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Review

EFFECT OF LIGHT ON THE AGING, CORROSION, AND DEGRADATION OF MATERIALS, IN RELATION TO THE ENHANCED REMOVAL OF ORGANIC POLLUTANTS

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Abstract

A review on advanced photochemical processes influencing properties of materials is presented. Particular emphasis is given on photolytic processes for the removal of pollutants. Separately are presented methods for the removal of biological pollution.

Major concern is paid to the methods for removal of persistent chemical pollutants. Two major groups of processes are known: homogenous and heterogeneous photocatalytic methods. The heterogeneous photocatalysis is usually done with semiconductor nanoparticles, capable to absorb light. In semiconductor the absorption of light quanta is connected with the promotion of electron(s) from valence to conduction band, leaving a positively charged hole(s) in CB. Electrons and holes can react with adsorbed molecules including water molecules. In this way the reactive intermediates are produced, which upon the sequence of reactions end with complete mineralization of ingredients.

The scaling-up of heterogeneous photocatalytic process is closely connected with efficacy of them. As a matter of fact, many factors are involved in kinetics of photocatalysis: concentration of pollutants; concentration of catalyst; temperature; radiant flux; quantum yield; dopants; etc. The interrelations among various parameters are mostly nonlinear, and construction of the photoreactor is very demanding task. In last 30 years a lot of study was done, and general conclusion is that TiO_2 *(mostly anatase) is most efficient photocatalyst, but there is a lot of work needed on improvement of such processes.*

Keywords: *photocatalysis, semiconductor photocatalysts, enhanced degradation of pollutants, doped photocatalysts.*

INTRODUCTION

Aging, corrosion and degradation of materials have common relation to effect of light. On the other hand, there are specific aspects of these changes which deserve their own elaboration. In this review, the issues of aging and corrosion will be briefly mentioned, and major subject will be removal of air- and water pollutants.

AGING

Aging is common feature of all materials, and there is a well defined distinction between physical and chemical aging [1]. The physical aging is easily monitored and predicted taking into account physical stress and temperature [2]. Generally, this aspect of aging is rather slow. Chemical aging is more complex and more efficient. It could be caused by chemical agents, but also by illumination and ionizing radiation, and similar ‘physical’ actions.

Particular concern is needed in the conservation of art and other collections because “Collections items damaged by light cannot be repaired or fixed by conservators. Light damage is permanent, irreversible, and cumulative, meaning that each exposure to light poses some damage that eventually causes significant change in the item including weakening, embrittlement, yellowing, darkening, color shift, and other issues depending upon the nature of the item exposed to light” [3, 4].

The importance of light for the changes of materials is well-known for a long time. It is a part of every accelerated aging test. For example, of dental materials [5, 6], polyvinyl acetate paints [7], acrylic paints [8, 9], of PVC/$CaCO_3$ composites [10], of chalcogenide glasses [11] (this is closely related to heterogeneous photocatalysis), of secondary organic aerosol material [12], of multi-crystalline silicon materials [13], and many other.

At this point we shall not offer a detailed account of light-assisted aging, but it will be explained along the general discussion of light-assisted degradation and removal of pollutants in air and water.

CORROSION

Corrosion is specific aspect of aging and degradation of metals [14].

The corrosion behavior of carbon steel was largely studied [15, 16]. Weight loss measurements were carried out in the three conditions, sunlight, shadow and dark conditions using the same solution. In polarization tests, an increase in the anodic current density and the corrosion rate of carbon steel appeared under UV light.

Since iron oxides exhibit a semiconductor-like behavior, the current density increases by the migration of photoelectrons and production of holes at the interface. EIS tests confirmed that in the presence of UV light the charge transfer resistance of the system decreases significantly, which is in agreement with polarization data.

The immersion test indicated that the sunlight increased the weight loss of the specimens within seven days. This is explained by the promotion of corrosion and rust formation due to the active oxygen generated by photoelectrochemical reactions under UV light.

The photo-corrosion is induced by an accumulation of photo-excited holes at the oxide surface, probably because the accumulation may increase the interfacial potential difference at the oxide surface and weaken the M-O bond of the oxide. The effect is due to photo-enhanced electromigration of charged defects like oxygen vacancies and interstitial Fe in the oxide film.

POLLUTANTS IN AIR AND WATER

Major types of pollutants, can be recognized as biological (bacteria and viruses) and chemical (natural or anthropogenic).

Bacterial pollutants - generally, pathogens are very common in the environment, and it is a subject of permanent concern of health and sanitary professionals. Air pollution by bacterial pollutants is serious only in closed space without proper ventilation and/or cleaning.

Because water is a natural medium for many microorganisms, biologically polluted water is more serious problem. Waterborne microbial species are known to be inactivated by solar disinfection, as given in Table 1 [17].

It was shown that pathogens listed in Table 1 are readily inactivated by exposure to sunlight in simple PET bottles.

Table 1. Several most common pathogen microorganisms and their susceptibility to light

Microbe Species		
Bacteria		
	Disease	Reduction with SODIS method (6h, 40 °C)
Escherichia coli	Indicator for water quality & enteritis	99.999%
Vibrio cholera	Cholera	99.999%
Salmonella species	Typhus	99.999%
Shigella flexneri	Dysentery	99.999%
Campylobacter jejuni	Dysentery	99.999%
Yersinia enterocolitica	Diarrhoea	99.999%
Virus		
	Disease	Reduction with SODIS method (6h, 40 °C)
Rotavirus	Diarrhoea, dysentery	90%
Polio virus	Polio	99.9 - 99.99%
Hepatitis virus	Hepatitis	Reports from users
Parasites		
	Disease	Reduction with SODIS method (6h, 40 °C)
Giardia species	Giardiasis	Cysts rendered inactive
Cryptosporidium spe.	Cryptosporidiasis	Cysts rendered inactive after > 10h exposure
Amoeba species	Amibiasis	Not rendered inactive. Water temperature must be above 50 °C for at least 1h to render inactive!

An additional list of microbial pathogens described in papers listed at SODIS site [18, 35].

Enterococcus sp.
Mycobacterium avium
Mycobacterium intracellulare
Pseudomonas aeruginosa
Salmonella typhimurium
Shigella dysenteriae type 1
Streptococcus faecalis
Staphylococcus epidermidis

Using advanced photolytic methods the removal of persistent microorganisms can be achieved [19]. Not only in water, but also on solid surfaces [20].

Chemical pollutants are equally versatile. Volatile organic compounds (VOC) are present in atmosphere stemming both from natural and anthropogenic sources. Importance of monitoring the status of VOC in atmosphere is well illustrated by World Meteorology Organization (WMO) in their “Statement Of Guidance For Atmospheric Chemistry” [21]. The photochemical transformations of VOCs are under extensive basic research for decades now [22-24].

The biggest source of chemical pollution is waste from chemical industry. Particularly, the organic raw industry waste [25, 26] may be a problem, because it is often hard to control its spreading. It is particularly true with gaseous pollutants [27] like formaldehyde [25, 28], (HCHO), automobile exhaust [29], liquid, gasoline [30, 31], benzene [32, 33]. Most of it can be readily removed using various standard methods. Crude, refractory organic compounds [34] (called persistent and/or recalcitrant) present the opposite problem and can be efficiently removed using only advanced photocatalytic methods [35]. It could be stated that the general approach for the removal of recalcitrant pollutants is their transformation to more reactive derivatives [36].

Pharmaceutical waste is another problem which is rarely seriously treated. Because of specific effect of waste drugs it’s important to completely remove them from water and soil [37]. On the other hand, it is equally important to monitor the effect of light on the drugs [38]. Similar status have pesticides [39] (and agrochemicals in general) [40].

Surfactants, and textile dyes (including their precursors) [41] are very common pollutants and their removal and monitoring of their degradation products attracted a lot of interest. As specific examples, one can point to the photoactive pollutants capable of producing harmful intermediates: photodegradation of 4-nitrophenol [42], chlorophenols [43, 44], and many others.

THE REMOVAL OF POLLUTANTS

Generally, most desirable methodology for the removal of pollutants is regular biological activity of specific organisms. In practice, it is hard to obtain efficient action of natural processes. The major reason is that high concentration of pollutants drastically inhibits the growth of biological material.

Research results are showing that particulate and dissolved natural organic material (NOM) in marine and surface waters, interstitial waters in sediments and soil solutions are influencing the (chemo)dynamics of inorganic and organic contaminants [45]. Among NOM components, the most interest attracted humic acids [46]. Humic substances (HS) are the largest constituent of soil organic matter (~60%) and are considered to be a key component of the terrestrial ecosystem, being responsible for many complex chemical reactions in soil [47]. They are very stable in natural medium because of their intimate interactions with soil mineral phases and are chemically too complex to be used by micro organisms. As far as soil is concerned, one of the most striking characteristics of HS is their ability to interact with metal ions, oxides, hydroxides, mineral and organic compounds [48], including toxic pollutants [49-51], to form water-soluble and water-insoluble complexes.

Formation of such complexes contributes to a reduction of toxicity through the passivation of harmful ingredients. Moreover, HS can interact with xenobiotic organic molecules such as pesticides [48, 52-54].

Very promising is the use of adapted microorganisms. Major problem is that much polluted (e.g. saline) waters are not fit for microorganisms [55]. Nevertheless, it can be a very cost-effective method for removal of pollutants.

Combination of various biological methods for the removal of pollutants is used for constructed wetlands. Constructed wetlands (wetland treatment systems) are wetlands designed to improve water quality. They use the same processes that occur in natural wetlands but have the flexibility of being constructed. As in natural wetlands, vegetation, soil, and hydrology are the major components. Different soil types and plant species are in use. Regarding hydrology, surface flow and subsurface flow constructed wetlands are the main types [56]. Subsurface flow constructed wetlands are further subdivided into horizontal or vertical flow.

Many constructed wetlands deal with domestic wastewater where BOD and COD (Biochemical and Chemical Oxygen Demand, respectively) are used as a sum parameter for organic matter. In general, the removal efficiency for organic contaminants is high.

ADVANCED METHODS FOR REMOVAL OF ORGANIC POLLUTANTS

Advanced oxidation comprises a range of similar but different chemical processes (AOP) aimed at tackling pollution in water, air and soil. Several directions are identified on advanced oxidation for water/wastewater treatment [57]. Water treatment by means of AOPs constitutes a core theme of research covering areas such as:

- industrial effluent treatment including, amongst others, distillery, agrochemical, craft-bleaching, pulp and paper, textile dye house, oilfield and metal-plating wastes;
- hazardous effluent treatment including hospital and slaughterhouse wastes;
- removal of pathogens and persistent, endocrine disrupting pharmaceutical residues from municipal wastewater treatment plant (WWTP) effluents (i.e. after secondary treatment);

AOPs can provide effective technological solutions for water treatment. Such solutions are vital for supporting and enhancing the competitiveness of different industrial sectors, including the water technology sector, in the global market. The main goals of academic, research and industrial communities through the development and implementation of environmental applications of AOPs will be:

- new concepts, processes and technologies in wastewater treatment with potential benefits for the stable quality of effluents, energy and operational cost savings and the protection of the environment;
- new sets of advanced standards for wastewater treatment;
- new methodologies for the definition of wastewater treatment needs and framework conditions;
- new know-how for contributing to enhancement of the European water industry competitiveness.

A specific feature of all advanced photolytic processes for treating of pollutants in air, soil and water is their ability for the microbial inactivation [20, 58]. General idea of AOPs is in the first place the use of reactive intermediates for the destruction of pollutants [26, 59, 60].

The major reactive species are OH radicals, singlet oxygen and ozone. The water photolysis is an obvious source for OH radicals.

Generally, photolytic methods [60, 61] can be divided on direct [59] and heterogeneous photocatalysis. Direct photolysis methods [62-64] usually involve use of photosensitizers, addition/generation of O_3 [66], and/or H_2O_2 [66]. More adequate term will be **homogeneous photocatalysis**. These methods are well described in classical works on photochemistry.

Direct irradiation with 206 nm UV of triphenyltin chloride (TPTCl), rhodamine B (RhB), and dimethyl phthalate (DMP) [68], proved that UV can directly decompose them without any oxidants or catalysts. It is reasonable to foresee that 206 nm UV would probably be suitable for the removal of most of organic pollutants in wastewater, which will provide alternative way to photo-degrade organic compounds in solution. However, intermediate products showed that only a part of targets can finally be mineralized into CO_2 under 206 nm UV irradiation.

Direct photolysis was applied for the removal of chlorophenols at various pH and using various light sources [43, 67]. The effect of wavelength and pH on the direct photolysis of 2-chlorophenol (2-CP), 4-chlorophenol (4-CP) and 2,4-dichlorophenol (2,4-DCP) in aqueous solution was studied by UV XeBr (282 nm) and KrCl (222 nm) excilamps. The highest pseudo-first order rate constants and quantum yields were found for molecular form of 4-CP (at pH 2 and 5.7) and anionic forms of 2-CP and 2,4-DCP (at pH 11) when irradiated by XeBr excilamp. The maximum removal efficiency of molecular 2-CP and 2,4-DCP with the lowest UV dose of absorbed energy was observed using KrCl excilamp. On the contrary, the XeBr excilamp needed the lowest dose ($\sim 2\ J\cdot cm^{-2}$) for complete degradation of molecular 4-CP and anionic 2-CP.

Some concerns are raised about the influence of UV irradiation on the quality of drinking water. A study was made [69] that showed that UV irradiation change the properties of DOM (dissolved organic matter), and increases the chlorine demand, but does not stimulate biological regrowth and biofilm formation in water distribution system.

Working at optimized experimental conditions (pH of 2, and H_2O_2 : EDTA molar ratio of 10), using a microwave-activated photochemical reactor and monitoring the EDTA degradation by total organic carbon analysis, mineralization ratios higher than 90% were observed at reaction times of 6 min [70].

It was found [28] that both background DOC (Dissolved Organic Carbon) and alkalinity have an inhibitory effect on the reaction rate of metaldehyde and therefore on EEos∗ especially for UV/TiO_2 where the alkalinity is a major issue and a chemical or physical process needs to be used to break the TiO_2 aggregates. Although more photons are absorbed by TiO_2 than by H_2O_2, the UV/H_2O_2 process remains more effective in term of quantum yield and energy consumption. The highest energy UV irradiation is affordable with so-called vacuum ultra violet (VUV) mercury lamps. A study of degradation of anatoxin-A [63] in aqueous solution showed that work with 172 nm lamp needs more than six time greater illumination in comparison with photolysis in the presence of moderate amount of H_2O_2. The optimization of reactor design, TiO_2 particles properties, and of the efficiency of light sources, will reduce the energy consumption and enhance use of AOPs as the drinking water treatment processes.

The photo-Fenton process [30, 31, 43, 60, 71] is one of the more widely studied AOPs. In the classical mechanism, hydroxyl radicals are generated by the cycle of oxidation and reduction reactions (outlined in eqs. 1 and 2) that requires the presence of ferrous ions (Fe^{2+}), hydrogen peroxide H_2O_2 and UV irradiation [72, 73]. In the first step, ferrous ions are oxidized by H_2O_2 (Fenton reaction), generating hydroxyl radicals (eq. 1). In the second step, the ferric ions (Fe3+) are reduced photochemically to the initial oxidation state (Fe2+), producing an additional hydroxyl radical, which reacts again via Eq. 1 as long as H2O2 is available.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{-} + OH^{-} \qquad (1)$$

$$Fe^{3+} + H_2O \qquad Fe^{2+} + H^{+} + OH^{-} \qquad (2)$$

∗ The electrical energy consumption currently represents the main part of the overall operating cost of AOPs and its evaluation is essential in order to evaluate the economic viability of a process. A figure of merit named electrical energy per order (EEo) has been introduced (Bolton, J.R., Bircher, K.G., Tumas, W., Tolman, C.A., Pure and Applied Chemistry 2001, 73, 627-637), which is defined as the electrical energy (in kWh) required to degrade a given volume of a pollutant, typically 1 m3, by one order of magnitude, and is expressed in kWh m^{-3}.

Being a homogeneous AOP system, the photo-Fenton process presents no limitations of mass transfer, favoring the kinetics of degradation relative to heterogeneous systems such as TiO2/UV. In some cases, the concentration of iron used in the photo-Fenton system may exceed the limit established by environmental legislation and may require removal of the ferric and/or ferrous ions at the end of the process.

An important barrier to industrial applications of AOP is the elevated cost of installing, operating, and maintaining artificial sources of UV radiation such as ionizers or lamps. Experiments on the degradation of raw gasoline in aqueous media demonstrated the feasibility of conducting the photo-Fenton process with medium-pressure mercury vapor lamps as the irradiation source. This suggested the possibility of using solar irradiation as the source of photons in this process. The experiments carried out in a falling film type solar reactor and three concentration variables were analyzed, *i.e.*, iron (Fe^{2+}) from 0.5 to 1.0 mM, total added hydrogen peroxide (H_2O_2) from 100 to 200 mmol/L, and sodium chloride (NaCl) from 200 to 2000 ppm.

As a matter of fact, an ecologically effective water treatment technique using electrochemically generated hydroxyl radicals [74], *i.e.* electro-Fenton process, was described as a good alternative to photo-Fenton reaction. It is worth mentioning the Fenton-like reactions as alternative, too, since it is not necessary to remove the ferric and/or ferrous ions at the end of the process and allow operation over a wide pH range [See Ref. 112].

Heterogeneous photocatalysis

Heterogeneous photocatalysis can be described as the acceleration of photoreaction in the presence of a solid catalyst. In the contexts of history and research, interest in heterogeneous photocatalysis can be traced back to many decades when Fujishima and Honda discovered in 1972 the photochemical splitting of water into hydrogen and oxygen in the presence of TiO_2 [75]. From this time, extensive research, much of it published, has been carried out to produce hydrogen from water in oxidation-reduction reactions using a variety of semiconductor catalyst materials.

In recent years (about two decades) heterogeneous photocatalysis arises as a major promising approach for efficient removal of pollutants [11, 35, 76-81]. In recent literature there are more than 2000 publications on the subject.

Semiconductors naturally emerged as photocatalysts, because of their specific energy gap between filled (valence) and empty (conducting) electron levels. Semiconductors have energy gap of few eV (ΔE in Fig. 1. Usually it is denoted as E_g – ‘energy gap’). The smaller the gap, the absorption is more in the visible part of spectrum. On the other hand, very small energy gap makes the material more reactive and susceptible to environmental conditions.

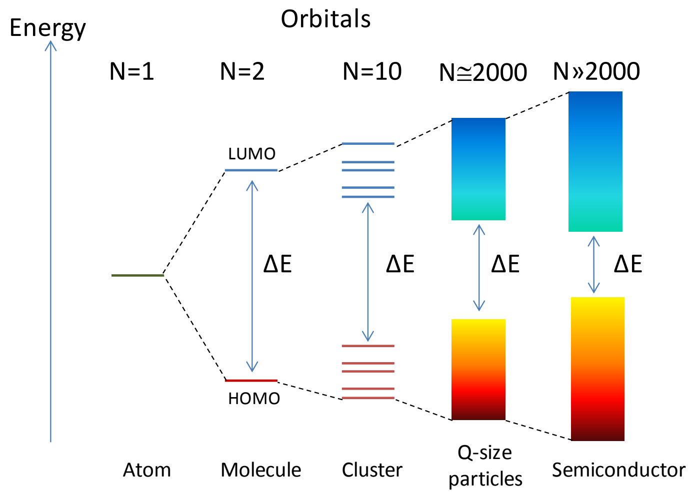

Figure 1. Change in the electronic structure of a semiconductor as the number N *of singly occupied orbitals present, increases from unity to clusters of more than 2000*

Several metal chalkogenides (oxides, sulfides and selenides) are viable photocatalysts: TiO_2, ZnO [82-85], CuO [86], CdS [87], CuSe [88], ZnSe [88], WO_3 [89], *etc*. But, in almost all practical applications, the catalyst used was non-porous titania (mainly anatase). Titania was sometimes modified either by iron doping or by deposition of a metal (Pt, Rh, or Ni).

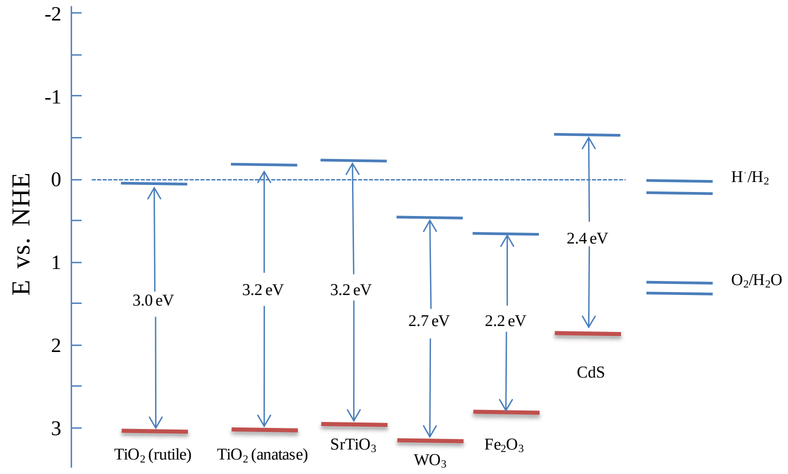

Figure 2. Valence and conductance band positions for various semiconductors and useful, relevant redox couples at pH≈0. In order to photoreduce a chemical species, the conductance band of the semiconductor must be more negative than the reduction potential of the chemical species; to photo-oxidize a chemical species, the potential of the valence band of the semiconductor must be more positive than the oxidation potential of the chemical species.

Inertness to chemical environment and long-term photostability has made TiO_2 an important material in many practical applications, and in commercial products ranging from drugs to foods, cosmetics to catalysts, paints to pharmaceuticals, and sunscreens to solar cells in which TiO_2 is used as a desiccant, brightener, or reactive mediator.

[*] The U.S. Food and Drug Administration permits up to 1% TiO_2 as an inactive ingredient in food products. While there are no known health effects associated with the use of TiO_2, a recent study found that 3-6 year old children are the most affected group of people that consume TiO_2 particles from food products. Many new properties of TiO_2 have been explored. It should be stated that regulatory framework for the use of TiO_2 in food products are yet to be firmly established in many countries, especially developing nations. The catalyst itself is unchanged during the process and no consumable chemicals are required. This results in considerable savings and simpler operation of the equipment involved.

Titanium dioxide is generally recognized as a most interesting photocatalyst [28, 60, 76, 90-93], which has a number of favorable properties: chemical inertness, does not change under prolonged irradiation, biologically neutral for almost all organisms. On the other hand, it has a number of unfavorable properties, too: a) Of the two important polymorphs of TiO_2, anatase begins to absorb UV light around 387 nm (band gap energy, E_{bg} ~3.2 eV), whereas the absorption onset of rutile occurs around 413 nm (E_{bg} ~3.0 eV) increasing sharply to shorter wavelengths. It means that TiO_2 absorbs a relatively small fraction (cca. 3-5%) of the solar radiation reaching the Earth's surface. b) The most important issue regards the notion that once photogenerated, e^- and h^+, tend to recombine more efficiently and rapidly, relative to otherwise slow redox chemistry at the TiO_2 surface (see Table 2).

The science that underlies heterogeneous photocatalysis has shown that the lowest energy level of the bottom of the conduction band (CB) of TiO_2 is a measure of the reduction potential of the photogenerated electrons, whereas the higher energy level of the valence band (VB) is a measure of the oxidation potential of photogenerated holes. pH-Dependent flat band potentials, V_{fb}, of the CB and VB bands of this metal oxide determine the energy of electrons and holes at the interface.

Accordingly, reductive and oxidative processes of couples with redox potentials more positive and more negative than the V_{fb} of CB and VB, respectively, can be driven by surface trapped electrons (e^-) and holes (h^+) that are poised to engage in various processes, the most important of which are photoreductions and photooxidations.

Corollary, the obvious strategy for the improvement of the performance of heterogeneous photocatalytic system is to lower the band-gap, to enable the absorption of the larger fraction of visible light. It can be achieved by doping of TiO_2 with various materials.

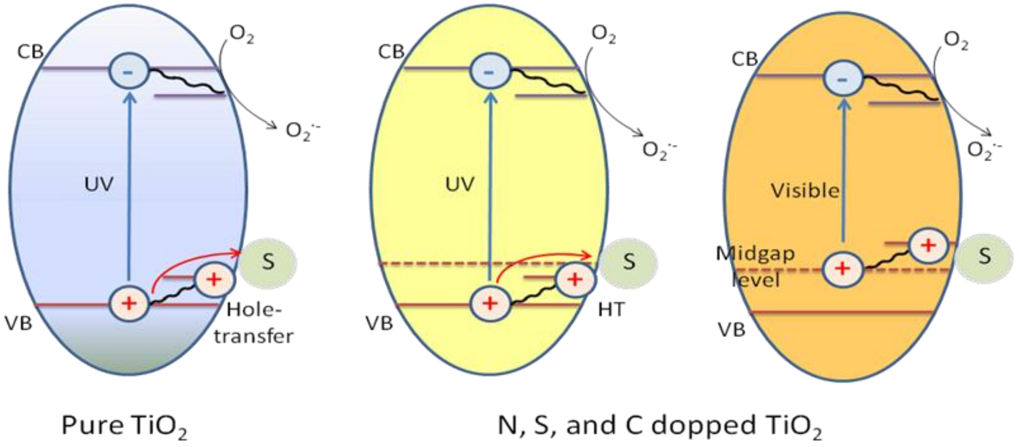

Figure 3. Doping of TiO_2 with p-block elements

Very good results were obtained by doping titania with p-block elements: N [94], C, S [95], B, F [96], as seen on Fig. 3. Although visible light absorption can be easily introduced by doping, absorption does not always result in satisfactory visible light photocatalytic activity, which is usually found to be not as good as that of pure TiO_2 under UV irradiation. As a matter of fact, several problems can be associated to single TiO_2 doping. High doping levels can hardly be attained because of the high formation energy, due to the unmatchable ionic charge and/or radius between the doped ions and host ones.

Absorption in the visible region remains rather limited, relative to the band-band absorption of pure TiO_2 in the UV region. Moreover, the recombination rate of the charge carriers is found to increase in doped samples, because of dopant-derived localized states in the band gap and bulk defects such as oxygen vacancies, acting as recombination centers. These also limit the mobility of the photogenerated carriers in the bulk, which hinders the migration of the carriers to the chemical species adsorbed on the photocatalyst surface. Also importantly, the introduction of electronic states above the valence band decreases the oxidation power under visible light irradiation.

The general working principle of photocatalysis is fairly well known and is the same in water and air. The process is initiated by activating the catalyst with light of sufficient energy, commonly this is ultraviolet (UV) light.

When this happens, an electron is excited from the filled valence band to the empty conduction band, leaving behind a hole in the valence band (Fig. 3). An electron-hole (e^-–h^+) pair is thus generated (reaction (3)), which can recombine again (either in bulk or on the surface, see Fig. 4) or which can migrate toward the catalyst surface and initiate redox reactions to reduce or oxidize the pollutants [78].

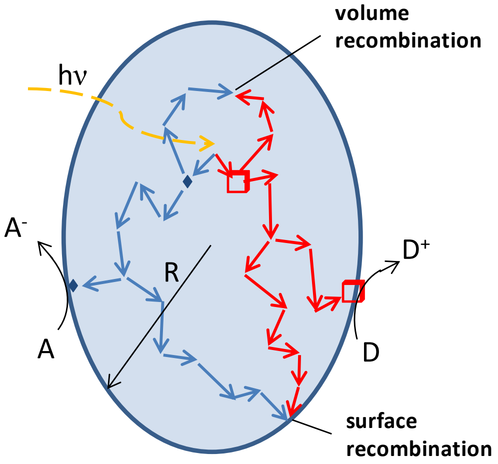

Figure 3. Fate of electrons and holes within a spherical particle of titania in the presence of acceptor (A) and donor (D) molecules

There are two distinct species present: a hole and an electron. The following reactions represent a couple of the possible reactions of e^- and h^+ on the surface, giving rise to reactive species

$$TiO_2 + h\nu \xrightarrow{h\nu > E_g} TiO_2(h^+ + e^-) \tag{3}$$

$$TiO_2(h^+) + {}^-OH_{(ads)} \rightarrow TiO_2 + OH^{\bullet}_{(ads)} \tag{4}$$

$$TiO_2(e^-) + O_{2(ads)} \rightarrow TiO_2 + O_{2(ads)}^{\bullet -} \tag{5}$$

The hole can react on the surface with adsorbed water or surface hydroxyl groups in order to form hydroxyl radicals (reaction (4)). These radicals are postulated to be very important for the oxidation processes because of their high activity. There exists a widespread agreement on the major role in TiO_2 photocatalysis of these hydroxyl radicals generated by adsorbed water species on the TiO_2 surface. Despite this consensus, several studies have questioned whether this mechanism is indeed reasonable to all TiO_2 photocatalytic oxidation reactions [97].

Apart from reactions with the positive hole, the electron can also initiate some reactions. It can, for instance, react with adsorbed oxygen to form the superoxide radical anion (reaction (5)).

It was concluded that free hydroxyl radicals can only be generated by the electroreduction of oxygen with photogenerated conduction band electrons because the photo-oxidation of nonadsorbed water molecules (or surface OH groups) with valence band holes is both thermodynamically and kinetically unfavorable. The detailed mechanism for the photocatalytic oxidation reactions thus remains a controversial issue.

The feasibility of these reactions depends on the redox potential of TiO_2. As can be seen in Fig. 5, the redox potential of the conduction band of TiO_2 is more negative than that of the $O_2/O_2^{\bullet-}$ redox couple. This means that oxygen can be reduced to superoxide radical anions (reaction (5)). The redox potential of several other species can be found in Fig. 5, where they are compared to the redox potential of TiO_2.

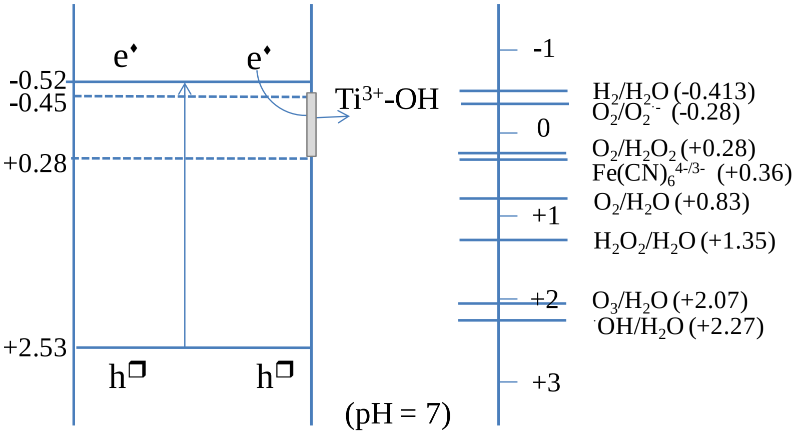

Figure 4. Schematic diagram showing the potentials for various redox processes occurring on the TiO_2 surface at pH 7

Other strategy for the improvement of photocatalytic efficiency is to change the surface of TiO_2 particles to increase the rate of oxidation/reduction of adsorbed substrate(s).

An important aspect of semiconductor photochemistry, in macrocrystalline and microcrystalline material, is the retardation of the electron-hole recombination process through charge carrier trapping [76]. As indicated earlier, in the preparation of semiconductor colloids, ideal crystal lattices are not produced in many cases, the colloid material can be so disorganized as to appear amorphous to X-ray diffraction. Thus most semiconductor colloid materials will have surface and bulk irregularities, *i.e.* defects, and these can act as electron-hole recombination centers or traps. The presence of such traps can alter significantly the photochemistry associated with the semiconductor colloid.

Table 2. Primary processes and associated characteristic time domains in the TiO_2-sensitized photomineralization of organic pollutants [126]

Primary process	Characteristic time
Charge carrier generation	
$TiO_2 + h\nu \rightarrow h^+ + e^-$	fs (very fast)
Charge carrier trapping	
$h^+ + {>}Ti^{IV}OH \rightarrow \{{>}Ti^{IV}OH^{\cdot +}\}$	10 ns (fast)
$e^- + {>}Ti^{IV}OH \leftarrow\rightarrow \{{>}Ti^{III}OH\}$	100 ps (shallow trap; dynamic equilibrium)
$e^- + {>}Ti^{IV} \rightarrow {>}Ti^{III}$	10 ns (deep trap)
Charge carrier recombination	
$e^- + \{{>}Ti^{IV}OH^{\cdot +}\} \rightarrow {>}Ti^{IV}OH$	100 ns (slow)
$h^+ + {>}Ti^{III}OH \rightarrow {>}Ti^{IV}OH$	10 ns (fast)
Interfacial charge transfer	
$\{{>}Ti^{IV}OH^{\cdot +}\}$ + organic pollutant $\rightarrow {>}Ti^{IV}OH$ + oxidized pollutant	100 ns (slow)
$\{{>}Ti^{III}OH\} + O_2 \rightarrow {>}Ti^{IV}OH + O^{\cdot -}$	ms (very slow)

Electron-hole recombination on most semiconductor materials is usually very fast [98], e.g. typically less than 10 ns for TiO_2 (see Table 2). However, if a hole scavenger is added to a semiconductor colloid, it is possible to remove some of the photogenerated holes and effectively trap the photogenerated electrons for a sufficient time to allow their transient absorption spectrum to be recorded. It was shown [99] that the specific-adsorbed anions such as F^-, PO_4^{3-}, and SO_4^{2-} are able to act as hole-scavenging agents. Similarly, if an electron scavenger is added, the transient absorption spectrum of trapped photogenerated holes can be determined. In a series of simple flash photolysis experiments conducted on TiO_2 colloids, were recorded the absorption spectra of trapped photogenerated electrons (using PVA/Polyvinylalcohol or thiocyanate as the hole scavenging agent) and of trapped photogenerated holes (using Pt or methyl viologen as the electron scavenging agent), which life-time is in microseconds.

The use of electron and hole scavengers in photochemical studies involving semiconductor colloids is widespread and often assumed rather than clearly stated. The most commonly used electron scavenger is dissolved oxygen, and the most commonly used hole scavenger is the PVA added to the colloid dispersion for steric stabilization or an added alcohol, such as isopropanol.

The study was done [100] which has shown that the recombination rate is in direct relation with light intensity. Fewer charge carriers - fewer recombinations. Because the charge carrier deactivation on the surface of particles is essential for the efficacy of the photocatalysis process, it is favorable to eliminate, as much as possible, the volume recombination of electrons and holes.

An interesting way is described by production of nano-flower structures which have extremely high surface to volume ratio [88].

There are reports [101] on the photodegradation of several dyes under exposure to visible light in the presence of TiO_2 nanoparticles. The visible-light irradiation mechanism (eqs 6-11) is clearly different from the UV-irradiation pathway described previously; the dye, not the semiconductor TiO_2, is excited by visible light:

$$\text{dye} + h\nu \rightarrow \text{dye}^* \tag{6}$$

$$\text{dye}^* + TiO_2 \rightarrow \text{dye}^{\cdot +} + TiO_2(e) \tag{7}$$

$$TiO_2(e) + O_2 \rightarrow TiO_2 + O_2^{\cdot -} \tag{8}$$

$$O_2^{\cdot -} + e + 2\,H^+ \rightarrow H_2O_2 \tag{9}$$

$$H_2O_2 + e \rightarrow {}^{\cdot}OH + OH^- \tag{10}$$

$$\text{dye}^{\cdot +} + O_2\ (\text{or } O_2^{\cdot -} \text{ or } {}^{\cdot}OH) \rightarrow \text{peroxide or hydroxyl intermediates}$$

$$\rightarrow \rightarrow \text{degraded or mineralized products} \tag{11}$$

The excited dye injects an electron to the conduction band of TiO_2, whence it is scavenged by preadsorbed oxygen, O_2, to form active oxygen radicals similar to those in UV irradiation processes. These active radicals drive the photodegradation or mineralization. The TiO_2 plays a significant role of an electron carrier, leading to separation of injected electrons and cationic dye radicals.

VERSATILE APPLICATIONS OF HETEROGENEOUS PHOTOCATALYSIS

Because of complex (photo)chemistry behind the heterogeneous photocatalytic processes, the search for the improved efficiency of these processes is mostly driven by researchers intuition, and every promising idea has to be tested experimentally for its validity. Here are several examples of these searches.

Photocatalyzed degradation of polymers in aqueous semiconductor suspensions [102] revealed that the photodegradation of water-insoluble polymeric films or particulates in TiO_2 aqueous dispersions is not very efficient. The blending of TiO_2 with PVC makes it more susceptible to the effect of light, but improvement is not much impressive.

Very efficient removal of chlorinated aromatics pollutants was achieved with photocatalytic membrane reactor [103]. The combination of dynamic membrane ($CaCO_3$) with photocatalysts (Fe-$ZnIn_2S_4$) is proved to be practicable for removal of halogenated compounds in water. This hybrid system can give rise of continuous photocatalysis, stirring, and separation of photocatalysts, in a single device. When the TiO_2 is used as photocatalyst, the performance is just 3-5 % lower than with Fe-$ZnIn_2S_4$.

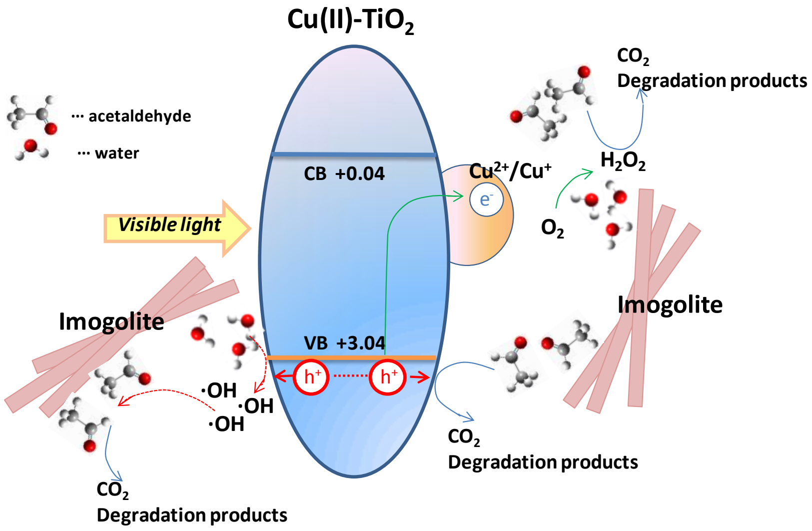

Figure 5. Possible photodegradation mechanisms of acetaldehyde under visible light irradiation; with Cu(II)-grafted TiO_2–imogolite composite as photocatalyst

Imogolite* with a nanotubular structure was synthesized hydrothermally and used to prepare imogolite–TiO_2 and imogolite–Cu(II)-grafted TiO_2 composites. The photocatalytic degradation of acetaldehyde by these composites was investigated [86]. Nanotubular imogolite had a high specific surface area (245 m2/g), with a strong surface affinity for water molecules. Under UV irradiation, photodegradation of acetaldehyde by the imogolite– TiO_2 composite was greater than that of TiO_2, indicating that imogolite plays an important role in adsorbing the acetaldehyde. The optimum mixtures of the TiO_2 as the photocatalyst, and imogolite as the adsorbent, lie between the compositions TiO_2:2-imo and TiO_2:3-imo. However, the photoactivity is also dependent on the relative humidity. With increasing relative humidity, the photodegradation activity decreases, but the photodegradation activity of the Cu(II)-grafted TiO_2–imogolite composite of composition Cu-TiO_2:3-imo was less affected by the relative humidity, and this composite also exhibited higher photoactivity under visible light irradiation than Cu(II)-grafted TiO_2 (Cu- TiO_2). The imogolite-containing composite has been suggested to be a very effective visible-light-driven photocatalyst and could be used to completely decompose or remove VOCs.

Nano-crystalline TiO_2 electrodes prepared by the electrophoretic immobilization of Degussa P25 on tin oxide glass showed [104] high efficiencies for the degradation of formic acid in one- and two-compartment photo-electrochemical cells (PEC). The application of +1.0 V to the TiO_2 electrode resulted in a marked increase in the rate of degradation of the formic acid when the concentration of dissolved O_2 was low.

*Imogolite is an aluminosilicate with a single-walled nanotubular structure consisting of a layer of aluminum(III) hydroxide (gibbsite), with isolated silicate groups bound on the inner wall.

There was not a marked increase in the rate in O_2 saturated solutions compared to the open circuit (OC) electrode. Similar results were obtained with nanocrystalline films of TiO_2 prepared on borosilicate and ITO (indium doped tin oxide) coated borosilicate glass, using a stirred tank reactor [105]. Photocatalytic and electrochemically assisted photocatalytic oxidation of formic acid under UVA and UVB irradiation shoved that the rate of formic acid oxidation under UVB irradiation was 30% greater as compared to UVA irradiation.

In a two-compartment PEC formic acid was photocatalytically degraded at the anode while Cu^{2+} was reduced to Cu^0 at the cathode when the illuminated TiO_2 anode was short-circuited to the copper mesh cathode. The initial IPCE (incident photon to current efficiency) for this system was 9.5%. This technology is worth testing whether it would work with ‘real’ industrial effluents and solar illumination.

Recently, a very marked improvement in doping of TiO_2 is achieved [106]. Usually, high doping will generate pronounced structure distortion that degrades the electron-hole separation. However, the substitutional replacement of surface bridging O’s (by surface bombardment with N atoms from adequate source) can retain the structure perfection even at the 9.4% doping level. The obtained samples combine beneficial effects of both extraordinary electronic structure at high doping level and superior charge separation efficiency with structure perfection.

The high activity of surface modified TiO_2 samples implies the importance of surface charge-trapping sites as compared to the bulk sites [107]. The surface N doping increases the photoactivity dramatically, but it does not show noticeable change of optical absorption. This is because only a small portion of the surface has been modified, which is not detectable by the UV-vis spectrometer. In the N-TiO_2 surface layer, the photogenerated electron can be captured by the π-conjugated structure of N *via* a percolation mechanism. Hence, the N sites act as the electron acceptors in the TiO_2, effectively suppressing the charge recombination and leaving more holes at Ti sites to form reactive species that promote the degradation of dyes/pollutants.

The results imply a conclusion that the photocatalytic activity is wavelength dependent. To interpret this, a schematic drawing of the energy diagram is shown in Figure 6.

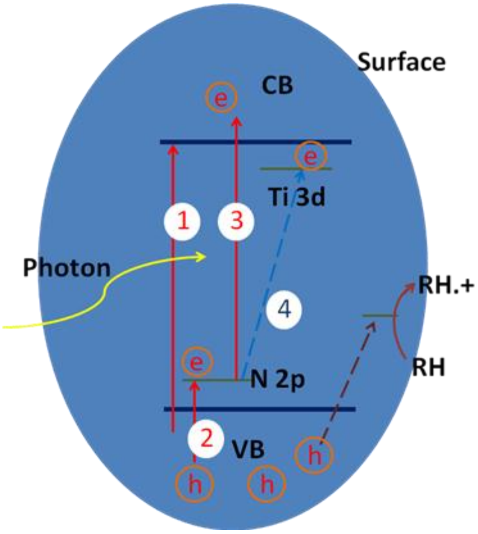

Figure 6. Schematic drawing of energy levels and the proposed processes of electron excitation in the N-TiO_2 samples

For the sample under UV irradiation, all the excitations of (1)−(4) will be facilitated, whereas only (2)−(4) are possible under visible light. The visible light activities for (2)−(4) are ~2.85 times lower than that under UV light. Therefore, the wavelength dependence of the external reaction efficiency (η) was found to be η(vis)/η(UV) = 0.35, which is in good agreement with the value of 0.3 for the charge separation efficiency ratio, Φ(vis)/Φ(UV) [108]. This implies that nearly all free charges generated by visible light excitation contribute to the photocatalytic reactions. The wavelength dependence of external reaction efficiency is reasonable because the final states of the electrons induced by visible light (Ti 3d ← N 2p transition) are different from that induced by UV excitation (Ti 3d ← O 2p and Ti 3d ← N 2p transition). Therefore, different redox potentials are generated by photons with different energies. The efficiency of this photocatalyst is twice that of the other doped TiO_2 [109], [110], probably due to the fact that modification is confined at the surface. Moreover, on the basis of XPS measurement and DFT calculations, broad states are formed at the VBM (valence band maximum), which benefits enhancing the lifetime of the photoexcited carriers [111]. The formation of broad states makes the diffusion of electrons easier inside the lattice, which retards the corresponding recombination.

A photoreaction generally takes place in water environment, and photogenerated electron−hole pairs can react with H_2O to form reactive oxygen species (ROS). Typically, the photogenerated electron combine with adsorbed oxygen to form superoxide anion ($O_2^{\cdot -}$), and the holes react with
OH^- to form hydroxyl radicals, ($OH^\bullet$). Subsequently, a chain reaction is activated to decompose the pollutants into small molecules. The majority of electron-hole pairs is trapped at bulk trapping sites and recombine there with release of heat.

Therefore, to have higher activity, not only the materials should absorb more photons, but also the amount of surface trapped electron-hole pairs should increase, competing with their recombination in the bulk. Surface nitridation can improve the photoactivity under visible light irradiation. However, the ability that the electron-hole pairs generated at N sites to migrate to the surface is also important. To achieve the best modified results, only the top ~10 nm of the surface needs to be engineered. Results suggest that the carrier diffusion dynamics may exhibit different behavior under UV and visible light irradiation.

As interesting alternative to TiO_2 photocatalyst, it was found [112] that tungsten oxide (WO_3) with a band gap sufficiently narrow for visible light absorption (*i.e.*, 2.6 eV) has the proper energy level of valence band (i.e., +3.1 V_{NHE}) for oxidation of absorbed water or hydroxide ions, into $^{\bullet}OH$, providing the potential capability for visible-light-induced water treatment and disinfection.

However, the conduction band (CB) potential (*i.e.*, +0.4 V_{NHE}) of WO_3 is not negative enough to reduce molecular oxygen as an electron acceptor ubiquitously present in aqueous environmental media. As a result, the photocatalytic reactions on pure WO_3 are limited due to the rapid recombination of electron-hole pairs.

The strategies to enable WO_3 to harness visible light for pollutant oxidation by facilitating charge separation include

(1) application of electron acceptors alternative to O_2 (*e.g.*, Cu(II), $S_2O_8^{2-}$),

(2) loading of co-catalyst (*e.g.*, CuO, Pt), and

(3) coupling of semiconductors with different band-gap structures.

For example, Cu(II) ions function as electron scavengers to retard the recombination of charge carriers, resulting in a two to three orders of magnitude improvement in the WO_3 photocatalytic surface mineralization of methanol.

The combination with Fenton-like reagent drastically accelerated WO_3-mediated photocatalytic oxidation under initially neutral pH conditions that favor the precipitation of Fe(III)-oxyhydroxides [89]. Although significant photo-reduction of Fe(III) to Fe(II) took place on WO_3 irrespective of pH conditions, the inability of Fe(III) as an electron scavenger to facilitate charge separation at neutral pH was confirmed, and is based on the negligible oxidative degradation in the WO_3/Fe(III) system.

On the other hand, the photo-generation of Fe(II) led to more rapid H_2O_2 decomposition in the WO_3/Fe(III)/H_2O_2 system (relative to the WO_3/H_2O_2 system), implying the possible involvement of the Fenton reaction in the enhanced photocatalytic degradation. The photolytic experiments with various probe compounds (benzoic acid, coumarin, and methanol) showed that the WO_3/Fe(III)/H_2O_2 system was more photoactive for the production of both $^{\bullet}OH$ and Fe(IV) than the WO_3/H_2O_2 system. The efficacy for hydroxylation of benzoic acid and coumarin (as $^{\bullet}OH$ probe) correlated well to the rate of photocatalytic 4-CP oxidation as initial pH of the aqueous suspensions of WO_3/Fe(III)/H_2O_2 increases, indicating that Fe(II)-mediated conversion of H_2O_2 to $^{\bullet}OH$ is responsible for the improved photocatalytic activity of the ternary system for organic oxidation. In addition to the iron-catalyzed decomposition of H_2O_2 to produce $^{\bullet}OH$ at circum-neutral pH, significant oxidative degradation under visible light irradiation was achieved in the WO_3/Fe(III)/H_2O_2 system.

The WO_3-modified TiO_2 nanotubes proved to be photocatalytically highly efficient [112] using solar light. Depending on the WO_3 content, either negative or positive effects were observed. It was proposed that the negative influence could result from the appearance of charge recombination centers, and by contrast, that the positive influence could be explained by a limitation of the photogenerated charge recombination induced by the modification. The formation of a $W_xTi_{1-x}O_2$ solid solution, leading to the emergence of intermediate energy levels depending on the tungsten content, was proposed. The TiNT-WO_3 4% composite material was found as the most effective photocatalyst for the degradation of organosulfur compounds such as diethyl sulfide.

Combination of photocatalytic methods with other AOPs is studied too. Effect of ultrasonication is very complex [122]. Ultrasound enhances the production of $HO\cdot$ and other free radicals, but, on the other hand, the light is scattered by cavitation bubbles attenuating the light flux.

Many pollutants like insecticides, pesticides, detergents as well as several chemical warfare agents (CWA) are organophosphorous compounds. The removal of dimethyl methylphosphonate (DMMP) and trimethyl phosphate (TMP) was obtained using the modified titania catalyst [123]. Deposition of Pt and Pd particles over TiO_2 Degussa P25 by mild chemical reduction allowed obtaining very active photocatalyst with activity much higher comparing to pure P25 and modified or unmodified Hombifine. The highest activity was observed at Pt content 1 wt.%, whereas almost same activity was at Pt and Pd content of 0.1%. Sulfuric acid additions further increased the activity at low Pt content but decreased it at high Pt content. Platinized photocatalyst demonstrated the same shape of reaction rate versus DMMP concentration dependence, with increased reaction rate constant that was attributed to a better charge separation. Photocatalytic oxidation of DMMP in 3 L recirculating batch reactor was studied with supported and suspended photocatalyst. The highest reaction rate was obtained with air bubbling and supported catalyst at the highest recirculation rate.

It was demonstrated that the increase in stirring rate or recirculation rate does not improve DMMP mass transfer. Instead, it improves the reaction rate *via* the increase of the dissolved oxygen concentration. The recirculating reactor demonstrated the same kinetic dependences as obtained in a beaker. The supported photocatalyst was stable in multiple uses whereas suspended photocatalyst was not.

The reverse processes, *i.e.* photocatalytic reduction which can enhance sequestration of CO_2, are subject of very intense studies [124]. Investigation is primarily directed to facilitating activation of two of the most thermodynamically stable molecules, CO_2 and H_2O. Conversions achieved so far are extremely small, <1%, occurring at a very slow rate, and catalysts tend to become deactivated very quickly. The CO_2 photoreduction process is highly complex, involving multi-electron transfer, and is non-selective, leading to a range of C_1 - C_3 compounds whose reaction pathways have not yet been fully established.

Another line of intensive research is the production of H_2 [125]. Despite a relatively low efficiency of the photocatalytic (TiO_2) hydrogen production system, for a capacity of 32.48 m^3/hr, the hydrogen production cost is around 3.00 US$, which is attractively low and acceptable, compared to the other water purification systems such as activated carbon or UV/O_3. There is a good chance to make the photocatalytic systems a better alternative way of hydrogen production.

ANALYSIS OF PARAMETERS FOR BUILDING OF LARGE SCALE EQUIPMENT FOR REMOVAL OF POLLUTANTS FROM WATER AND AIR

Potential of heterogeneous photocatalytic processes was recognized more than 30 years ago, but its implementation for large-scale removal of pollutants from water was very slow [80]. At the start, two major problems were recognized. How to provide uniform light distribution inside the reactor through the absorbing and scattering liquid to the catalyst, and how to provide the high surface areas for catalyst coating per unit of reactor volume. On this line were done the analyses of several other parameters influencing the yield and kinetics of photocatalysis [77, 113]:

Mass of catalyst

Either in static, or in slurry, or in dynamic flow photoreactors, the initial rates of reaction were found to be directly proportional to the mass *m* of catalyst. This indicates a true heterogeneous catalytic regime. However, above a certain value of *m*, the reaction rate levels off, and become independent of *m*. This limit depends on the geometry and on the working conditions of the photoreactor. It was found equal to 1.3 mg TiO_2 per square centimeter of a cross-section of a fixed bed, and to 2.5 mg TiO_2 per cubic centimeter of suspension.

These limits correspond to the maximum amount of TiO_2 in which all the particles - *i.e.* all the surface exposed - are totally illuminated. For higher quantities of catalyst, a screening effect by excess particles occurs, which masks part of the photosensitive surface. For applications, this optimum mass of catalyst has to be chosen in order (i) to avoid an unnecessary excess of catalyst and (ii) to ensure a total absorption of efficient photons.

One major barrier to the development of a photocatalytic reactor is that the reaction rate is usually slow compared to conventional chemical reaction rates, due to low concentration levels of the pollutants. Other crucial hurdle is the need to provide large amounts of active catalyst inside the reactor. Even though the effective surface area of the porous catalyst coating may be high, there can only be a thin coating (about 1 μm thick) applied to a surface. Larger thickness of catalyst layer washes away during experiments due to poor adhesion. Thus, the amount of active catalyst in the reactor is limited and, even if individual degradation processes can be made relatively efficient, the overall conversion efficiency will still be low. This problem severely restricts the processing capacity of the reactor and the time required to achieve high conversions is measured in hours, if not days.

Wavelength

The variations of the reaction rate as a function of the wavelength follows the UV-visible absorption spectrum of the catalyst, with a threshold corresponding to its band gap energy. For TiO_2 with $E \cong 3.02$ eV, this requires: $\lambda \leq 400$ nm. One must be aware of possibility of light absorption by reactants, too.

Initial concentration

The kinetics, generally, follows a Langmuir-Hinshelwood mechanism with the rate *r* varying proportionally with the coverage as:

$$r = k(KC/(1 + KC))$$

For diluted solutions ($C < 10^{-3}$ M), KC becomes << 1 and the reaction is first order, whereas for concentrations > *cca*. 5×10^{-3} M, ($KC >> 1$), the reaction rate is at maximum and is of the zeroth order. Similar Langmuir-Hinshelwood expressions including partial pressures P instead of C have been found for gaseous reactants. In some cases, such as in alcohol dehydrogenation, the rate follows a square root variation:

$$r = k[\, K^{1/2}C^{1/2} / (1 + K^{1/2}C^{1/2})\,]$$

This indicates that the active species react in the dissociated adsorbed state. In other cases, such as in the photocatalytic degradation and mineralization of chlorobenzoic acids, a zero kinetic order was found, even at low concentrations. This is due to a strong chemisorption on titania with the saturation of the hydroxylic adsorption sites. For a maximum yield, reactions should be performed with initial concentrations equal to, or higher than, the threshold of the plateau.

Temperature

Because of the photonic activation, the photocatalytic systems do not require heating. The true activation energy is nil, in agreement with an experimental activation energy E_a very small (a few kJ/mol). Photocatalysis is generally operating at room temperature. At low temperature (<0 °C), the activation energy E_a increases and tends to become equal to the heat of desorption of the reaction product. This is exemplified by the case of hydrogen in alcohol dehydrogenation or alkane-deuterium isotopic exchange, carried out on bifunctional Pt/TiO_2 photocatalysts [114, 115]. This means that at these low temperatures, the rate-limiting step becomes desorption of the H_2 (or HD) from the metallic part of the catalyst.

By contrast, at 'high' temperatures ($\theta \geq 70$ °C) for various types of photocatalytic reactions (as those that use mirror-focused solar light), the activity decreases and the apparent activation energy becomes negative [116]. This indicates that the adsorption of the reactant becomes the rate limiting step.

As a consequence, the optimum temperature is generally comprised between 20 and 80 °C. This explains why solar devices which use light concentrators require coolers. This absence of heating is attractive for photocatalytic reactions carried out in aqueous media and in particular for environmental purposes (photocatalytic water purification). There is no need to waste energy in heating water which possesses a high heat capacity. Photocatalysis has been presented as competitive with incineration for VOC treatment in air [117].

Radiant flux

The light power invested is determined by measuring the radiant flux. The total light power emitted corresponds to *cca*. 20% of the electrical power consumed. It has been shown, for all types of photocatalytic reactions, that the rate of reaction r is proportional to the radiant flux, Φ. This confirms the photo-induced nature of the activation of the catalytic process, with the participation of photo-induced electrical charges (electrons and holes) to the reaction mechanism. However, above a certain value estimated to be *cca*. 250 W/m², the reaction rate r becomes proportional to $\Phi^{1/2}$. It can be demonstrated that the rate of electron-hole formation becomes greater than the photocatalytic rate, which favors the electron-hole recombination:

$$e^- + p^+ \rightarrow N + E$$

(N: neutral center; E: energy (light $h\nu' \leq h\nu$, or heat).

The optimal light power utilization corresponds to the domain where r is proportional to Φ.

The problem of photon energy absorption has to be considered regardless of reaction kinetics mechanisms. The high degree of interaction among the transport processes, reaction kinetics, and light absorption leads to a strong coupling of physico-chemical phenomena - a major obstacle in the development of photocatalytic reactors [81].

The illumination factor is of utmost importance since the amount of catalyst that can be activated determines the water treatment capacity of the reactor. The volume of photocatalytic reactor, assuming a well-mixed reactor, can be expressed as

$$V_R = \frac{QC_{in}X}{\eta\kappa\mathfrak{R}}$$

where Q is the volumetric flow rate (m^3/s), C_{in} is the inlet pollutant concentration (mol/m^3), X is the fractional conversion desired, η is the effectiveness factor (the ratio of actual rate to observed rate), κ is illuminated catalyst surface area in contact with reaction liquid inside the reactor volume (m^2/m^3) and $\mathfrak{R}$ is the average mass destruction rate ($mol/m^2/s$). Hence, smallest reactor volume will be obtained when κ and $\mathfrak{R}$ are as large as possible for specified values of Q, C_{in}, and X. $\mathfrak{R}$ is a reaction specific parameter as it expresses the performance of catalyst for the breakdown of a specific model component, while κ is a reactor specific parameter representing the amount of catalyst inside a reactor that is sufficiently illuminated so that it is active, and is in contact with the reaction liquid. An increase in $\mathfrak{R}$ can be accomplished by modifying the physical nature of the catalyst in terms of its structure and morphology, or by the addition of additional oxidizing agents. Improving the degradation rates would lead to the need of reduced amount of catalyst to be illuminated, and, therefore, a smaller reactor volume. The parameter κ, illuminated specific surface area, helps to compare design efficiency of different photocatalytic reactors as it defines the efficacy to install as much active catalyst per unit volume of reaction liquid in the reactor.

Quantum yield

By definition, it is equal to the ratio of the reaction rate in molecules per second (or in mol per s) to the efficient photonic flux in photons per second (or in Einstein per second (an Einstein is a mol of photons)). This is a kinetic definition, which is directly related to the instantaneous efficiency of a photocatalytic system. Its maximum value is equal to 1. It may vary on a wide range according (i) to the nature of the catalyst; (ii) to the experimental conditions used and (iii) especially to the nature of the reaction considered. We have found values comprised between 10^{-4} and 0.7. The knowledge of this parameter is fundamental. It enables one (i) to compare the activity of different catalysts for the same reaction, (ii) to estimate the relative feasibility of different reactions, and (iii) to calculate the energetic yield of the process and the corresponding cost.

Quantum yield highly depends on electron-hole recombination in bulk. If the path to surface is shorter, the efficacy of chemical transformation of adsorbed molecule is improved. Producing the catalyst with mesoporous structure and suspended on reticulated support, having high surface to volume ratio, proved to be very effective [118, 119].

Modifications of the catalyst by noble metal deposit and ion-doping

As generally observed, the maximum quantum yields are always obtained with titania. In addition, anatase is the most active allotropic form among the various ones available, either natural (rutile and brookite) or artificial (TiO_2-B, TiO_2-H). In photocatalytic reactions involving hydrogen, either as a reactant (deuterium-alkane isotopic exchange) or as a product (alcohol dehydrogenation), the system requires the presence of a metal acting as a co-catalyst necessary (i) to dissociate the reactant (D_2) and (ii) to recombine H and D into dihydrogen (or HD). Additionally, the metal (i) attracts electrons, by photoinduced metal-support interaction (PMSI), (ii) decreases the electron-hole recombination and (iii) maintains the turn-over number constant [120].

Another modification was aimed at extending the photosensitivity of titania to the visible region to efficient harvest cheaper and more abundant solar photons. This was done by ion doping, either *n*-type (Nb^{5+}, Sb^{5+}, Mo^{6+}, Ta^{5+}) or *p*-type (Ga^{3+}, Cr^{3+}, Al^{3+}). Unfortunately, ion doping was found to strongly inhibit the reaction and decrease the quantum yield. This was explained by the fact that both pentavalent donor impurities and trivalent acceptor impurities behave as electron-hole recombination centers. However, this drawback could be turned into advantage by using ion doping as a means of passivating TiO_2-based pigments in paintings and plastics against weathering [121].

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