

PHOTOCATALYSIS - A REVIEW ON APPLICATIONS

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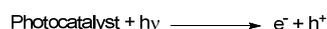
Abstract

“Photocatalysis” an emerging field focuses on the environmental applications. Organic reactions such as photooxidation, photoreduction, heterocyclic organic compound synthesis, cyclization reactions, mineralization of azo dyes, degradation reactions of organic pollutants, polymers, plastics etc., has been mainly focused on this review.

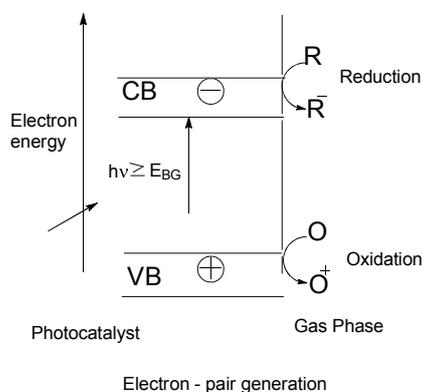
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1. Introduction

Photocatalysis refers to the acceleration of the rate of chemical reactions (oxidation/reduction) brought about by the catalyst, usually a semiconductor oxide by UV or visible radiation. Photocatalysis has become an integral part of the advanced oxidation process (AOP) which employs oxidizing agents like H₂O₂, O₃, Fentons reagent etc., for the effective detoxification of various organic pollutants.



Mechanism of the UV Photocatalysis involves the generation of valence band holes and the conduction band electrons, when a semiconductor photocatalyst absorbs light photon of energy greater than or equal to its band gap. The holes mediate the oxidation of organic compounds by the formation of hydroxyl radicals and the electrons mediate the oxidation and reduction reactions by the formation of superoxide radicals. The charge is transferred between the electron-hole pairs and an adsorbed, ground state, reactant on the photocatalyst surface.



1.1 The Photocatalytic reaction

The series of events following the illumination of a photocatalyst-reactant interface may be initiated by either (A) light absorption by the catalyst, which leads to the activation of the reactant, or by (B) direct excitation of the reactant, which is then quenched by the catalyst. Mechanisms (A) and (B) may operate simultaneously at a semiconductor-reactant interface, though (A) is generally considered to be the primary step for photocatalytic oxidation.

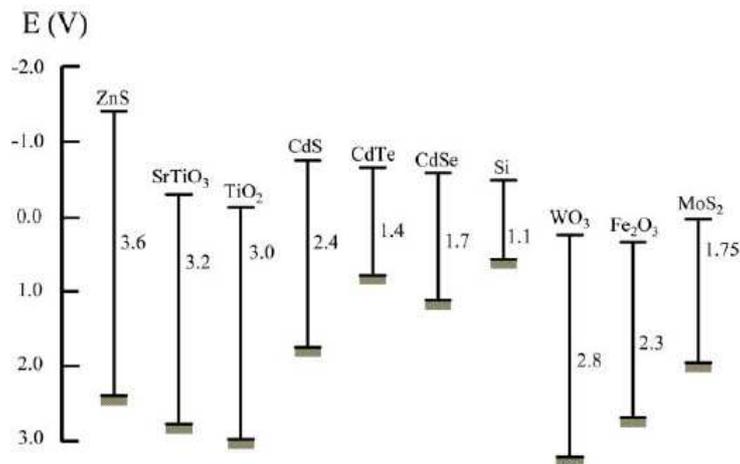
In the presence of electron-hole pairs on the catalyst surface, and water as vapour form in air, produce the oxidizing agents such as reactive oxygen species (ROS) which include oxygen (O_2), superoxide (O_2^-), peroxide (O_2^{2-}), and hydroxide (OH) radicals. These species can participate in a host of oxidation-reduction (redox) reactions, which are highly effective at the chemical destruction of VOC's (volatile organic compounds), particulate matter, microbes, ozone, NO_x, and SO_x.

Excited state conduction-band electrons and valence-band holes can recombine and dissipate the input energy as heat, get trapped in meta stable surface states, or react with electron donors and acceptors adsorbed on the semiconductor surface or within the surrounding electrical double layer of the charged particles. In the absence of suitable electron and hole scavengers, the stored energy is dissipated within a few nanoseconds by recombination [1]. If a suitable scavenger or surface defect state is available to trap the electron or hole, recombination is prevented and subsequent redox reactions may occur. The valence band holes are powerful oxidants, while the conduction-band electrons are good reductants.

2. Photocatalytic semiconductor materials:

Several simple oxide and sulfide semiconductors have band-gap energies sufficient for promoting or catalyzing a wide range of chemical reactions of environmental interest. They include TiO₂ ($E_g = 3.2\text{ eV}$), WO₃ ($E_g = 2.8\text{ eV}$), SrTiO₃ ($E_g = 3.2\text{ eV}$), ZnO ($E_g = 3.2\text{ eV}$), and ZnS ($E_g = 3.6\text{ eV}$). The redox potential of valence band hole and conduction band must be positive and negative respectively to generate hydroxyl and superoxide radicals. The band gap energy and the redox potentials [2] of the most common semiconductors, used as photocatalysts are shown below. The metal sulfide semiconductors are unsuitable based on the stability requirements in that they readily undergo photo anodic corrosion, while the iron oxide

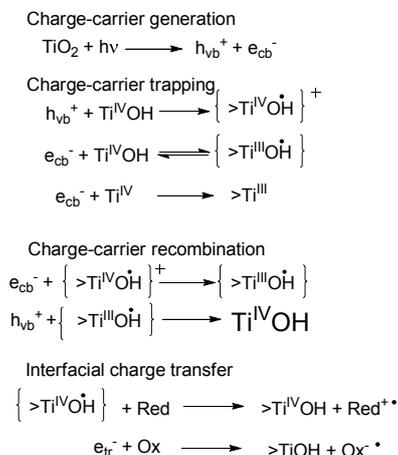
polymorphs are not suitable semiconductors, even though they are inexpensive and have nominally high band gap energies, because they readily undergo photo cathodic corrosion [3]. Titanium dioxide in the anatase form appears to be the most photoactive [4, 5] and the most practical semiconductor for widespread environmental application such as water purification, wastewater treatment, hazardous waste control, air purification, and water disinfection.



ZnO appears to be a suitable alternative to TiO₂; however, ZnO is unstable with respect to incongruous dissolution [6,7,8] to yield Zn(OH)₂ on the ZnO particle surfaces and thus leading to catalyst inactivation over time.

Titanium dioxide has different crystalline forms. The most common forms are anatase and rutile. The third crystalline form is brookite, which is uncommon and unstable. In the photocatalysis applications, it is known that, anatase is more efficient than rutile. Although TiO₂ exist in two forms as anatase and rutile, anatase with $E_{BG}=3.2\text{eV}$ is more active for Photocatalysis applications, even though rutile with $E_{BG}=3.0\text{eV}$, indicating the possibility of absorption of longer wavelength radiation. This is because of CB position of anatase form is more negative when compared to rutile form, which results in the higher reducing property of anatase.

2.1 Mechanism for the TiO₂ Photocatalytic reaction:



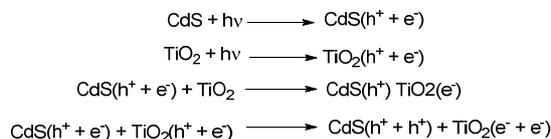
where $>\text{TiOH}$ represents the primary hydrated surface functionality of TiO_2 , [1] e_{cb}^- is a conduction-band electron, e_{tr}^- is a trapped conduction-band electron, h_{vb}^+ is a valence-band hole, Red is an electron donor (i.e., reductant), Ox is an electron acceptor (i.e., oxidant), $\{ >\text{Ti}^{\text{IV}}\text{OH} \}^+$ is the surface-trapped VB hole (i.e., surface-bound hydroxyl radical), and $\{ >\text{Ti}^{\text{III}}\text{OH} \}$ is the surface-trapped CB electron. Because of reversible changing in the oxidation state from +4 to +3, TiO_2 was found to be a most favored photocatalyst.

The ideal photocatalyst should possess the following properties: (i) photoactivity, (ii) biological and chemical inertness, (iii) stability toward photocorrosion, (iv) suitability towards visible or near UV light, (v) low cost, and (vi) lack of toxicity [9]. With these advantages, along with environmentally benign, low cost and the ease of synthesis makes TiO_2 as mostly used photocatalyst.

2.2 Mixed semiconductors

Generally speaking, any semiconductor doped with a secondary dopant would increase its activity. Several metals have been used for doping; these include Pt, Li^+ , Zn^{2+} , Cd^{2+} , Ag^+ , Co^{3+} , Cr^{3+} , Fe^{3+} , Al^{3+} , etc., [10]. The presence of transition metals increases the photocatalytic activity either by scavenging electrons that reduce the recombination of charges and therefore favors the $\text{HO}\cdot$ formation, or by modifying the surface properties of the material regarding the active sites, presence of defects etc., which could increase the adsorption and favor the interfacial reactions. In mixed semiconductor photocatalysts, the synthesis procedure has a marked effect on the

catalytic activity of the hybrid photocatalyst as reported in the case of TiO₂-SiO₂ [11], TiO₂-V₂O₅ [12], etc. This might perhaps be because the recombination is increased by crystallite defects.



Photocatalytic activity such as degradation, oxidation, reduction etc., were depend upon the presence of doped metal or non-metal or co-doped ion with TiO₂ was reported by Chen et al.,[13] as shown in table 1.

Table 1

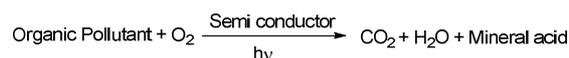
Photocatalytic effect of various metal ions, non-metal and co-doped with TiO₂

| Metal ion doped TiO ₂ | Photocatalytic activity |
|---|--|
| Sn ⁴⁺ | Photodegradation of phenol |
| Fe ³⁺ | Photocatalytic disinfection of E.Coli |
| V ²⁺ | Photooxidation of phenol |
| Pt ⁴⁺ | Photodegradation of dichloroacetate and 4-chloro phenol |
| Ag ⁺ | Photodegradation of 2,4,6-trichloro phenol |
| Au ³⁺ | Photodegradation rate of salicylic acid |
| V ²⁺ | Reduced photocatalytic activity for the oxidation of 4-chloro phenol |
| Cr ⁶⁺ | Oxidation of oxalic acid, propene, 2-propanol |
| Cu ²⁺ , Fe ³⁺ , Zn ²⁺ , Al ³⁺ | Reduced photodegradation of Rhodamine B |
| Cr ⁶⁺ , Ag ⁺ | Enhanced photodegradation rate for Rhodamine B |
| Co-doped TiO ₂ | |
| Cr/N | Reduced photocatalytic efficiency in the degradation of methylene blue |
| Li ⁺ , Na ⁺ , K ⁺ | Degradation of organic pollutants |
| Au/N | Higher photocatalytic activity for the degradation of methyl orange |
| Au/Fe | Enhanced activity for CO oxidation |
| Non-Metal doped TiO ₂ | |
| N | Higher photocatalytic activity for the decomposition of methylene blue and for the oxidation of isopropanol to acetone |
| C | Higher photocatalytic activity for the degradation of Cl ₃ COOH |
| F | Higher photocatalytic activity for the oxidation of acetone to CO ₂ |
| N/F | Higher photocatalytic activity for the decomposition of acetaldehyde and trichloroethylene. |

3. Application of Photocatalysis:

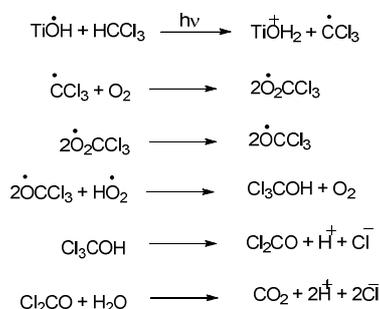
3.1 UV Photocatalytic degradation of organic compounds:

The complete mineralization of organic chloro solvents (pollutants) into HCl and CO₂ using TiO₂ as a photocatalyst has been demonstrated by Ollis and coworkers [14].



3.2 Degradation of Chloro compounds:

Kormann et al., [15] have proposed the following mechanism for chloroform oxidation after generation of the electron-hole pair due to excitation at wavelengths less than 380 nm.



Among the chloro compounds, the relative ease of degradation as follows:

Chloroolefins > chloroparaffins > chloro acetic acid

Bromo compounds like CHBr₃ and CH₂Br₂ exhibit higher degradation rates compared to corresponding chloro compounds. The semiconductor sensitizer for the above reactions must be photoactive, able to utilize visible and UV light, biologically and chemically inert, photostable and inexpensive.

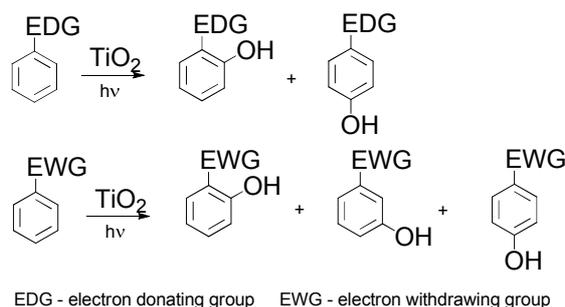
3.3 Photodegradation of phenol:

The degradation of phenolic compounds proceeds primarily by the attack of the hydroxyl radicals, which results in the hydroxylation of the parent compound at the ortho or para-position, due to the ortho- or para-directing nature of the phenolic -OH group [16, 17]. These are the primary intermediates, which on further exposure results in the formation of a fully hydroxylated secondary intermediate species. Further oxidation results in the fragmentation of the benzene ring to form C-6 and C-5 aliphatic carboxylic acids and aldehydes. In the case of chloro or nitro

substituted phenols, the hydroxyl group replaces the substituent group before the ring fragmentation.

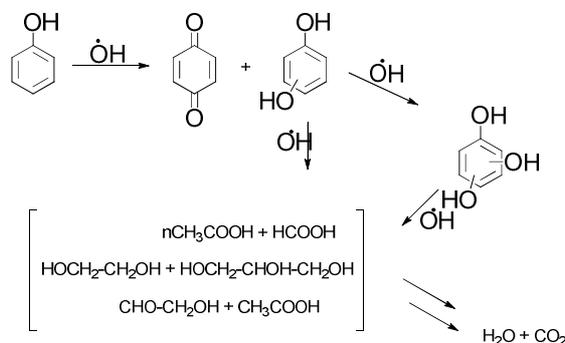
The longer (C-6, C-5, C-4) chain organic acids and aldehydes on longer exposure periods yield C-3, C-2 and C-1 organic acids. Finally, these shorter chain compounds mineralize to form CO₂ and H₂O. The degradation order of phenols as follows:

pentachlorophenol > trichlorophenol > dichlorophenol > 4-chlorophenol ≈ 2-chlorophenol > 2-methyl phenol ≈ 3-methyl phenol > phenol.



Chloro-methyl phenols (cresols) degrade much faster compared to chloro-nitrophenols, which can be attributed to the ring deactivating nature of the nitro group for the hydroxyl radicals to react with the phenolic compound. Moreover, it was found that the degradation is independent of the position of the substituents, but depends on the nature of the substituent group. In another study, nitro substitution was found to retard the degradation rate of nitrobenzene, while chloro- and hydroxy substitution resulted in an enhancement in the degradation rate [18].

TiO₂ catalyzed photocatalysis can be used to obtain mono-hydroxylated aromatic derivatives in fairly good yields [19, 20]. Under irradiation, the aromatic compounds adsorbed on the catalyst surface undergo two competing reaction pathways: (i) hydroxylation of the aromatic ring or, (ii) multi-step oxidation reactions to complete mineralization.



Photocatalytic degradation of phenolic compounds

3.4 Degradation studies of dyes

3.4.1 General considerations

Most of the dyes are toxic and potentially carcinogenic in nature and their removal from the industrial effluents is a major environmental problem. Various methods have been suggested to handle the dye removal from water; these include the biodegradation, coagulation, adsorption, advanced oxidation process (AOP) and the membrane process [21-26]. The various AOPs include the following:

- (1) Photolysis (UV or UV-V),
- (2) Hydrogen peroxide oxidation
- (3) Ozone (Ozonation, photo ozonation) and
- (4) Photocatalysis

Titanium dioxide mediated photocatalytic oxidation has been applied more extensively for dye studies. This is mainly because of its low cost, stable nature and its optical absorption in the UV region. The use of TiO_2 has also guaranteed good results in detoxification of water samples loaded with molecules like anilines, alcohols, and organo chlorides. A quick comparison between TiO_2 and other semiconductors such as ZrO_2 reveals that the photocatalytic efficiencies are quite different. Although the band gap energies for both TiO_2 and ZrO_2 are the same (3.1eV) the higher activity of TiO_2 could be assigned to a higher efficiency in the separation of the photo generated charges (less e^-/h^+ recombination rate) due to the structure of the material.

The degradation of a dye can be characterized in two ways: percent decolorization and percent mineralization. Decolorization refers to the reduction in concentration of the parent dye molecule under consideration at its characteristic wavelength, but does not refer to the complete removal of the organic carbon content. This is due to the formation of colored dye intermediates, which absorb at different wavelengths. Hence, complete degradation or mineralization occurs when all the organic carbon is converted to CO_2 . Therefore, analyzing the mineralization of the dyes in terms of the total organic carbon (TOC) content assumes importance.

The radical formed as a result of this reaction can undergo further transformation to yield other intermediates with smaller size. The presence of electron withdrawing groups was found to retard the degradation rate of the dye. They have attributed the degradation of the dye to both

photosensitized oxidation and reduction mechanisms. The anionic dyes exhibited higher decolorization rates compared to the cationic dyes.

3.4.2 Effect of substituents

The substituents attached to the naphthalene group of a dye molecule were hydroxylated more easily than those linked to the triazine group. Most of intermediates were aromatic and aliphatic carboxylic acids, which were further oxidized slowly to CO₂. The mineralization rates of the selected dyes were much slower than the decoloration rates.

3.4.3 Effect of TiO₂ form on dye degradation

Since various forms of TiO₂ forms are available such as P-25 Degussa TiO₂, Tiona PC 100, TiO₂ Tiona PC 500 and nano-sized TiO₂, the use of nano sized TiO₂ catalyst increases the surface area of the catalyst which can lead to more degradation of dye molecules at the end. Anatase forms of TiO₂ were effective catalysts for the degradation dye, whereas rutile TiO₂ does not efficiently induce the oxidation of the dye. Consequently, the catalytic ability of titanium dioxide is dramatically dependent on its crystalline form. Photo oxidation should occur with the same efficiency for both anatase and rutile. Samples of mixed morphology (TiO₂ P-25) were found to be generally the most photoactive [27].

TiO₂ adsorbed almost only cationic dyes, TiO₂ particles have a negative charge and, therefore, more readily adsorb cationic molecules. The highest values of photocatalytic degradation rate constant are observed for cationic dyes. There was a linear correlation between absorbance of illuminated solution of dyes and reverse values of the dyes photodegradation rate constant. Only cationic dyes could be adsorbed on the surface of the photocatalyst. Simultaneously, their photocatalytic degradation is faster than that of anionic dyes.

3.4.4 Effect of the initial concentration of dye

Percentage degradation decreases with increasing amount of dye concentration as dye concentration increases, more organic substances are adsorbed on the surface of TiO₂, whereas less number of photons are available to reach the catalyst surface and therefore less •OH are formed, thus causing an inhibition in degradation percentage [28].

3.4.5 Effect of additives

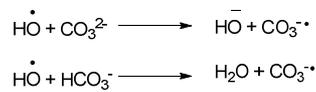
As ions which are initially added to the dye solution as ionic compounds in order to improve the industrial process. However on release of wastewater, the ions become an integral

part of the effluent. Many common ions present in dye wastewater are Fe^{2+} , Zn^{2+} , Ag^+ , Na^+ , Cl^- , PO_4^{3-} , SO_4^{2-} , BrO_3^- , CO_3^{2-} , HCO_3^- and persulphate ions. Each of these added ions causes a certain decrease in percentage degradation of the dye solution [29].

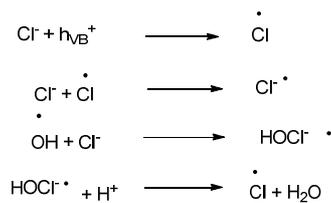
Fe^{2+} ions most likely undergo the following chemical reaction in solution with $\text{HO}\cdot$ radicals already produced in solution:



Dye degradation decreases in the presence of CO_3^{2-} and HCO_3^- ions, which scavenge the $\text{HO}\cdot$ radicals according to the following reactions thus causing a decrease in percentage degradation.



A decrease in degradation value in the presence of Cl^- is due to its hole and hydroxyl radical scavenging effect, which occurs as follows [30]:



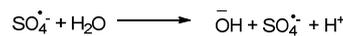
The presence of sulphate ions in solution also causes a decrease in percentage degradation because these ions can react with $\text{HO}\cdot$ radicals in solution and result in their depletion as follows [31]:



Addition of a strong oxidizing agent such as persulphate ions also decreases the degradation percentage because of the reason that it can produce sulphate ions in solution:

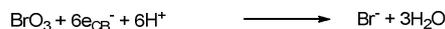


The sulphate ions can then react with $\text{HO}\cdot$ radicals as shown above. The sulphate radicals can further react with water molecules to produce more sulphate ions as follows:

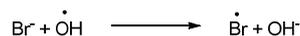


Since $\text{SO}_4^{\cdot-}$ is less reactive than $\text{HO}\cdot$ radicals, therefore SO_4^{2-} concentration increases in solution which leads to less dye degradation. The addition of bromate ion (BrO_3^-) can also

decrease percentage degradation. This can be explained on the basis that this species is an efficient electron scavenger and can react in the solution as follows [30]:



The bromide ions produced in the reaction can react with HO^\bullet radicals in solution, thus decreasing their concentration which result in less degradation.



The addition of ethanol can inhibit the photo degradation of a dye solution. This is because of the reason that ethanol can quench hydroxyl radicals which are the main source of dye degradation chemistry [32]. The degradation becomes less in the absence of oxygen and this has been attributed to the recombination of photo generated hole-electron pairs. Oxygen adsorbed on the surface of a semiconductor prevents the recombination process by trapping electrons according to the reaction



3.4.6 Effect of temperature

An increase in temperature increases the recombination of charge carriers and also the desorption process of adsorbed reactant species, thereby resulting a decrease of photocatalytic activity [33].

3.4.7 Degradation of an azo dye

Azo bonds are the most active bonds in azo-dye molecules [27] and can be oxidized by positive hole or hydroxyl radical or reduced by electron in the conduction band. The cleavage of N=N bonds leads to the decoloration of dyes. Interaction with solar light results initially in cleavage of the dye molecule in the vicinity of the azo bond followed by the formation of molecules containing naphthalene and benzene-type rings. Diazo dyes are less degradable than mono azo dyes. Major intermediates identified in these studies were aromatic amine, phenolic compounds and several organic acids. The results also indicated that in the photo catalytic degradation of azo dye, adsorption of dye to TiO_2 is one of the important factors which determine the degradation rate. Photocatalytic degradation of azo dye was proposed to proceed predominantly through oxidation by positive hole (or $\bullet\text{OH}$) and reduction by conduction band electron. Acridine, aryl methane, anthraquinone, nitro, xanthenes and quinine-amine dyes has been degraded with photocatalyst.

3.5 Other Applications:

Since 1972, when Fujishima and Honda discovered the photocatalytic splitting of water using TiO₂ electrodes; research on the heterogeneous photocatalysis started growing rapidly [34].

The environmental applications of heterogeneous photocatalysis include removing heavy metals such as (Hg), chromium (Cr), lead (Pb), Cadmium (Cd), lead (Pb), Arsenic (As), nickel (Ni) copper (Cu). The photoreducing ability of photocatalysis has been used to recover expensive metals from industrial effluent, such as gold, platinum and silver [35].

3.5.1 Destruction of organics:

Photocatalysis has been used for the destruction of organic compounds such as alcohols, carboxylic acids, phenolic derivatives, or chlorinated aromatics, into harmless products e.g, carbon dioxide, water, and simple mineral acids [36]. Water contaminated by oil can be treated efficiently by photocatalytic reaction [37]. Herbicides and pesticides that may contaminate water such as 2,4,5 trichlorophenoxyacetic acid, 2,4,5 trichlorophenol, triazine herbicides and DDT can be also mineralized [38].

3.5.2 Removal of inorganic compounds:

In addition to organic compounds, wide ranges of inorganic compounds are sensitive to photochemical transformation on the catalyst surfaces. Inorganic species such as bromate, or chlorate [39], azide, halide ions, nitric oxide, palladium and rhodium species, and sulfur species can be decomposed [40]. Metal salts such as AgNO₃, HgCl and organometallic compound (e.g CH₃HgCl) can be removed from water, as well as cyanide, thiocyanate, ammonia, nitrates and nitrites [41].

3.5.3 Water disinfections

Photocatalysis can also be used to destroy bacteria and viruses. *Streptococcus mutans*, *Streptococcus natuss*, *Streptococcus cricetus*, *Escherichia coli*, *scaccharomyces cerevisisas*, *Lactobacillus acidophilus*, poliovirus 1 were destructed effectively using heterogeneous photocatalysis [42]. The increasing incidence of algal blooms in fresh water supplies and the consequent possibility of cyanobacterial microcystin contamination of potable water *Microcystin toxins* is also degraded on immobilized titanium dioxide catalyst [43].

3.5.4 Degradation of natural organic matter

Humic substances (HS) act as a source of methyl groups and thus react with hypochlorite ion which is used as a biocide in water treatment plants, to produce disinfectant by-products e.g., trihalomethanes, haloacetic acids, other chlorinated compounds and nitriles, some of which are suspected to be carcinogenic [44]. Advanced oxidation has been applied to decreasing the organic content in water including humic acid [45, 46] It has the advantage of not leaving any toxic byproducts or sludge. Degradation of the humic acid or other fraction of humic substances has not been studied in detail. The first work in this field was carried out by Bekbolet in 1996, who studied the effectiveness of photocatalytic treatment on the degradation of humic acid [47].

3.5.5 Pesticides

The mineralization of the pesticides should result in the conversion of these hazardous compounds to innocuous products of N, S and P along with CO₂ and H₂O. During mineralization, phosphorous is converted to orthophosphoric acid (H₃PO₄), nitrogen to NO₃⁻ and NH₄⁺ ions, and sulphur to SO₄²⁻ ions [48].

3.5.6 Pharmaceutical compounds

Recently, photocatalytic degradation of pharmaceutical compounds and drugs are widely studied, the time taken for the complete mineralization is longer compared to the removal of the parent compound, indicating that the degradation intermediates are quite stable. Moreover, toxicity tests prove that the intermediates formed during the degradation are more toxic compared to the parent pharmaceutical compound.

3.5.7 Polymers and plastics

Photo degradation is an important mode of polymer degradation wherein the incident light radiation itself induces the scission of the macromolecule by the initiation of polymer radicals, or results in the generation of hydroxyl (·OH) radicals in presence of oxidizing agents and/or catalysts, which then attack the polymer backbone to initiate the radicals [49]. Photo degradation of the polymers can be carried out either in the solid or liquid phase. In the solid state, the polymeric materials are exposed to UV radiation or sunlight in the form of thin films or sheets, while in the liquid phase; the polymers are dissolved in aqueous or organic solvents. Although the degradation of polymers in the solid state is more realistic from a practical

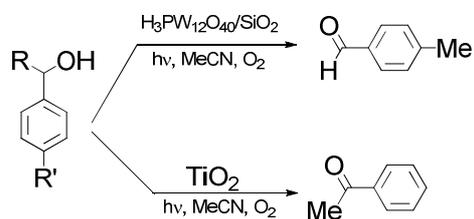
viewpoint, liquid phase degradation is faster, owing to the homogeneous medium which offers enhanced mass transfer of the reactants and products.

The first step in the Photocatalytic degradation of the polymers [P] is the formation of the hydroxyl radicals ($\cdot\text{OH}$) from the TiO_2 surface. In the presence of organic solvents or in the absence of moisture, surface hydroxyl groups present in TiO_2 serve as the key source of hydroxyl radicals. The UV photon and/or the $\cdot\text{OH}$ radicals generated attacks the polymer, resulting in the generation of polymer α -radical. These α -radicals are the precursors of chain breakage. The next step is the reaction of [P.] with atmospheric oxygen to form polymer peroxy radicals [POO.]. These combine bi molecularly with one another and form [POO-OOP] species. Thus, with the exclusion of oxygen, polymer oxy radicals are formed [PO.].

3.6 Applications of Photocatalysis in synthesis

3.6.1 Photooxidation and oxygenation reactions

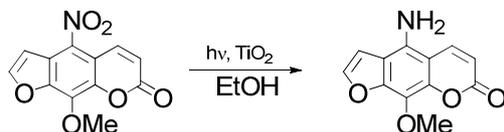
Upon photocatalysis, benzylic and allylic alcohols give carbonyl derivatives by using O_2 rather than inorganic oxidants based on noxious metals, improving both economic and environmental aspects. TiO_2 (anatase) was found suitable for the oxidation of 1-phenylethanol in dry acetonitrile under a slow stream of oxygen [50].



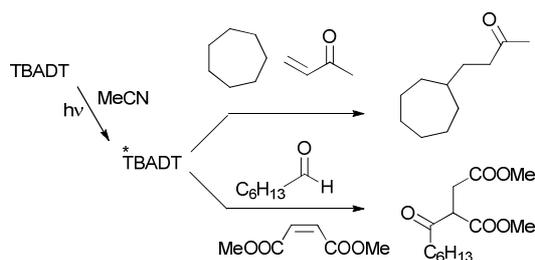
Alkylaryl and diaryl sulfides were cleanly oxidized using the photocatalyst 2,4,6-triphenylthiopyrylium salt (TPTP) encapsulated within a HY zeolite through a ship-in-the-bottle synthesis. The oxidation of thioanisole to sulfoxide in 85% yield upon irradiation by blue light. The Photocatalytic method employs safe, easy-to-handle reagents and avoids the use of elemental fluorine or of highly reactive derivatives usually required [51]. Oxidation to the radical cation and deprotonation give the benzyl radical that, after further oxidation to the cation, adds fluoride.

3.6.2 Photoreduction

When a suspension of titanium dioxide (anatase, 5.0 g/L) in ethanol containing 5-nitro-8-methoxypsoralen is irradiated under nitrogen, 5-amino-8-methoxypsoralen is formed in 85% yield [52].

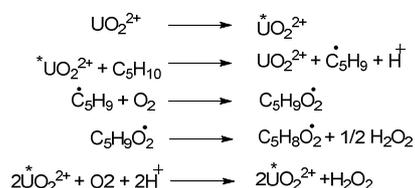


Photocatalysis gives preparatively useful results in the alkylation of electrophilic alkenes by activating R–H and RCO–H bonds under mild conditions, thus skipping the preliminary conversion into the more reactive derivatives R–X and RCO–X and the use of a chain transfer agent that are required in the corresponding thermal processes. Thus, polyoxotungstate salts (e.g. tetrabutylammonium decatungstate, have been used as photocatalysts in the radical conjugate addition of electron-poor olefins by cycloalkanes [53, 54]. TBADT was active for at least 50 cycles and was easily separated. Thus, 4-cycloheptyl-2-butanone was prepared in 56% yield from 3-buten-2-one and cycloheptane. Hydrogen abstraction from aldehydes likewise smoothly occurred and the acylation of α,β -unsaturated nitriles, ketones and esters was again successful. Noteworthy, equimolar amounts of aldehyde and olefin were used, in contrast to thermal methods where a large excess of aldehyde is required. Moreover, the reaction could be carried out at a low temperature, thus preventing the decarbonylation of the intermediate acyl radicals that competes or predominates in thermal reactions. This made acylation successful also with α -substituted aldehydes [54].

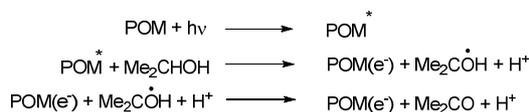


The titania-assisted photodegradation of aromatics is the mineralization of phenol with *p*-benzoquinone, hydroxylated aromatic compounds and aliphatic compounds as intermediates. [54] Hydroquinone and catechol accumulate, consistent with initial ortho-para attack by OH radicals. Indeed, the photodegradation rate for *o*-substituted phenols correlates with the stability

of adducts with the OH radical. A homogeneous inorganic catalyst UO_2^{2+} absorbs visible light to produce a long-lived, strongly oxidizing excited state, $^*\text{UO}_2^{2+}$, which is capable to catalyse the aerobic oxidation of cyclopentane to cyclopentanone [55].

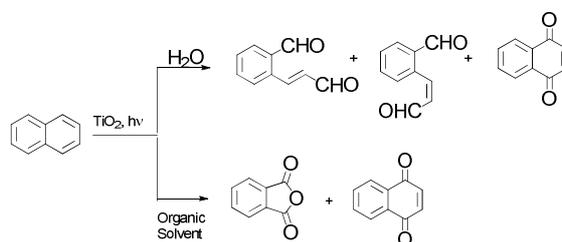


Polyoxometalates (POMs) also induce reversible redox reactions upon irradiation, acting as multielectron and oxygen relays [56]. The reaction route commonly proposed for the conversion of organic substrates (mainly alcohols) is H-abstraction, as shown in the case of 2-propanol oxidation.

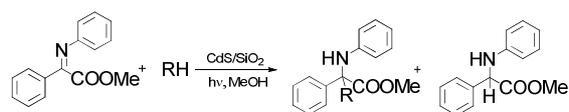


Phthalocyanine and porphyrin complexes have been widely studied as photocatalysts for hydrocarbon aerobic oxidation such as in the case of iron(III) mesotetrakis (2,6-dichlorophenyl)porphyrin, working in aqueous solutions of appropriate surfactants to form micelles, where the oxygenation of alkenes to epoxides smoothly takes place [57].

Water (containing 1% CH_3CN) and organic solvents give different selectivities in the attractive oxidation of naphthalene and its derivatives [58]. In the former case 2-formylcinnamaldehydes together with 1,4-naphthoquinone were formed, with a maximum yield of 11% when conversion was ca. 50%. Conversely when using organic solvents the main product was phthalic anhydride and considerable quantities of 1,4-naphthoquinone were also formed.

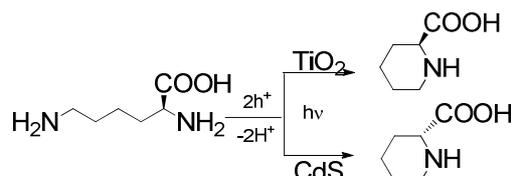


Novel unsaturated N-phenyl- α -amino esters can be obtained by irradiation at 350 nm of silica-supported CdS methanolic suspensions. The involved reagents are methyl (2Z)-phenyl(phenylimino)acetate and various cyclic olefin [59].

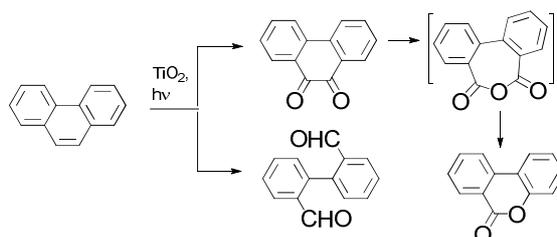


3.6.3 Heterocyclic compound synthesis

Amino acids in deaerated aqueous suspensions [60] of TiO_2 and CdS are successfully cyclized via a combination of oxidation and reduction with full retention of (S)-configuration in the product (pipercolinic acid) when the reaction was promoted by TiO_2 .



Irradiating solutions of phenanthrene and acetonitrile at 340 nm in the presence of TiO_2 yields a coumarin compound at room conditions; with 8% water and oxygen as oxidant, [61] this type of compound retains appeal since they are intermediates for many chemicals, including pharmaceuticals and fluorescent dyestuffs.



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