatalytic degradation of organic pollutants. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, Vol. 6, pp. 186-205, ISSN 1389-5567

Chattopadhyay, D., & Rakshit, P.C. (Eds.) (2010). *Electronics: Fundamentals and Applications*, New Age International (P) Ltd., Publishers ISBN : 978-81-224-3147-6, New Delhi-110 002, India

Chen, C.T., Kao, J.Q., Liu, C.Y., & Jiang, L.Y. (2011). Oxidative, photo-activated TiO_2 nanoparticles in the catalytic acetylation of primary alcohols, *Catalysis Science & Technology*, Vol. 1, pp. 54–57

Chen, X., Zhang, J., Fu, X., Antonietti, M., & Wang, X. (2009). Fe-g-C_3N_4-Catalyzed Oxidation of Benzene to Phenol Using Hydrogen Peroxide and Visible Light, *Journal of the American Chemical Society*, Vol. 131, pp. 11658–11659, ISSN 1520-5126

Ciamician, G. & Silber, P. (1900). *Chemische Berichte*, Vol. 33, p. 2911-2913

Deanna, H.C., Agrios, A.G & Gray, A.k. (2003). Explaining the Enhanced Photocatalytic Activity of Degussa P25 Mixed-Phase TiO_2 Using EPR. *The Journal of Physical Chemistry B*, Vol. 107, pp. 4545-4549, ISSN 1520-5207

Dindar, B., & İçli, S. (2001). Unusual photoreactivity of zinc oxide irradiated by concentrated sunlight. *Journal of Photochemistry and Photobiology A: Chemistry*, Vol. 140, pp. 263-268, ISSN 1010-6030

Dondi, D., Cardarelli, A.M., Fagnoni, M., & Albini, A. (2006). Photomediated synthesis of β-alkylketones from cycloalkanes. *Tetrahedron*, Vol.62, pp. 5527-5535, ISSN 0040-4020

Du, J., & Yoon, T.P. (2009). Crossed Intermolecular [2+2] Cycloadditions of Acyclic Enones via Visible Light Photocatalysis. *Journal of the American Chemical Society*, Vol.131, 14604-14605, ISSN 1520-5126

Enache, D.I., Edwards, J.K., Landon, P., Solsona-Espriu, B., Carley, A.F., Herzing, A.A., Watanabe, M., Kiely, C.J., Knight, D.W., & Hutchings, G.J. (2006). Solvent-Free Oxidation of Primary Alcohols to Aldehydes Using Au-Pd/TiO_2 Catalysts, Science, Vol. 311, pp. 362-365, ISSN 1095-9203

Esposti, S., Dondi, D., Fagnoni, M., & Albini, A. (2007). Acylation of Electrophilic Olefins through Decatungstate-Photocatalyzed Activation of Aldehydes. *Angewandte Chemie. International Edition*, Vol.46, pp. 2531-2534, ISSN 1521-3773

Esswein, A.J., & Nocera, D.G. (2007). Hydrogen Production by Molecular Photocatalysis. *Chemical Review*, Vol. 107, pp. 4022-4047, ISSN 1520-6890

Evans, P., & Sheel, D.W. (2007*)*. Photoactive and antibacterial TiO_2 thin films on stainless steel. *Surface and Coatings Technology*, Vol. 201, pp. 9319–9324, ISSN 0257-8972

Fan, F.-R.F., Leempoel, P., & Bard, a.J. (1983). Semiconductor electrodes. *Journal of The Electrochemical Society*, Vol. 130, pp. 1866-75, ISSN 0013-4651

Farhadi, S., Afshari, M., Maleki, M., & Babazadeh, Z. (2005). Photocatalytic Oxidation of Primary and Secondary Benzylic Alcohols to Carbonyl Compounds Catalyzed by $H_3PW_{12}O_{40}/SiO_2$ under an O_2 Atmosphere. *Tetrahedron Letters*, Vol.46, pp. 8483-8486, ISSN 0040-4039

Fox, M.A., & Dulay, M. (1993*)*. Heterogeneous Photocatalysis. *Chemical Review*, Vol. 83, pp. 341-357, ISSN 1520-6890

Fox, M.A. (2001). Synthetic Applications of Photocatalytic Oxidation and Reduction Reactions of Organic Reactants on Irradiated Semiconductor Surfaces, In: *Electron Transfer in Chemistry*, Balzani V. (Ed.), pp. 272-311, Wiley-VCH, ISBN 3-527-29912-2, Weinheim (Germany)

Frank, S.N., & Bard, A.J. (1997). Heterogeneous photocatalytic oxidation of cyanide ion in aqueous solutions at titanium dioxide powder. *Journal of the American Chemical Society*, Vol. 99, pp. 303-304, ISSN 1520-5126

Friedrich, W. (1828). Ueber künstliche Bildung des Harnstoffs. *Annalen der Physik und Chemie*, Vol. 88, No. 2, pp. 253–256

Fu, G., Vary, P.S., & Lin, C.T. (2005). Anatase TiO_2 Nanocomposites for Antimicrobial Coatings. *The Journal of Physical Chemistry B*, Vol. 109, pp. 8889-8898, ISSN 1520-5207

Fujishima, A., & Honda, K. (1972). Electrochemical Photolysis of Water at a Semiconductor Electrode. *Nature*, Vol. 238, p. 37, ISSN 0028-0836

Füldner, S., Pohla, P., Bartling, H., Dankesreiter, S., Stadler, R., Gruber, M., Pfitzner, A., & König, B. (2011). Selective Photocatalytic Reductions of Nitrobenzene Derivatives Using $PbBiO_2X$ and Blue Light. *Green Chemistry*, Vol.13, pp.640-643, ISSN 1463-9270

Gambarotti, C., Punta, C., Recupero, F., Caronna, T., & Palmisano L. (2010). TiO_2 in Organic Photosynthesis: Sunlight Induced Functionalization of Heterocyclic Bases. *Current Organic Chemistry*, Vol. 14(11), pp. 1153-1169, ISSN 1385-2728

Gan, W.Y., Lam, S.W., Chiang, K., Amal, R., Zhao, H., & Brungs, M.P. (2007). Novel TiO_2 thin film with non-UV activated superwetting and antifogging behaviours. *Journal of Materials Chemistry*, Vol. 17, pp. 952–954, ISSN 1364-5501

Gaya, U.I., & Abdullaha, A.H. (2008). Heterogeneous photocatalytic degradation of organic contaminants over titanium dioxide: A review of fundamentals, progress and problems. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, Vol. 9, pp. 1–12, ISSN 1389-5567

Guo, Y., Zhang, X., Zou, H., Liu, H., Wang, J., & Yeung, K.L. (2009). Pd–silicalite-1 composite membrane for direct hydroxylation of benzene. *Chemical Communications*, pp. 5898–5900, ISSN 1364-548X

Guzman, M. I., & Martin, S. T. (2010). Photo-production of lactate from glyoxylate: how minerals can facilitate energy storage in a prebiotic world. *Chemical Communications*, pp. 2265-2267, ISSN 1359-7345

Hariharan, C. (2006). Photocatalytic degradation of organic contaminants in water by ZnO nanoparticles: Revisited. *Applied Catalysis A: General*, Vol. 304, pp. 55-61, ISSN 0926-860X

Hashimoto, K., Irie, H., & Fujishima, A . (2005). TiO_2 Photocatalysis: A Historical Overview and Future Prospects. *Japanese Journal of Applied Physics*, Vol. 44, pp. 8269-8285, ISSN 1347-4065

Heller, A., Degani, Y., Johnson, D.W., & Gallagher, P.K. (1987). Controlled Suppression and Enhancement of the Photoactivlty of Titanium Dioxide (Rutile) Pigment. *The Journal of Physical Chemistry*, Vol. 91, pp. 5987-5991, ISSN 0022-3654

Heller, A. (1995*).* Chemistry and Applications of Photocatalytic Oxidation of Thin Organic Films. *Accounts of Chemical Research*, Vol. 28, pp. 503-508, ISSN 1520-4898

Hoffmann, M.R, Martin, S.T, Choi, W., & Bahnemann, D.W. (1995*).* Environmental Applications of Semiconductor Photocatalysis. *Chemical Review*, Vol. 95, pp. 69-96, ISSN 1520-6890

Hoffmann, M.R., Moss, J.A., & Baum, M. M. (2011). Artificial Photosynthesis: Semiconductor Photocatalytic Fixation of CO_2 to Afford Higher Organic Compounds. *Dalton Transactions*, Vol.40, pp. 5151-5158, ISSN 1364-5447

Hu, J-S., Ren, L-L., Guo, Y-G., Liang, H-P., Cao, A-M., Wan, L-J., & Bai, C-L. (2005*).* Mass Production and High Photocatalytic Activity of ZnS Nanoporous Nanoparticles. *Angewandte Chemie International Edition*, Vol. 44, pp. 1269 -1273, ISSN 1521-3773

Iizuka, M., & Yoshida, M. (2009). Redox system for perfluoroalkylation of arenes and a-methylstyrene derivatives using titanium oxide as photocatalyst, *Journal of Fluorine Chemistry*, Vol. 130, pp. 926–932, ISSN 0022-1139

Ischay, M.A., Anzovino, M.E., Du, J., & Yoon, T. P. (2008). Efficient Visible Light Photocatalysis of [2+2] Enone Cycloadditions. *Journal of the American Chemical Society*, Vol.130, 12886-12887, ISSN 1520-5126

Karraway, E.R., Hoffman, A.J., & Hoffmann, M.R. (1994). Photocatalytic Oxidation of Organic Acids on Quantum-Sized Semiconductor Colloids. *Environmental Science & Technology*, Vol. 28, pp. 786-793, ISSN 1520-5851

Kisch, H. (2001). Semiconductor photocatalysis for organic synthesis, In: *Advances in Photochemistry*, Vol. 26, Neckers, D.C., Bünau, G.V., Jenks, W.S. (Eds.), 93-143, John Wiley & Sons, Inc., ISBN 0-471-39467-X, USA

Kormann, C., Bahnemann, D.W., & Hoffmann, M.R. (1988). Photocatalytic Production of H_2O_2 and Organic Peroxides in Aqueous Suspensions of TiO_2, ZnO, and Desert Sand. *Environmental Science & Technology*, Vol. 22, pp. 798-806, ISSN 1520-5851

Li, C., Yuan, J., Han, B., Jiang, L., & Shangguan, W. (2010). TiO_2 nanotubes incorporated with CdS for photocatalytic hydrogen production from splitting water under visible light irradiation. *International Journal of Hydrogen Energy,* Vol. 35, pp. 7073-7079, ISSN 0360-3199

Linsebigler, A.L., Lu, G., & Yates, J.T. (1995). Photocatalysis on TiO_2 Surfaces: Principles, Mechanisms, and Selected Results. *Chemical Review* , Vol. 95, pp. 735-758, ISSN 1520-6890

Liu, M., Piao, L., Zhao, L., Ju, S., Yan, Z., He, T., Zhou, C., & Wang, W. (2010). Anatase TiO_2 single crystals with exposed {001} and {110} facets: facile synthesis and enhanced photocatalysis, *Chemical Communications*, Vol. 46, pp. 1664–1666, ISSN 1364-548X

Liu, Y., Wanga, X., Yanga, F., & Yang, X. (2008). Excellent antimicrobial properties of mesoporous anatase TiO_2 and Ag/TiO_2 composite films. *Microporous and Mesoporous Materials*, Vol. 114, pp. 431–439, ISSN 1387-1811

Łukasiak, L., & Jakubowski, A. (2010). History of Semiconductors. *JTIT*, vol. 1, pp. 3-9, ISSN 1899-8852

Macyk, W., & Kisch, H. (2001). Photosensitization of Crystalline and Amorphous Titanium Dioxide by Platinum(iv) Chloride Surface Complexes. *Chemistry - A European Journal*, Vol. 7, pp. 1862-1867, ISSN 1521-3765

Maeda, K., & Domen, K. (2007). New Non-Oxide Photocatalysts Designed for Overall Water Splitting under Visible Light. *The Journal of Physical Chemistry C*, Vol. 111, pp. 7851-7861, ISSN 1932-7455

Maira, A. J., Yeung, K.L., Soria, J., Coronado, J.M., Belver, C., Lee, C.Y., & Augugliaro, V. (2001). Gas-phase photo-oxidation of toluene using nanometer-size TiO_2 catalysts. *Applied Catalysis B: Environmental*, Vol. 29, pp. 327-336, ISSN 0926-3373

Malato, S., Blanco, J., Alarcón, D.C., Maldonado, M.I., Fernández-Ibáñez, P., & Gernjak, W. (2007). Photocatalytic decontamination and disinfection of water with solar collectors. *Catalysis Today*, Vol. 122, pp. 137-149, ISSN 0920-5861

Maldotti, A., Andreotti, L., Molinari, A., Tollari, S., Penoni, A., & Cenini, S. (2000). Photochemical and Photocatalytic Reduction of Nitrobenzene in the Presence of Cyclohexene. *Journal of Photochemistry and Photobiology A: Chemistry*, Vol.133, pp. 129-133, ISSN 1010-6030

Maldotti, A., Molinari, A., & Amadelli, R. (2002a). Photocatalysis with Organized Systems for the Oxofunctionalization of Hydrocarbons by O_2. *Chemical Reviews*, Vol. 102, pp. 3811-3836, ISSN 1520-6890

Maldotti, A., Molinari, A., Varani, G., Lenarda, M., Storaro, L., Bigi, F., Maggi, R., Mazzacani, A., & Sartori, G. (2002b). Immobilization of $(n-Bu_4N)_4W_{10}O_{32}$ on Mesoporous MCM-41 and Amorphous Silicas for Photocatalytic Oxidation of Cycloalkanes with Molecular Oxygen. *Journal of Catalysis*, Vol. 209, pp. 210-216, ISSN 0021-9517

Marinković, S., & Hoffmann, N. (2001). Efficient Radical Addition of Tertiary Amines to Electron-Deficient Alkenes Using Semiconductors as Photochemical sensitisers. *Chemical Communications*, pp. 1576-1578, ISSN 1364-548X

Marinković, S., & Hoffmann, N. (2003). Semiconductors as Sensitizers for the Radical Addition of Tertiary Amines to Electron Deficient Alkenes. *Internationa Journal of Photoenergy*, Vol.5, pp. 175-182, ISSN 1687-529X

Martra, G. (2000). Lewis acid and base sites at the surface of microcrystalline TiO2 anatase: relationships between surface morphology and chemical behavior. *Applied Catalysis A: General*, Vol. 200, pp. 275-285, ISSN 0926-860X

Mccullagh, C., Robertson, J.M.C., Bahnemann, D.W., & Robertson, P.K.J. (2007). The application of TiO_2 photocatalysis for disinfection of water contaminated with pathogenic micro-organisms: a review. *Research on Chemical Intermediates*, Vol. 33, pp. 359-375, ISSN 1568-5675

Meissner, D., & Memming, R. (1988). Photoelectrochemistry of Cadmium Sulfide. 1. Reanalysis of Photocorrosion and Flat-Band Potential. *The Journal of Physical Chemistry*, Vol. 92, pp. 3476-3483, ISSN 0022-3654

Mills, A., & Le Hunte, S. (1997). An Overview of semiconductor photocatalysis. *Journal of Photochemistry and Photobiology A: Chemistry*, Vol. 108, pp. 1-35, ISSN 1010-6030

Mills, A., & Lee, S-K. (2002). A web-based overview of semiconductor photochemistry-based current commercial applications. *Journal of Photochemistry and Photobiology A: Chemistry*, Vol. 152, pp. 233-247, ISSN 1010-6030

Minisci, F., Vismara, E., Fontana, F., Morini, G., Serravalle, M., & Giordano, C. (1987). Polar effects in free-radical reactions. Solvent and isotope effects and effects of base catalysis on the regio- and chemoselectivity of the substitution of protonated heteroaromatic bases by nucleophilic carbon-centered radicals. *The Journal of Organic Chemistry*, Vol. 52, pp. 730-736, ISSN 1520-6904

Molinari, A., Amadelli, R., Mazzacani, A., Sartori, G., & Maldotti, A. (1999). Heterogeneous Photocatalysis for Synthetic Purposes: Oxygenation of Cyclohexane with $H_3PW_{12}O_{40}$ and $(nBu_4N)_4W_{10}O_{32}$ Supported on silica. *Journal of Chemical Society, Dalton Transactions*, pp. 1203-1204, ISSN 1472-7773

Molinari, A., Amadelli, R., Carassiti, V., & Maldotti, A. (2000). Photocatalyzed Oxidation of Cyclohexene and Cyclooctene with $(nBu_4N)_4W_{10}O_{32}$ and $(nBu_4N)_4W_{10}O_{32}$/FeIII [meso-Tetrakis(2,6-dichlorophenyl)-porphyrin] in Homogeneous and Heterogeneous Systems. *European Journal of Inorganic Chemistry*, pp. 91-96, ISSN 1099-0682

Molinari, R., Caruso, A., & Poerio, T. (2009a). Direct benzene conversion to phenol in a hybrid photocatalytic membrane reactor, Catalysis Today, Vol. 144, pp. 81–86, ISSN 0920-5861

Molinari, A., Montoncello, M., Rezala, H., & Maldotti A. (2009b). Partial oxidation of allylic and primary alcohols with O_2 by photoexcited TiO_2, *Photochemical & Photobiological Sciences*, 2009, 8, 613–619, ISSN 1474-905X

Montalti, M., Credi, A., Prodi, L., Gandolfi, M-T. (2006) *Handbook of Photochemistry* (3rd edition), Taylor & Francis Group, LLC, ISBN 0-8247-2377-5, Boca Raton, FL (USA)

Murata, C., Yoshida, H., & Hattori, T. (2001). Visible light-induced photoepoxidation of propene by molecular oxygen over chromia–silica catalysts. *Chemical Communications*, pp. 2412-2413, ISSN 1364-548X

Narayanam, J. M. R., & Stephenson, C. R. J. (2011). Visible Light Photoredox Catalysis: Applications in Organic Synthesis. *Chemical Society Reviews*, Vol.40, pp. 102-113, ISSN 0306-0012

Ohama, Y., & Van Gemert, D. (Eds.). (2011). *Application of Titanium Dioxide Photocatalysis to Construction Materials*, Springer, ISBN 978-94-007-1296-6, Dordrecht Heidelberg London New York

Ouidri, S., & Khalaf, H. (2009). Synthesis of benzaldehyde from toluene by a photocatalytic oxidation using TiO₂-pillared clays, *Journal of Photochemistry and Photobiology A: Chemistry*, Vol. 207, pp. 268-273, ISSN 1010-6030

Palmisano, G., Augugliaro, V., Pagliaro, M., & Palmisano, L. (2007a). Photocatalysis: a promising route for 21st century organic chemistry. *Chemical Communications*, pp. 3425–3437, ISSN 1364-548X

Palmisano, G., Yurdakal, S., Augugliaro, V., Loddo, V., & Palmisano, L. (2007b). Photocatalytic Selective Oxidation of 4-Methoxybenzyl Alcohol to Aldehyde in Aqueous Suspension of Home-Prepared Titanium Dioxide Catalyst, *Advanced Synthesis & Catalysis*, Vol. 349, pp. 964 – 970, ISSN 1615-4169

Park, C.B., Lee, S.H., Subramanian, E., Kale, B.B., Lee, S.M., & Baeg, J.-O. (2008). Solar Energy in Production of L-Glutamate through Visible Light Active Photocatalyst-Redox Enzyme Coupled Bioreactor. *Chemical Communications*, pp. 5423-5424, ISSN 1364-548X

Parkin, P.I., & Palgrave, R.G. (2005). Self-cleaning coatings. *Journal of Materials Chemistry*, Vol. 15, pp. 1689–1695, ISSN 1364-5501

Pastori, N., Gambarotti, & C., Punta, C. (2009). Recent Developments in Nucleophilic Radical Addition to Imines: the Key Role of Transition Metals and the New Porta Radical-Type Version of the Mannich and Strecker Reactions. *Mini-Reviews In Organic Chemistry*, Vol. 6(3), pp. 184-195, ISSN 1570-193X

Pham, P.V., Nagib, D.A., & MacMillan, W. C. (2011). Photoredox Catalysis: A Mild, Operationally Simple Approach to the Synthesis of α-Trifluoromethyl Carbonyl Compounds. *Angewandte Chemie. International Edition*, Vol.50, pp. 6119-6122, ISSN 1521-3773

Pillai, U.R., & Sahle–Demessie, E. (2002). Selective Oxidation of Alcohols in Gas Phase Using Light-Activated Titanium Dioxide, *Journal of Catalysis*, Vol. 211, pp. 434–444, ISSN 0021-9517

Pouretedal, H.R., Norozi, A., Keshavarz, M.H., Semnani, A. (2009). Nanoparticles of zinc sulfide doped with manganese, nickel and copper as nanophotocatalyst in the degradation of organic dyes. *Journal of Hazardous Materials* Vol. 162, pp. 674-681, ISSN 0304-3894

Radhakrishnan,C., Lo, M.K.F., Warrier, M.V, Garcia-Garibay, M., A., & Monbouquette, H.G. (2006). Photocatalytic Reduction of an Azide-Terminated Self-Assembled Monolayer Using CdS Quantum Dots. *Langmuir*, Vol.22, pp. 5018-5024, ISSN 1520-5827

Ravelli, D., Dondi, D., Fagnoni, M., & Albini, A. (2009). Photocatalysis. A multi-faceted concept for green chemistry. *Chemical Society Reviews*, Vol. 38, pp. 1999–2011, ISSN 0306-0012

Ravelli, D., Albini, A., & Fagnoni, M. (2011). Smooth Photocatalytic Preparation of 2-Substituted 1,3-Benzodioxoles. *Chemistry - A European Journal*, Vol.17, pp. 572-579, ISSN 1521-3765

Reber, J.F., & Rusek, M. (1986). Photochemical Hydrogen Production with Platinized Suspensions of Cadmium Sulfide and Cadmium Zinc Sulfide Modified by Silver Sulfide. *The Journal of Physical Chemistry*, Vol. 90, pp. 824-834, ISSN 0022-3654

Sakai, N., Fujishima, A., Watanabe, T., & Hashimoto, K.(2003). Quantitative Evaluation of the Photoinduced Hydrophilic Conversion Properties of TiO$_2$ Thin Film Surfaces by the Reciprocal of Contact Angle. *The Journal of Physical Chemistry B*, Vol. 107, pp. 1028-1035, ISSN 1520-5207

Selloni, A. (2008). Crystal growth: Anatase shows its reactive side, *Nature Materials*, Vol. 7, pp. 613-615, ISSN 1476-1122

Selvam, K., & Swaminathan, M. (2010). Au-doped TiO$_2$ nanoparticles for selective photocatalytic synthesis of quinaldines from anilines in ethanol, *Tetrahedron Letters*, Vol. 51, pp. 4911–4914, ISSN 0040-4039

Selvam, K., Krishnakumar, B., Velmurugan, R., & Swaminathan, M. (2009). A simple one pot nano titania mediated green synthesis of 2-alkylbenzimidazoles and indazole from aromatic azides under UV and solar light, *Catalysis Communications*, Vol. 11, pp. 280–284, ISSN 1566-7367

Shiraishi, Y., & Hirai, T. (2008). Selective organic transformations on titanium oxide-based photocatalysts, *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, *Vol.* 9, pp. 157–170, ISSN 1389-5567

Shiraishi, Y., Sugano, Y., Tanaka, S., & Hirai, T. (2010). One-Pot Synthesis of Benzimidazoles by Simultaneous Photocatalytic and Catalytic Reactions on Pt@TiO$_2$ Nanoparticles, *Angewandte Chemie International Edition*, Vol. 49, pp. 1656 –1660, ISSN 1521-3773

Sivaranjani, K., & Gopinath, C.S. (2011). Porosity driven photocatalytic activity of wormhole mesoporous TiO$_{2-x}$N$_x$ in direct sunlight, *Journal of Materials Chemistry*, Vol. 21, pp. 2639-2647, ISSN 1364-5501

Skorb, E.V., Antonouskaya, L.I., Belyasova, N.A., Shchukin, D.G., Möhwald, H., & Sviridov D.V. (2008). Antibacterial activity of thin-film photocatalysts based on metal-modified TiO$_2$ and TiO$_2$:In$_2$O$_3$ nanocomposite. *Applied Catalysis B: Environmental*, Vol. 84, pp. 94-99, ISSN 0926-3373

Subba Rao, K. V., & Subrahmanyam, M. (2002). Synthesis of 2-Methylpiperazine by Photocatalytic Reaction in a Non-Aqueous Suspension of Semiconductor-Zeolite Composite Catalysts. *Photochemical & Photobiological Sciences*, Vol.1, pp. 597-599, ISSN 1474-905X

Sunada, K., Kikuchi, Y., Hashimoto, K., & Fujishima, A. (1998). Bactericidal and Detoxification Effects of TiO$_2$ Thin Film Photocatalysts. *Environmental Science & Technology*, Vol. 32, pp. 726–728, ISSN 1520-5851

Sunada, K., Watanabe,†T., & Hashimoto, K. (2003). Bactericidal Activity of Copper-Deposited TiO$_2$ Thin Film under Weak UV Light Illumination. *Environmental Science & Technology*, Vol. 37, pp. 4785-4789, ISSN 1520-5851

Tanaka, T., Ooe, M., Funabiki, T., & Yoshida, S. (1986). Formation of an Epoxide Intermediate in the Photo-Oxidation of Alkenes over Silica-Supported Vanadium Oxide. *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases*, Vol.82, pp. 35-43, ISSN 0956-5000

Tanaka, T., Takenaka, S., Funabiki, T., & Yoshida, S. (2000). Photocatalytic Oxidation of Alkane at a Steady Rate Over Alkali-Ion-modified Vanadium Oxide Supported on Silica. *Catalysis Today*, Vol.61, pp.109-115, ISSN 0920-5861

Tani, M., Sakamoto, T., Mita, S., Sakaguchi, S., & Ishii, Y. (2005). Hydroxylation of Benzene to Phenol under Air and Carbon Monoxide Catalyzed by Molybdovanadophosphoric Acid. *Angewandte Chemie International Edition*, Vol. 44, pp. 2586–2588, ISSN: 1521-3773

Tlili, A., Xia, N., Monnier, F., & Taillefer, M. (2009). A Very Simple Copper-Catalyzed Synthesis of Phenols Employing Hydroxide Salts, *Angewandte Chemie International Edition*, Vol. 48, pp. 8725–8728, ISSN: 1521-3773

Tricoli, A., Righettoni, M., & Pratsini, S.E. (2009). Anti-Fogging Nanofibrous SiO_2 and Nanostructured SiO_2–TiO_2 Films Made by Rapid Flame Deposition and In Situ Annealing. *Langmuir*, Vol. 25, pp. 12578–12584, ISSN 1520-5827

Ullah, R., & Dutta, J. (2008). Photocatalytic degradation of organic dyes with manganese-doped ZnO nanoparticles. *Journal of Hazardous Materials* Vol. 156, pp. 194-200, ISSN 0304-3894

Wang, R., Hashimoto, K., Fujishima, A., Chikuni, M., Kojima, E., Kitamura, A., Shimohigoshi, M., & Watanabe, T. (1997). Light-induced amphiphilic surfaces. *Nature*, Vol. 388, pp. 431-432, ISSN 0028-0836

Ward, D., White, J.R., & Bard, A.J. (1983). Electrochemical Investigation of the Energetics of Particulate Titanium Dioxide Photocatalysts. The Methyl Viologen- Acetate System. *Journal of the American Chemical Society*, Vol. 105, pp. 27-31, ISSN 1520-5126

Warrier, M., Lo, M. K. F., Monbouquette, H., & Garcia-Garibay, M. A. (2004). Photocatalytic Reduction of Aromatic Azides to Amines Using CdS and CdSe Nanoparticles. *Photochemical &Photobiological Sciences*, Vol.3, pp. 859-863, ISSN 1474-905X

Watanabe, T. et al. (1992): Proc. 1st Int. Conf. TiO_2 Photocatalyst, ed. H. Al-Ekabi

Weber, M., Weber, M., & Kleine-Boymann, M. (2005). Phenol, In: *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, ISBN: 9783527306732, Weinheim (Germany)

Weissermel, K., & Arpe, H.J. (1997). *Industrial organic chemistry* (3rd edition), Wiley-VCH, ISBN 3-527-28838-4 Gb, Weinheim (Germany)

White, J.M., Szanyi, J., & Henderson, M.A. (2003*).* The Photon-Driven Hydrophilicity of Titania: A Model Study Using TiO_2(110) and Adsorbed Trimethyl Acetate. *The Journal of Physical Chemistry B* , Vol. 107, pp. 9029-9033, ISSN 1520-5207

White, J.R., & Bard, A.J. (1985). Electrochemical Investigation of Photocatalysis at CdS Suspensions in the Presence of Methylviologen. *The Journal of Physical Chemistry*, Vol. 89, pp. 1947-1954, ISSN 0022-3654

Yang, C-C., Yu, Y-H., von der Linden, B., Wu, J.C.S., & Mul, G. (2010). Artificial Photosynthesis over Crystalline TiO_2-Based Catalysts: Fact or Fiction?. *Journal of the American Chemical Society*, Vol.132, pp. 8398-8406, ISSN 1520-5126

Yoshida, H., Murata, C., & Hattori, T. (1999). Photooxidation of Propene to Propene Oxide by Molecular Oxygen over Zinc Oxide Dispersed on Silica. *Chemistry Letters*, Vol.28, pp. 901, ISSN 0366-7022

Zhang, G., Yi, J., Shim, J., Leea, J., & Choi, W. (2011). Photocatalytic hydroxylation of benzene to phenol over titanium oxide entrapped into hydrophobically modified siliceous foam, *Applied Catalysis B: Environmental*, Vol. 102, pp. 132–139, ISSN 0926-3373

Zhang, Z., Hossain, Md F., & Takahashi, T. (2010). Photoelectrochemical water splitting on highly smooth and ordered TiO_2 nanotube arrays for hydrogen generation. *International Journal of Hydrogen Energy*, Vol. 35, pp. 8528-8535, ISSN 0360-3199

Zheng, Z., Huang, B., Qin, X., Zhang, X., Dai, Y., & Whangbo, M-H. (2011). Facile in situ synthesis of visible-light plasmonic photocatalysts $M@TiO_2$ (M=Au, Pt, Ag) and evaluation of their photocatalytic oxidation of benzene to phenol, *Journal of Materials Chemistry*, Vol. 21, pp. 9079-9087, ISSN 1364-5501

Zou, Y-Q., Lu L-Q., Fu, L., Chang, N.J., Rong, J., Chen, J-R., & Xiao, W-J. (2011) Visible-Light-Induced Oxidation/[3+2] Cycloaddition/Oxidative Aromatization Sequence: A Photocatalytic Strategy to Construct Pyrrolo[2,1-α]isoquinolines. *Angewandte Chemie International Edition*, Vol.50, pp. 1-6, ISSN 1521-3773

Zubkov, T., Stahl, D., Thompson, T.L., Panayotov, D., Diwald, O., & Yates, J.T. Jr. (2005). Ultraviolet Light-Induced Hydrophilicity Effect on $TiO_2(110)(1\times1)$. Dominant Role of the Photooxidation of Adsorbed Hydrocarbons Causing Wetting by Water Droplets. *The Journal of Physical Chemistry B*, Vol. 109, pp. 15454-15462, ISSN 1520-5207
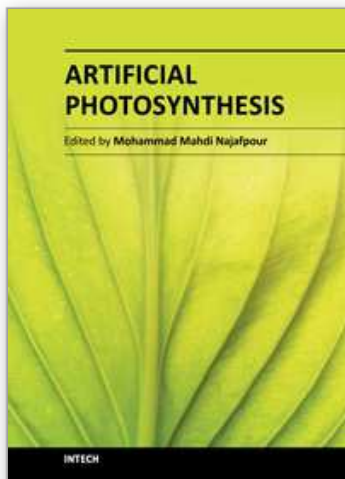
Artificial Photosynthesis

Edited by Dr Mohammad Najafpour

Photosynthesis is one of the most important reactions on Earth, and it is a scientific field that is intrinsically interdisciplinary, with many research groups examining it. We could learn many strategies from photosynthesis and can apply these strategies in artificial photosynthesis. Artificial photosynthesis is a research field that attempts to replicate the natural process of photosynthesis. The goal of artificial photosynthesis is to use the energy of the sun to make different useful material or high-energy chemicals for energy production. This book is aimed at providing fundamental and applied aspects of artificial photosynthesis. In each section, important topics in the subject are discussed and reviewed by experts.

How to reference

In order to correctly reference this scholarly work, feel free to copy and paste the following:

Cristian Gambarotti, Lucio Melone and Carlo Punta (2012). Semiconductors in Organic Photosynthesis, Artificial Photosynthesis, Dr Mohammad Najafpour (Ed.), ISBN: 978-953-307-966-0, InTech, Available from: http://www.intechopen.com/books/artificial-photosynthesis/semiconductors-in-organic-photosynthesis

INTECH
open science | open minds