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Materials for selective photo-oxygenation *vs* photocatalysis: preparation, properties and applications for environment and health.

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Abstract

This perspective papers compares the properties and applications in environmental and health fields of organic photosensitizers (embedded in solid organic or inorganic inert supports) and of TiO_2-based photocatalysts. The basic principles of photosensitization and photocatalysis are recalled and the properties of the reactive oxygen species (ROS) produced under irradiation in both cases are reviewed.

Various families of organic photosensitizers (PSs) and their immobilization on different supports are then described. The properties of these materials are summarized. A chapter is dedicated to their applications for fine chemistry, disinfection, photodynamic therapy (PDT), degradation of water persistent pollutants and solvent-free oxygenation of selected chemicals.

After a short reminder of the latest reviews on TiO_2-based photocatalysis, some selected applications of supported TiO_2 materials are reported in the fields of water treatment, of active photocatalytic indoor air remediation/disinfection and of passive materials designed not only for self-cleaning but also for air pollutants and microorganisms removal.

Both types of materials are quite complementary and their advantages/drawbacks are highlighted. The selectivity and extended lifetime of singlet oxygen ($^1O_2$) produced under visible-light by PS-containing materials make them highly attractive for the selective oxygenation of persistent pollutants in wastewater containing complex matrices or for PDT. On the other hand, TiO_2-base photocatalysts are devoted to the complete mineralization of pollutants. However, their large field use under visible irradiation is still to be developed.

1. Introduction

Photo-oxidation in the presence of a *catalyst* under room temperature and pressure conditions, which makes use of oxygen of air and water as the only chemical species and either UVA (315-400 nm) or visible (400 to 760 nm) radiation as energy is considered as a green process. The most often used *photocatalysts* are semi-conductors, mainly titanium dioxide (TiO_2), which when irradiated under UVA give rise to *redox reactions* of various species (water, oxygen, organic or mineral pollutants) adsorbed on its surface both in solution and in the gas phase.[1,2,3,4,5] Alternatively, organic photosensitizers or dyes may be included, adsorbed or grafted on various inorganic or organic supports, giving rise to *photosensitizing materials* also able to induce the formation of *reactive oxygen species* (ROS) when irradiated mainly in the visible range and leading most often to photo-oxygenation reactions.[6,7] In the following the distinction will be made between *photocatalysts* and *photosensitizing materials* and their different reactivity will be explained.

Photocatalysis has been extensively investigated and used as an advanced oxidation process (AOP) with several well-known environmental applications, such as self-cleaning and defogging surfaces,[8] water purification,[9] air purification,[10,11,12] disinfection.[13] Other applications deal with energy concerns such as hydrogen generation[14,15,16] or carbon dioxide reduction[17,18,19,20]. The number of papers on these topics is steadily increasing. As an AOP, photocatalysis is aimed at oxidizing pollutants up to their mineralization (transformation into carbon dioxide, water and eventually mineral acids), avoiding as far as possible the formation in significant amount of incompletely oxidized side-products, which have to be carefully controlled for any application.

Alternatively, *photosensitizing materials* involving an *organic photosensitizer included in a supporting inert material* are very useful in some selected cases: mild and selective oxygenation of high-added value products in fine chemicals synthesis,[21,22,23,24] treatment of special wastes containing sulfur compounds,[25,26] or bactericidal photodynamic inactivation (PDI),[27,28,29] besides better known applications for wastewater treatment[30] and photodynamic therapy (PDT).[31,32]

This perspective paper will describe the mechanisms of *photocatalysis vs photosensitization* and the main reactive oxygen species (ROS) expected in both cases. It will give some general information on various photosensitizing materials and on their possible applications. Owing to the huge amount of papers on photocatalytic materials, only review papers on TiO_2-derived materials will be recalled here with selected applications for the purpose of comparison with PS-containing materials. Self-cleaning or superhydrophilic surfaces as well as sensitized TiO_2 will be excluded from the discussion.

2. Photocatalysis *vs* photo-oxygenation: basic mechanisms

2.1. Unselective reactions of photo-produced radicals by photocatalysis

Photocatalysis is based on the excitation of narrow band-gap semi-conductors (usually TiO_2) to generate electrons and holes under UV radiation (Figure 1). “When a photocatalyst absorbs a photon of energy equal to or greater than its band-gap (E_g), an electron-hole pair is generated. Subsequently the pair is separated into a free electron and a free hole (h^+, e^-). The electron and hole walk randomly to the surface where they are trapped (h^+_{tr}, e^-_{tr}, path (a) Figure 2). The trapped holes h^+_{tr} react with adsorbed donor molecules (oxidation step, path c) while the trapped electrons e^-_{tr} react with an acceptor (reduction step (d)). However one of the most significant deactivation pathways is recombination of the electron-hole pair at surface trapping sites with the release of heat (path (b) Figure 1).”[33] When the photogenerated holes react with surface-adsorbed water, they give the highly reactive hydroxyl radical ($HO^•$) as the main ROS, while in the presence of oxygen, superoxide radical anion ($O_2^{-•}$) and alternatively singlet oxygen ($^1O_2$)[34] are the other produced ROS.[33] Hole trapping by adsorbed molecules also gives rise to radical cation $RH^{•+}$ further giving radical species $R^•$, able to readily react with ground state oxygen. This oversimplified picture is generally agreed but does not take into account some features derived from fundamental studies that were extensively reviewed recently.[5] For instance the formation of hydroxyl radicals $HO^•$ by direct hole trapping of adsorbed water are discussed and alternative routes for their formation are proposed. Hole trapping by adsorbed molecules (alcohols, benzene) is thoroughly analyzed. The so-called “antenna effect”, resulting from aggregates regarded as arrays of nanowires that should allow the transport of charge carriers is also emphasized.

The high reactivity of radicals, especially hydroxyl radicals $HO^•$, makes heterogeneous photocatalysis an efficient, albeit un-selective method for photo-oxidation, ultimately leading to mineralization (transformation into carbon dioxide, water and eventually mineral acids), avoiding as far as possible the formation in significant amount of incompletely oxidized side-products, which have to be carefully controlled for any application. Since TiO_2 mainly absorbs UVA light, a great interest appeared these last 15 years in the development of modified TiO_2 extending its absorption spectrum in the visible range in order to take more advantage of solar or even indoor lighting.[35] The main strategies towards visible-light absorbing TiO_2 are metal (transition metals or noble metals) or non-metal (nitrogen, carbon, sulfur, fluorine) doping, dye sensitization, coupling of semi-conductors and defect introduction.[36]

Although the number of wide field applications of photocatalysis for water treatment remains rather low, the number of papers devoted to this topic is still quite high. Recent reviews aimed at rationalizing the influent parameters of this process,[13,37,38] or gathering the latest technological achievements,[9,39] A lot of papers and patents were also recently devoted to solid-gas photocatalysis for the mineralization of organic Volatile Organic Compounds (VOCs) in air.[10] For indoor air, decontamination or deodorization, [3,12,40,41,42] as well as its disinfection[12] is sought. In the case of outdoor air, nitrogen oxides (NO_x) degradation is mainly studied.[43,44,45] The less investigated use of photocatalytic reactions for fine chemical synthesis, in the presence (oxidation) or absence of oxygen was also reviewed.[46,47,48]

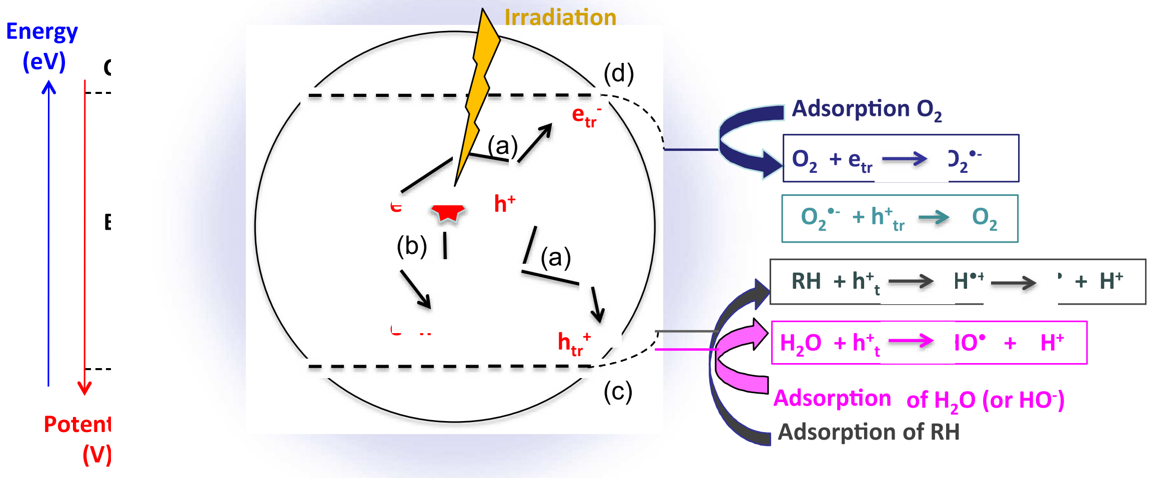


Figure 1 : Schematic of TiO_2 photocatalytic mechanism; (a): trapping of the electrons and holes photogenerated by the surface to give surface trapped holes (h_{tr}) and electrons (e_{tr}) ; (b): charge recombination; (c) oxidation of H_2O or RH (and alternatively of $O_2^{\bullet -}$) by trapped holes; (d) reduction of O_2 by trapped electrons. Adapted from ref. [33].

2.1. Photosensitization: singlet oxygen formation and photooxygenation

Photosensitized reactions are defined as the absorption of a radiation by a molecular species, called photosensitizer (PS), which induces the modification of another molecular species, either by *electron transfer* (type I mechanism) or by *energy transfer* (type II mechanism), with regeneration of the PS to its ground state without its chemical alteration. The structure of the more often used PSs is recalled in Figure 2.

Starting from ground state oxygen $O_2(X^3\Sigma_g^-)$, the type II photooxidation mechanism involves the formation of singlet oxygen, in its highly reactive $O_2(a^1\Delta_g)$ state (referred to as $^1O_2$ in the following).[49] The production of singlet oxygen $^1O_2$, a powerful electrophile, by energy transfer from the triplet state of the PS (T1, Figure 3a) to $O_2(X^3\Sigma_g^-)$ is an important process enabling photo-oxygenation (*i.e.* selective oxidation by oxygen uptake) of various electron-rich substrates (activated double bonds, sulphides, amines, phenols, anions,…) in several kinds of media. Singlet oxygen is very useful as a versatile synthetic reagent for fine chemical synthesis or wastewater treatment (insecticides and pesticides degradation).[30,50] It is also known for its cytotoxicity[51,52] and is the active oxidizing agent in photodynamic processes, *i.e.* damage of living tissue by the combination of a photosensitizer, visible light, and oxygen, including blood sterilization, photodynamic therapy (PDT), or photodynamic inactivation (PDI).

For efficient singlet oxygen production by energy transfer, the following conditions have to be fulfilled by the PS: high absorption coefficient in the spectral region of the excitation light, high ISC (inter system crossing) quantum yield, long triplet lifetimes and triplet energy higher than the energy gap between the ground and the $a(^1\Delta_g)$ states of O_2 (94.2 kJ mol^{-1}). The singlet oxygen generating ability of a photosensitizer is measured by its quantum yield Φ_Δ. Some of these data on well-known PSs are gathered in Table 1.

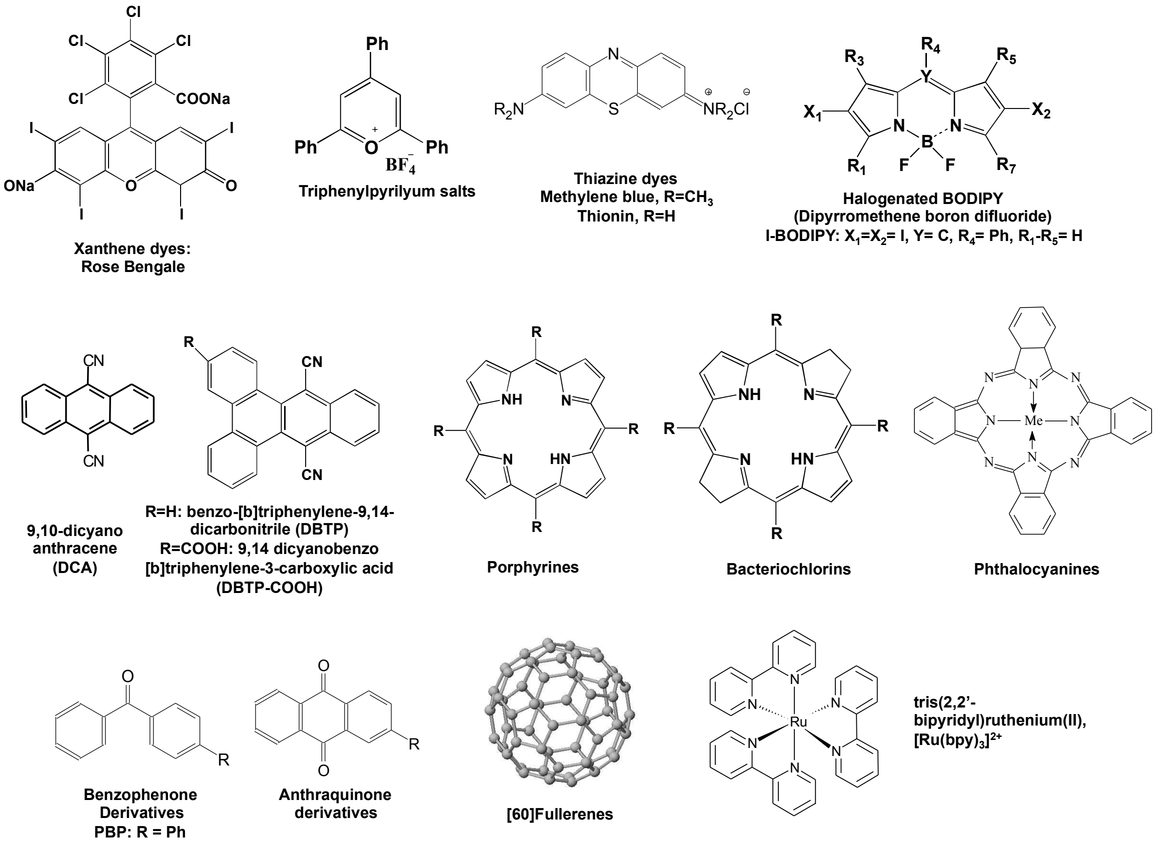
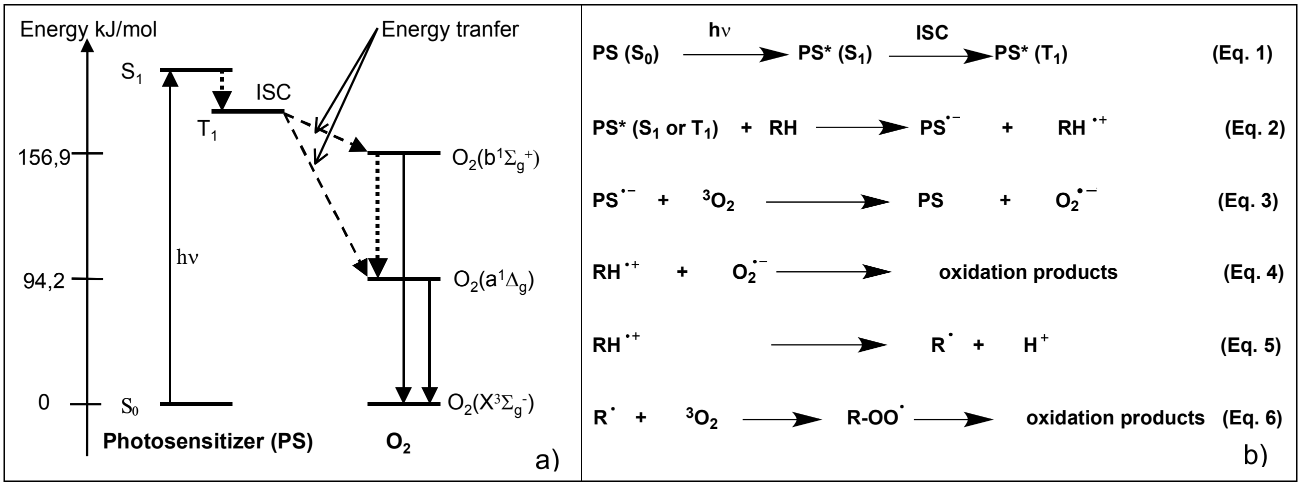


Figure 2 : Chemical strucuture of various organic photosensitizers (PSs)

Sensitizer	E_T (kJ mol^{-1})	τ_t (µs)	λ_{abs} (nm)	Φ_Δ	Solvent (for Φ_Δ)	Ref.
Benzo-[b]triphenylene-9,14-dicarbonitrile (DBTP)	ND (>94,2)	□□□	340-430	0.91	CH_3CN	[53]
Phthalocyanine Zn(II)	109	270, *p*	500-750	0.53	CH_3CN	[54,55,56]
Methylene Blue	138	450	630-660	0.51	MeOH	[54,56]
Tetraphenylporphyrine	140	1500	300-700	0.78	C_6H_6	[54,57]
C_{60} Fullerene	151	205, *n*	340-510	0.98	C_6H_6	[54,58,59]
Rose Bengal	164	130	490-570	0.76	MeOH	[54,60]
9,10-dicyano-anthracene	175	100, *n*	340-430	2.06*	CH_3CN	[54,61]
tris(2,2'-bipyridyl)ruthenium(II), $[Ru(bpy)_3]^{2+}$	197	0.72, *p*	180-450	0.73	MeOH	[62]
Triphenylpyrylium tetrafluoroborate	221	10	300-450	-	-	[63]
4-phenylbenzophenone (PBP)	254	40, *n*	250-380	0.75	EtOH	[54,64]
9,10-Anthraquinone	261	0.11, *n*	300-430	0.62-0.70	CH_3CN	[54,65]
I-BODIPY	ND	ND	450-600	0.83	CH_3CN	[66]

Table 1: Triplet energy, triplet lifetimes, broad absorption range of the PS family and singlet oxygen production in various solvents of selected PS from Figure 3 (ND: not determined; n: non-polar solvent; p: polar solvent, * upper limit at infinite oxygen concentration).

In some cases, if the excited singlet or triplet state of the PS is a strong oxidant enough (i.e. a good electron acceptor), it may react with an electron donor RH to yield a radical-cation $RH^{\bullet+}$ (Figure 3b). Then, depending on the redox potential of the ground state PS, type I mechanism may lead to the formation of superoxide radical anion, $O_2^{\bullet-}$, by reducing ground state molecular oxygen. The thermodynamc feasibility of the first electron transfer reaction is evaluated using the well-known Rehm-Weller equation (Figure 4). It is thus easily recognized that under these conditions the same reactive species ($RH^{\bullet+}$, $O_2^{\bullet-}$) as with TiO_2 might be produced.[67] Typical reduction potentials and excitation energy of several PS's, together with values for the free enthalpy of ground state oxygen reduction to superoxide radical-anion, $O_2^{\bullet-}$, are given in Table 2. From this table, it is concluded that almost all the excited PSs, except triphenylpyrylium salts, are able to reduce ground state oxygen to superoxide radical-anion $O_2^{\bullet-}$. As stated by Silva *et al.*, energy and electron transfer are "exquisitely entangled in PSs such as porphyrins and bacteriochlorins". For instance, bacteriochlorin triplet quenching involves charge transfer species (singlet oxygen, superoxide anion, hydrogen peroxide, hydroxyl radical), while the quenching of porphyrin triplets by molecular oxygen leads essentially to singlet oxygen.[68] The photophysical basis of these results in this series,[68] in the cyanoanthracene family,[53] and for several other PSs was extensively discussed.[69,70,71,72]



$$\text{PS }(S_0) \xrightarrow{h\nu} \text{PS* }(S_1) \xrightarrow{\text{ISC}} \text{PS* }(T_1) \qquad \text{(Eq. 1)}$$

$$\text{PS* }(S_1 \text{ or } T_1) + \text{RH} \longrightarrow \text{PS}^{\bullet-} + \text{RH}^{\bullet+} \qquad \text{(Eq. 2)}$$

$$\text{PS}^{\bullet-} + {}^3O_2 \longrightarrow \text{PS} + O_2^{\bullet-} \qquad \text{(Eq. 3)}$$

$$\text{RH}^{\bullet+} + O_2^{\bullet-} \longrightarrow \text{oxidation products} \qquad \text{(Eq. 4)}$$

$$\text{RH}^{\bullet+} \longrightarrow \text{R}^{\bullet} + \text{H}^{+} \qquad \text{(Eq. 5)}$$

$$\text{R}^{\bullet} + {}^3O_2 \longrightarrow \text{R-OO}^{\bullet} \longrightarrow \text{oxidation products} \qquad \text{(Eq. 6)}$$

Figure 3 : General schemes of photosensitized reactions a) singlet oxygen production by energy transfer (Type II reactions); ISC : intersystem crossing); b) oxygenation reactions by electron transfer (Type I reactions).

Figure 4 : Rehm-Weller equation, $E^0_{(D^{\cdot+}/D)}$: standard redox potentiel of the electron donor D (V), $E^0_{(A/A^{\cdot-})}$= $E^0_{(PS/PS^{\cdot-})}$: standard redox potential of the electron acceptor A (V), ΔE_{00} (kJ mol^{-1}): excitation energy of the PS, ε : dielectric constant of the solvent, d : distance between the two radical ions $A^{\cdot-}$ and $D^{\cdot+}$ (m)).

Photosensitizer	ΔE_{00} /eV (nm)	E_{red} (V)	E_{red*} (V)	ΔG^0 (kJ mol^{-1})	Ref.
Triphenylpyrylium tetrafluoroborate	2,82	-0,29	2,53	28.0	[73]
9,10-dicyanoanthracene	2,89	-0,83	1,91	-24.1	[74,75]
Benzo[b]triphenylene-9,14-dicarbonitrile (DBTP)	2.99	-0.92	2.07	-32.8	[74,75]
Zn(II)tetraphenylporphyrin	2.05	-1.35	0.70	-74.3	[73]
$Ru(bpy)_3^{2+}$	2.12)	-1.35	0.77	-74.3	[73]
9,10-anthraquinone	2,73	-0,86	1,87	-27.0	[73]
Benzophenone	2,98	-1,83	1,17	-120.6	[73]

Table 2 : Excitation energy ΔE_{00}, redox potential of the ground (E_{red}= $E_{PS/PS^{\cdot-}}$) and excited (E_{red}*= $E_{PS*/PS^{\cdot-}}$) states of several electron accepting PS's (*vs* SCE) and values of the free enthalpy of reduction of ground state oxygen to superoxide radical-anion, $O_2^{\cdot-}$. ΔG(kJ mol^{-1}) = 96.48($E_{PS/PS^{\cdot-}}$ - $E_{O_2/O_2^{\cdot-}}$), with $E_{O_2/O_2^{\cdot-}}$= -0.58 V *vs* Saturated Calomel Electrode (SCE) in CH_3CN.[76] See text for definitions.

As an introductory example, the versatility of triphenypyrylium salts is representative of the two previously mentioned type I and type II mechanisms. Actually, triphenylpyrylium salts (TP^+) were known as unable to generate either singlet oxygen or superoxide radical anion in solution, but to be strong oxidants in their excited singlet (S1) or triplet (T1) states ($E_{TP^*(S1)/TP^{\cdot-}}$ = 2.5 and $E_{TP^*(T1)/TP^{\cdot-}}$ = 2.0 V vs SCE).[63] They were thus proposed as clean-electron transfer photosensitizers (Type I reactions). The incorporation of the dye inside NaY zeolite strongly increases its resistance against hydrolysis in neutral water at room temperature and thus its stability. Upon photoexcitation, TP@NaY can generate hydroxyl radicals $HO^{\bullet}$ making them suitable for the degradation of organic pollutants in water and TP@NaY was shown to be more active than TiO_2 for the solar degradation of 4-chlorophenoxyacetic acid.[77,78]

On the other hand, although singlet oxygen phosphorescence at 1270 nm could not be detected from a CH_3CN solution of TP,BF_4, singlet oxygen phosphorescence was clearly observed in D_2O or in decafluoropentane when TP^+ was incorporated in NaY zeolite or in MCM-41, indicating that the molecular photochemistry of TP^+ salts is modified by encapsulation inside the confined space of the zeolite cavity.[79] This enhanced singlet oxygen formation (type II mechanism) was attributed to the much longer lifetimes of TPT triplet state in the solid matrix (ms range) than in solution (μs range). Accordingly the sulfide-containing chemical warfare agent yperite was successfully oxidized with TP@NaY in dichloromethane solutions. Type II mechanism could account for the obtained products (sulfoxide, sulfone, disulfide), although no detailed data on the product composition was given.[80]

In other words, depending on the conditions (water, deuterated water, fluorinated solvent or aerated dichloromethane) and on the substrate, either type I reactions with hydroxyl radicals or type II reaction with singlet oxygen may occur with these zeolite materials.

2.2. Properties of the different ROS

Singlet oxygen in its first excited state $O_2(a^1\Delta_{\square})$ is a powerful oxidant, with a variable lifetime (τ_Δ) depending on the solvent/medium: 3.1 μs in water, 9.5 μs in methanol, 59 μs in $C_{10}F_{18}$, 50 μs in silicone rubber, 38-28 μs in poly(methyl methacrylate) and polystyrene (PS) respectively at $T>T_g$ (glass temperature). In the gas phase, τ_Δ is calculated to be 86 or 54 ms for air at 0% or 100% relative humidity, respectively, at 1 bar and 298 K.[69]

Since the average value of the square of distance d, which an O_2 molecule travels during time t depends on its diffusion coefficient D_0 according to $d^2 = 6D_0t$, the diffusion length, d, of $^1O_2$ is estimated to be 2.7 mm in air of 100 % relative humidity ($D_0 = 0.232$ cm^2 s^{-1} for O_2 gas at 298 K and $\tau_\Delta = 54$ ms). This means that singlet oxygen is able to diffuse and react with suitable reactants in the gas phase. For instance Majima *et al*. demonstrated that it was possible to detect single $^1O_2$ molecule at a distance >1 mm from the place of its creation (TiO_2 surface) in ambiant air.[81] Likewise in water, with $D_0 = 2\times10^{-5}$ cm^2 s^{-1} for O_2 and $\tau_\Delta = 3.1$ μs, the diffusion length of $^1O_2$ is estimated to be 193 nm, which reduces to 155 nm inside cells.[51,69] According to Ogliby, this means that the initial effects of singlet oxygen will be spatially confined in cells (typical diameter of eukaryiotic cells ~ 10-30 μm) and that it will be able to cross over the cell membrane into the extracellular environment making singlet oxygen "a *selective* not a *reactive* intermediate". Several papers dealt with the study of singlet oxygen diffusion at the air-solid interface[82] or at the liquid–solid interface.[83,79,84].

These considerations are to be compared with the time scales of the various photocatalytic processes and to the very short lifetimes of radical species, and specifically hydroxyl radicals (ns range[85]) formed in the *photocatalytic* process limiting their diffusion from the source: in this case the radical species have to react quickly with molecules pre-adsorbed on the surface of the photocatalyst (distance of photocatalysis efficiency < 10 nm from[86]).

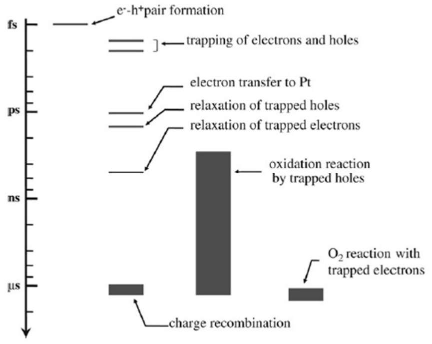


Figure 5 : Time scales in photocatalysis. From [33] with permission of copyright owner.

On the other hand, superoxide radical anion, formed by reduction of ground state oxygen is a Brönsted base that reacts via formation of $HO_2^{\bullet}$ in solvents containing water (Eq. 7) and a strong nucleophile in non-aqueous solvents. It is thus prone to hydrogen abstraction to hydroperoxyl radicals $HO_2^{\bullet}$ and fast disproportionation reactions leading to hydrogen peroxide.[87,] (Eqs. 8 & 9).

$$O_2^{\bullet-} + H_3O^+ \longrightarrow HO_2^{\bullet} + H_2O \quad pKa= 4.75- 4.88 \qquad \text{(Eq. 7)}$$

$$2\ HO_2^{\bullet} \xrightarrow{k_8 =8.1\ 10^5\ M^{-1}\ s^{-1}} H_2O_2 + O_2 \qquad \text{(Eq. 8)}$$

$$2\ O_2^{\bullet-} + 2\ H^+ \xrightarrow[pH\ 7.4]{k_9 =2.4\ 10^5\ M^{-1}\ s^{-1}} H_2O_2 + O_2 \qquad \text{(Eq. 9)}$$

It should also be recalled that superoxide radical-anion reacts through the so-called Haber-Weiss reaction with H_2O_2, leading with much lower rate constants to the formation of hydroxyl radicals (Eqs. 10 &11).[68,88]

$$O_2^{\bullet-} + H_2O_2 \xrightarrow{k_{10} =16\ M^{-1}\ s^{-1}} HO^{\bullet} + HO^- + O_2 \qquad \text{(Eq. 10)}$$

$$HO_2^{\bullet} + H_2O_2 \xrightarrow{k_{11} =3.7\ M^{-1}\ s^{-1}} HO^{\bullet} + H_2O + O_2 \qquad \text{(Eq. 11)}$$

3. Design of materials for selective photo-oxygenation

The development of stable “photosensitizing materials” is an active research field, with numerous applications including oxidation reactions of high-added value products under mild conditions for fine chemicals synthesis, wastewater treatment, bactericidal treatments, photodynamic therapy (PDT). For all these applications, the photosensitizer has to be deposited, embedded or grafted on different supports (silica, alumina, polymers, zeolites, Layered Double Hydroxides (LDH), cellulose, dendrimers, carbon nanotubes,…) with different macroscopic forms (films, powders, beads, glasses, fibers) and various specific surface area, surface properties and transparency. For an optimized stability, grafting of the PS on the support is obviously preferred if reactions are to be carried out in suspensions (liquid-solid). Other advantages of these supported PS’s are the control of aggregation and self-quenching of the dye, the increase of their photostability, their easy separation from the other reactants and products, the possible use of solvents where PS’s are poorly soluble or their use in solvent-free reactions (gas-solid interface).[6,7] This strategy allows tuning the absorption range and the oxidation properties by proper choice of the sensitizer. Moreover, as with triphenylpyrylium salts for instance, the nature (organic, inorganic) and structuration (micro or meso-structuration) of the support may further influence the properties of the dye.

This short review does not aim at an extensive list of the numerous photosensitizing materials that have been prepared and studied. Only selected recent examples will be given with the purpose of making a parallel with TiO_2-based photocatalytic materials.

3.1. Rose Bengal (RB)

Rose Bengal is a well-known PS, soluble in polar solvents including water, easily graftable through its carboxylate function, active in the visible range (λ_{max} 490-570 nm, Figure 6) with a high singlet oxygen quantum yield. Since the earlier work of Nilsson and Kearns, and of Schaap *et al*. in 1975, a lot of papers have dealt with the immobilization of Rose Bengal on to polymers (polyamides, polymethacrylate, polyethylene glycol, N-isopropylacrylamide-co-vinylbenzene, chlomethylated poly(styrene-co-vinylbenzene), which led to the development of commercial Merrifields beads known as Sensitox®), silica gels, bromomethylated glass, cotton, cyclo- et poly-phosphazenes,…. All these materials are cited in the review of Wahlen *et al.*.[7] More recent papers focused on the immobilization of RB onto various fabrics: dyied nylon[89] or wool,[90] water-soluble chitosan,[91] silanized cellulose,[92] hydrophilic and various polymers,[93,94,95] or polymers bonded to nylon micro- and nano-structured fabrics.[96] A polymer consisting of N-isopropylacrylamide and RB units demonstrated a temperature–controlled changeable oxidation selectivity by singlet oxygen in water.[97]

Most of these studies emphasize the role of the amount of PS loaded on the support and the drop of efficiency related to aggregation phenomena, for instance when RB is adsorbed on silica nanoparticles.[51] From the comparison between the photophysical properties of Rose Bengal adsorbed or grafted on different kinds of silica or adsorbed on cellulose, it was concluded that singlet oxygen production was correlated with RB concentration and with the type of bonding to the support.[52,53] One of the main issues with these materials is their stability, since RB is readily prone to photobleaching.

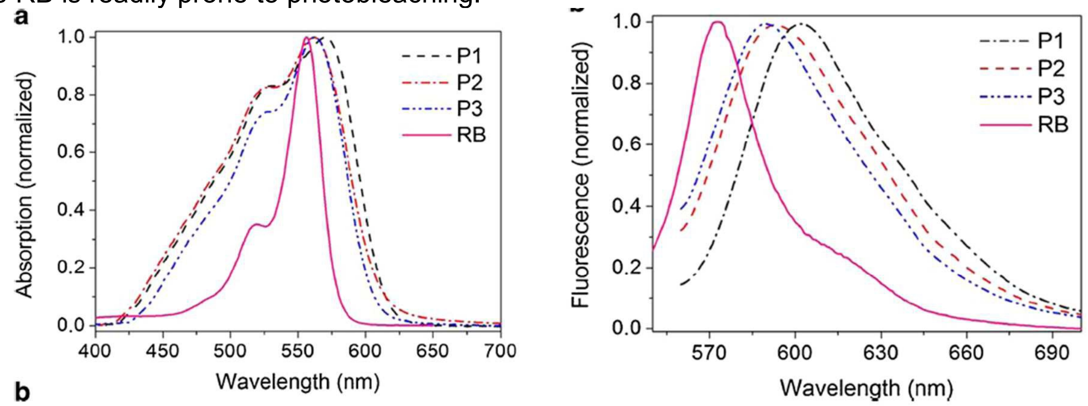


Figure 6: Normalized a) absorption spectra ; b) fluorescence spectra (λexc 550 nm) of solid polymers P1-P3 and RB dianion in MeOH (10 μM). From [93] by permission of the copyright owner.

3.2. Triphenylpyrylium salts

Triphenylpyrylium salts (TP^+) absorb photons in the 300-450 nm range (Figure 7) and are highly oxidant in their excited state (Table 2), but they are not able to produce either singlet oxygen or superoxide anion in the presence of oxygen, at least under usual homogeneous solution photooxygenation conditions. They are prone to hydrolysis although more stable in acidic media than in neutral water.[63]

However, when TP^+ is entrapped inside zeolites micropores, its properties are significantly modified: it generates singlet oxygen with quantum yields of the same order of magnitude as metal phthalocyanines, due to the increase of TP^+ triplet state lifetime inside the confined space of the zeolite cavity.[79] It also led to the formation upon irradiation of an aqueous slurry containing the reactive $HO^{\bullet}$ radical together with the pyrylium radical, which was exploited for the photochemical hydroxylation of benzene.[98] Triphenylpyrylium salts were also synthesized inside zeolites cavities (ship in the bottle),[77] adsorbed on silica[99] or grafted on a Merrifield resin (chloromethylated polystyrene).[100]

These results emphasize the role of TPT^+ entrapment inside zeolites or mesoporous silica cavities leading to significant improvement of their stability, efficiency and reactivity.

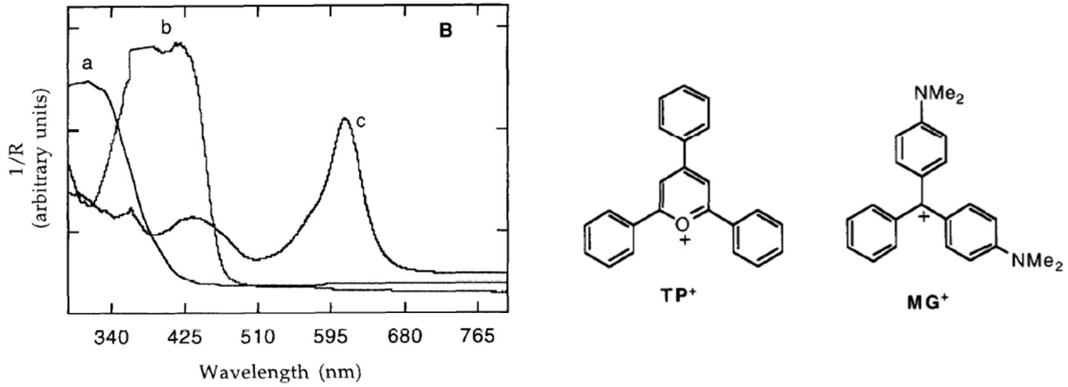


Figure 7 : Normalized diffuse reflectance spectra of (a) TiO_2, (b) (TP^+) prepared within the voids of Y zeolite (TPY), and (c) malachite green (MG^+) prepared within the voids of Y zeolite (MGY). From [78] with permission of the copyright owner .

3.3. Ruthenium salts

Ru(II) coordination complexes with polyazaheteroaromatic ligands display a broad absorption band in the 180–550 nm range, ISC quantum yields close to unity, long excited state lifetimes, significant $^1O_2$ production quantum yield and good thermal and photochemical stability. Tris(2,2'-bipyridyl)ruthenium(II) dichloride ($[Ru(bpy)_3]Cl_2$) belongs to this family of stable sensitizers able to react both by energy transfer and by electron transfer.[101] The preparation, photochemical characterization and evaluation of the photodisinfection power of singlet oxygen photosensitizing materials prepared from Ru(II) complexes immobilized on porous silicone polymers was reported by Orellana's group (Figure 8).[50,102] High $^1O_2$ production in water was achieved due to efficient quenching of the long-lived sensitizer triplet state of the Ru(II) sensitizer by dissolved O_2. Longer $^1O_2$ emission lifetimes than in water were measured (25-32 µs), depending on the ionic or neutral nature of the supporting silicone. Stability and re-use of these disinfection materials were carefully investigated.[103] Alternatively, Ru(bipy)$_3^{2+}$ and other complexes were grafted on a hydrophilic polymer,[104] encapsulated in biocompatible poly($_{\text{D,L}}$-lactide-co-glycolide)nanoparticles,[105] while Ru, Ir and Re complexes with dicarboxylic functionalities were incorporated in metal-organic frameworks (MOF)[106] or in mesoporous silica.[107]

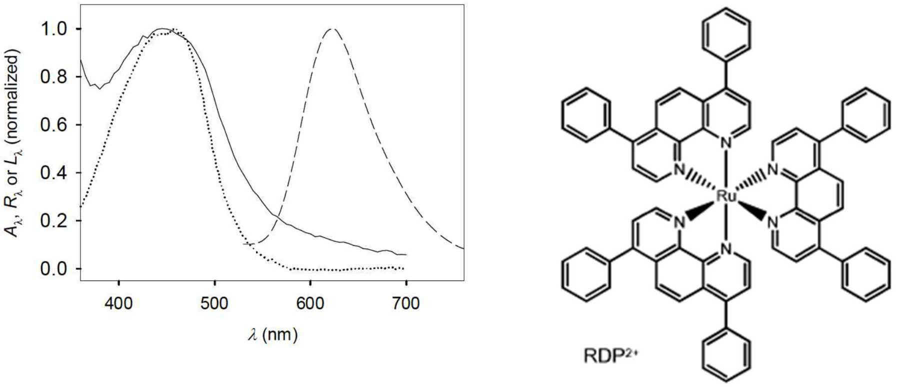


Figure 8 : Normalized absorption A (——), reflectance R (·····) and emission L (-----) spectra of RDP^{2+}/pSil photosensizing material (RDP^{2+} : [tris(4,7-diphenyl-1,10-phenanthroline)ruthenium(II)] dichloride.[50] With permission of the copyright owner.

3.4. Cyanoaromatics

Cyano derivatives of anthracenes and other cyano aromatics are often used for sensitized photooxygenation reactions and photo-induced electron transfer (PET) reactions.[108, 109,110] 9,10-dicyanoanthracene (DCA), which absorbs light at wavelengths longer than 400 nm has been extensively studied.[65] Reaction mechanisms may proceed through energy transfer leading to formation of singlet oxygen, a($^1\Delta_g$) with high quantum yields.[61,111] Alternatively, depending on the reactants, photo-induced electron transfer is possible, giving rise to redox reactions. In the presence of ground state oxygen, the superoxide radical anion is easily produced (Table 1).[112,113,] Dicyanoanthracene, dicyanonaphtalene, di- and tetra-cyanobenzene, grafted on styrenic polymers were successfully used for photoinduced electron transfer oxygenation reactions of cyclopropane.[114] A dicyanoanthracene derivative with a carboxylic functionality (DBTP-COOH, Figure 2) was also grafted on silica and used for benzylic ethers and sulfides photooxidation in acetonitrile solution: although evidence for electron transfer mechanisms was obtained,[115,116] high singlet oxygen quantum yields were also achieved (solid-gas[117] or solid-liquid[53] interface).

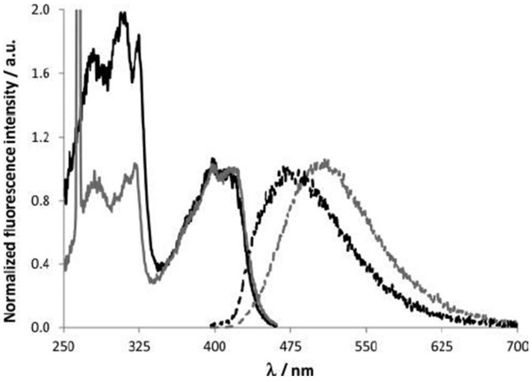


Figure 9 : Fluorescence excitation (λ_{em} 470 nm) and emission (λ_{exc} 385 nm) of DBTP-based silica monoliths (DBTP: benzo-[b]triphenylene-9,14-dicarbonitrile). Grey: encapsulated DBTP; black: grafted DBTP-COOH. From [117] with permission of the copyright owner.

3.5. Porphyrins

Porphyrins derivatives (either free bases or their metal complexes, soluble either in non-polar or polar solvents) are able to produce singlet oxygen or superoxide radical anion under visible light irradiation (400 to 700 nm, Figure 10), but they undergo fast photobleaching. A huge number of papers (see Wahlen's review[7] for selected examples before 2004 and the following list is still far from exhaustive) deal with their adsorption, deposition, impregnation or grafting on silica,[118] Vycor glass,[84] silicon,[119] polydimethylsiloxane,[120] polyethyleneglycol,[121] and on various polymers (polystyrene,[122,123,124,125] polypropylene,[126] nylon fibers,[127] chitosan,[128] cellulose[129,130,131]). Singlet oxygen emission at 1270 nm recorded on bactericidal nanofabrics based on tetraphenylporphyrin (TPP) deposited on polyurethane was assigned to the long lifetimes of the TPP triplet state in this environment.[132] The material stability under irradiation conditions is sometimes (but not always) addressed by recycling experiments and should be more carefully considered for the application of these materials under real conditions.[124,133,134]

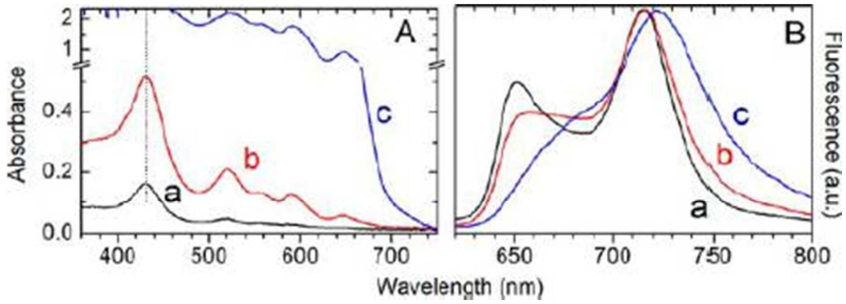


Figure 10 : (A) Absorption and (B) normalized fluorescence spectra (λ_{exc} 430 nm) of sulfonato-polystyrene nanofibers with a cationic porphyrine derivative (5,10,15,20-tetrakis(1-methylpyridinium-4-yl)porphyrin or TMPyP) at low (a), medium (b) and high (c) TMPyP loading. From [125] with permission of the copyright owner.

3.6. Phthalocyanines

Under visible light irradiation (Q band around 700 nm), and in the presence of oxygen some metal complexes of phthalocyanines, where the metal has closed *p* or *d* configuration (Mg(II), Al(III), Si(IV) or Zn(II)) are able to produce singlet oxygen and hydrogen peroxide though formation of superoxide radical-anion, $O_2^{\bullet -}$.[135,136,137,138] In aqueous solution, the formation of the reactive hydroxyl radicals, $HO^{\bullet}$ issued from $O_2^{\bullet -}$ was also reported with (octakis(pyridiniomethyl)phthalocyaninotitanyl octachloride).[139] As in the porphyrin series, a lot of papers were recently published on oxidation materials based on phthalocyanines and only selected examples will be given here. Metallophthalocyanines were mainly grafted on polymers[140,141,142,143,144,145,146] silica,[147,148,149,150] or embedded in zeolites[151,152,153] or clay minerals.[154,155,156] All these materials were successfully used for photooxidation of various compounds and singlet oxygen involvement was demonstrated. Provided that aggregation is controlled, phthalocyanines are excellent for the development of phototherapeutic agents owing to their low toxicity, high stability, efficient $^1O_2$ generation, and intense light absorption in the therapeutic window.

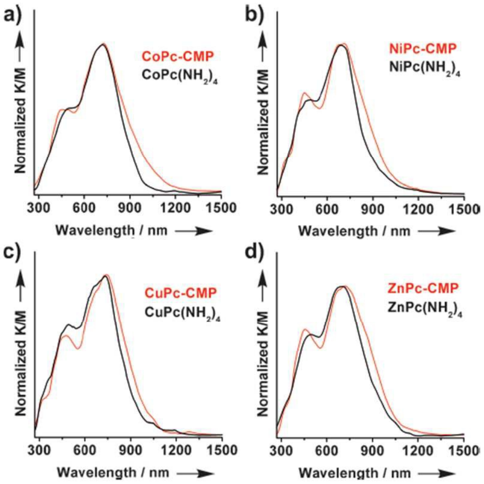


Figure 11 : Absorption spectra of metallophthalocyanines(MPc)-conjugated microporous polymers (CMP) compared with their monomers. From[146] with permission of copyright owner.

3.7. Boron-dipyrromethene (BODIPY) complexes

Halogenated BODIPY derivatives were more recently studied for singlet oxygen production under visible light and their possible use in PDT.[157,158] A non-halogenated derivative could be integrated in a high internal phase emulsion (HIPE) polymerisation process yielding a porous polymer with a high efficiency and recyclability for sulfide oxidation although no evidence for singlet oxygen formation was given.[159] More recently, iodinated BODIPY derivatives grafted on silica nanoparticles or on mesoporous silica were successfully used respectively for singlet oxygen induced cytotoxicity against cancer cells[160] and for the tandem photoredox [3+2] cycloaddition of tetrahydroisoquinoline with N-phenylmaleidimines.[161]

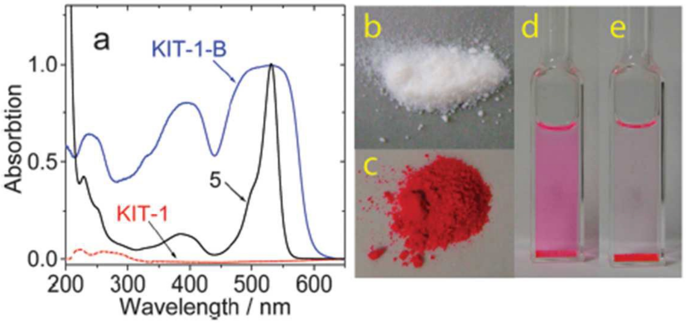


Figure 12 : UV-Vis absorption spectra of the triethoxysilyl derivative of the BODIPY (curve 5) and of the grafted silica (KIT-1-B) ; b and c : pictures of the initial (KIT-1) and grafted (KIT-1-B) silica powders ; d and e : suspension of KIT-1-B in acetonitrile before and after deposition of the material in the cuvette. From [161] with permission of the copyright owner.

3.8. Methylene Blue and derivatives of thionin

Thionin and derivatives like Methylene Blue (MB) are good singlet oxygen photosensitizers with a maximum absorption in the 600-700 nm range (Figure 13). A lot of papers reviewed by Wahlen,[7] were devoted to the ability of zeolites containing Methylene Blue to drastically influence the regioselectivities of singlet oxygen oxygenation of olefins and the selectivity of sulfides oxidation to sulfoxides, sulfones and other products arising from C-S bond cleavage. Methylene Blue was embedded in silica[162] or bentonite[163] for the selective oxidation of phenol, naphtol and anthracene derivatives. A cross-linked poly-N-isopropylacrylamide nanocapsule containing thionine or benzophenone promoted $^1O_2$ oxygenation controlled by temperature:[164,165] at low temperature, the capsules exists as the swollen single capsule, allowing $^1O_2$ diffusion towards bulk water and high oxygenation activity of phenol. A rise in temperature leads to contraction of the capsule and suppresses $^1O_2$

diffusion leading to a decreased activity. A very useful application was devoted to the development of a well-defined solid system based on Methylene Blue supported on Nafion films as convenient reference material for singlet oxygen production with a quantum yield of 0.24 in the air-equilibrated solid phase.[83]

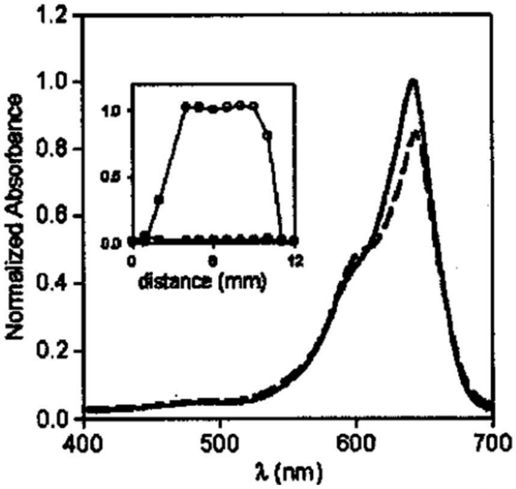


Figure 13 : Normalized absorption spectra of Methylene Blue in an air-equilibrated Nafion®-Na film after preparation (—) and a week later (-----). The inset shows the absorption profile at the absorption maximum (642 nm) of a MB-dyed and non-dyed film. From[83] with permission of copyright owner.

3.9. Fullerenes

Fullerenes (C_{60} and C_{70}) owe their photochemical activity to their strong absorbance throughout the UV spectrum and to their conjugated structure (*Figure 14*). They are able to produce singlet oxygen in non polar solvents (Type II mechanism) and peroxides radicals issued from $O_2^{\bullet-}$ in polar solvents such as water (Type I mechanism) in the presence of UV or visible light.[166,167] However, they are poorly soluble in usual solvents and a lot of efforts are devoted to the grafting of their functionalized derivatives on various supports enabling their use in water : polymer,[168,169] siloxane,[170] silica.[171,172,173,174] High concentration of fullerene in water was achieved (7.8 mM) with a water-soluble polymer, consisting of C_{60} incorporated into a polyvinylpyrrolidone (NVP) copolymer. The biological activity was confirmed by formation of $O_2^{\bullet-}$ and DNA cleavage.[175]

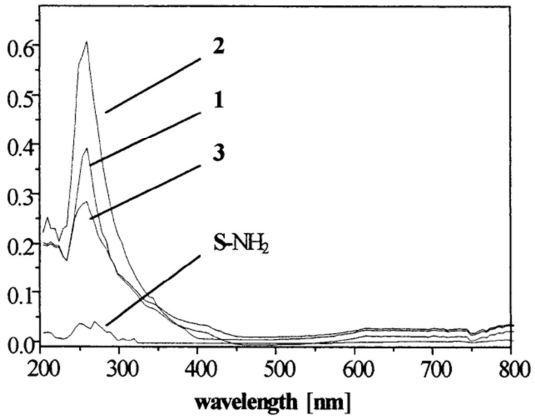


Figure 14: Diffuse reflectance UV/VIS spectra of NH_2-containing polymer S-NH_2 (carbohydrate hydrophilic polymeric matrix functionalized with amino moieties) and fullerene-C60-containing polymers 1, 2, and 3 (different fullerene concentrations in the range 3.61 – 6.66 10^{-3} mol.g^{-1}). From[168] with permission of the copyright owner.

3.10. Miscellaneous aromatics

In addition to the reference sensitizer 1*H*-phenalen-1-one (or phenalenone) with a high singlet oxygen quantum yield under UV excitation independent of the solvent polarity,[176] other aromatic ketones like 2-acetonaphtone, 4-phenylbenzophenone (PBP in Figure 2), 4-benzanthrone, 9H-fluoren-9-one or anthraquinone and their derivatives may also act as excellent sensitizers for photooxygenation reactions (Table 1, Table 2). Anthraquinone, able to produce singlet oxygen, is also a good oxidant in its excited state, making type I reaction possible.[24] Benzophenone excited state is a weaker oxidant but can produce readily superoxide anion (Type I reaction) and singlet oxygen (Type II reaction). The main drawback of these aromatic ketones is related to their absorption in the UV-A or near visible: benzophenone and its derivatives display a weak n-π* absorption band in the 325-400 nm range (Figure 15A), while this band lies in the 400-425 nm range for anthraquinone derivatives (Figure 15B). Benzophenone derivatives are easily grafted on polymer backbone,[177,165] and on mineral supports.[178] Lifetimes and quantum yields of singlet oxygen production were determined in the absence on solvent inside silica monoliths containing anthraquinone and benzophenone.[179]

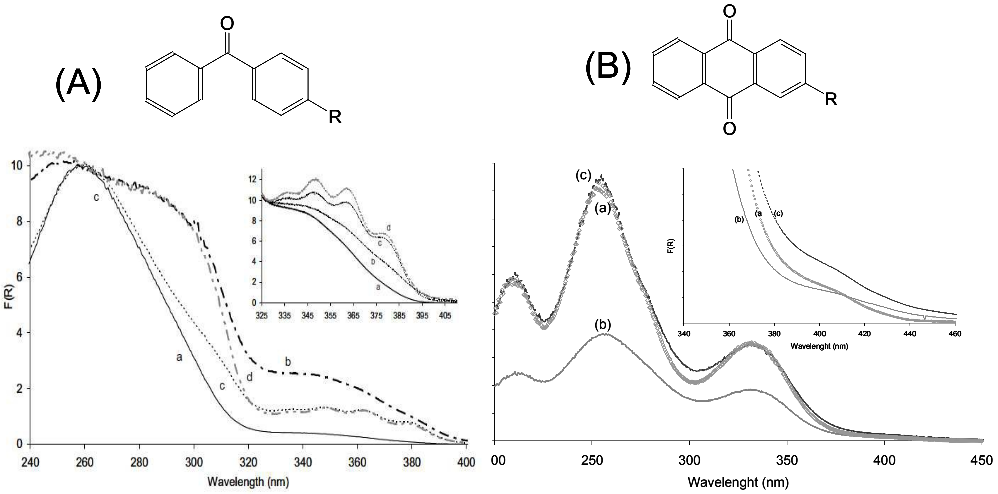


Figure 15 : Diffuse reflectance spectra of (A) 4-benzoybenzoate sodium salt (R = COO$^-$NA$^+$) (a) adsorbed on a double layered hydroxide; (b) intercalated in a on a double layered hydroxide; (c) in mechanical mixture with a double layered hydroxide and (d) pure; Insert: DRUV spectra normalized at 325 nm. From [180] with permission of the copyright owner ; (B) DRUV spectra of commercial silicagel beads grafted with anthraquinone-2-carboxylic acid (R= COOH) (a) before irradiation, (b) after irradiation at 420 nm under continuous flow of gaseous dimethylsulfide in air and (c) after regeneration by washing. From [26] (by permission of the copyright owner.

3.11. Polyoxometallates

Polyoxometalates (POM's) or decatungstate ($W_{10}O_{32}^{4-}$) are able to photosensitize oxidation reactions according to radical processes derived from Type I mechanisms. It is generally accepted that illumination of the $W_{10}O_{32}^{4-}$ complex CT band (λ_{max} 324 nm) generates a charge transfer excited state $W_{10}O_{32}^{4-*}$ which decays in about 30 ps to a longer-lived higly reactive species (wO) which does not react with oxygen, but enables hydrogen abstraction from organic substrates (RH) or electron transfer to give radicals (type I' mechanism).[181] Owing to their acidic nature, POM's are very soluble in water and difficult to extract from the reaction medium. Immobilization of POM's onto solids to create hybrid catalysts is necessary to improve their specific surface area, recovery and recyclability. In addition to classical Keggin-type POM's ($H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$), a wide variety of more stable transition metal-substituted POM's with a weak absorption band in the visible range may also be grafted on different kinds of silica[182,183,184,185] zirconia,[186] impregnated on polystyrene[187] or fluoropolymeric films[188]. All these materials were claimed to be more stable than crude POM's and to be efficient for oxidation of various hydrocarbons under UV irradiation in aqueous solutions or under solvent-free conditions.

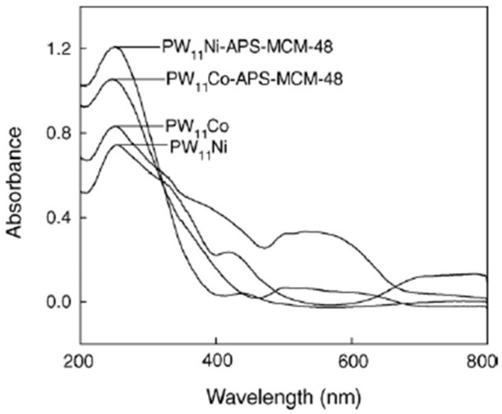


Figure 16: UV-Vis diffuse reflectance spectra of $PW_{11}Co$ and $PW_{11}Ni$ (with $PW_{11}M = K_5[M(H_2O)PW_{11}O_{39}]$) and their corresponding hybrid catalysts obtained by co-ordination of the metal center on amino modified MCM-48. From [182] with permission of the copyright owner.

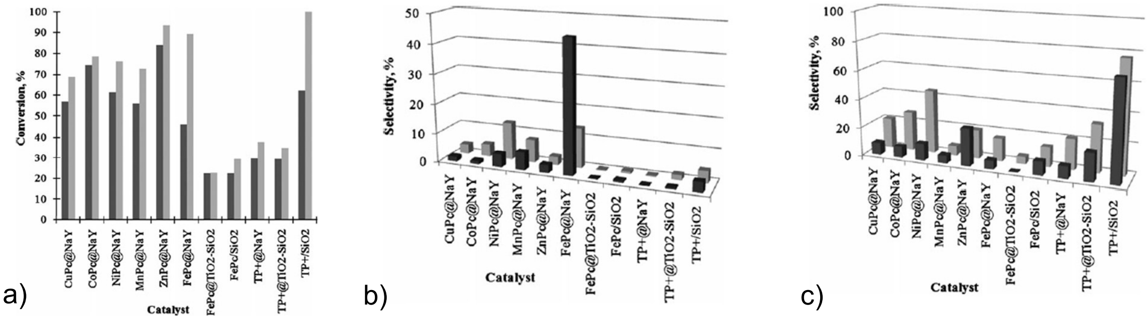
4. Applications of photosensitizing materials

Although less numerous than the papers dealing with *photocatalytic* materials, a great number of studies are nowadays focusing on *photosensitizing* polymer films and fibers and on nanoparticles for PDT applications, which both could be used in aqueous medium. A special attention is also currently paid to easy particles recovery by various methods (filtration, magnetic separation or electrocoagulation).

4.1.1. Fine chemistry

Selective and efficient oxidation of sulfides, often used as simulants of warfare agents like yperite, to sulfoxides with minor or negligeable sulfone formation, can be achieved with a large variety of materials suspended in organic solvents:

- RB dyied Nylon fabrics,[89]
- TPT^+ encapsulated inside zeolites or mesoporous channels of MCM-41, or supported on silica or titania-silica (with a cooperative effect in which the host intervenes by adsorbing yperite, favoring the contact between the photoactivated species and the substrate)[189,190] Under identical conditions (emission of the light source not defined) conversion only reached 37 % after 3.5 hours with TiO_2 Degussa P25.
- porphyrin-containing MOF (through singlet oxygen generation and porosity of the material favoring adsorption of the chemical),[191]
- benzophenone derivative intercalated in the channels of a Layered Double Hydroxide (more selective than in homogeneous solution and recyclable).[180]



a) b) c)

Figure 17: a) Photocatalytic activity of the photosensitizing materials for dipropylsulfide decomposition under UV light irradiation(dark grey: 60 min, light grey: 120 min); b) selectivity to dipropyldisulfide; c) selectivity to dipropylsulfoxide. From [190] with permission of the copyright owner.

Other selected examples concern the oxidation of various chemicals under visible irradiation:

- Oxidation of olefins to ketones by zeolites encapsulated TPT^+[192]

- Oxidation of furans to butenolides with Rose Bengale (RB) immobilized on wool[93], and of furoic acid to 5-hydroxy-5H-furan-2-one with RB in hydrophilic polystyrene polymers[90]
- Oxidation of thioanisole and aerobic amine coupling reactions with Ru and Ir-MOF[106]
- Oxidation of α-pinene and sulfides in solution with anthraquinone derivative, RB, or DBTP-COOH grafted on silica.[24] Different mechanisms with electron transfer evidence and radicals involvement for the anthraquinone-based material were observed.
- Oxidation of various olefinic compounds by porphyrin-functionalized pyrimidine dendrimers, claimed as synthetically useful PS's that could be recycled after nanofiltration, even if they were prone to photodegradation.[193]
- Photooxygenation of various organic compounds either solvent-free or in chloroform solutions with polystyrene beads doped or grafted with several porphyrin derivatives.[133,194] The performance, recyclability and efficiency of these materials were commented.
- Selective oxidation of diols[185] and alcohols[186] with silica bound $W_{10}O_{32}^{4-}$.
- Oxidation of α-terpinene and methionine using C_{60} fullerene covalently linked to Tentagel® and silica gel matrices in microstructured continuous flow reactors.[21]

Last, a smart singlet oxygen generating photochromic MOF including a Zn-porphyrin was recently designed and allowed the reversible control of singlet oxygen generation demonstrated by oxidation of selected probes.[195] Rhenium complexes embedded in a flexible self-standing polymeric silsesquioxane film yielded high singlet oxygen emission under irradiation at 467 nm.[196]

4.1.2. Disinfection

A lot of papers are devoted to the bactericidal or antimicrobial activity of photosensitizing materials under visible light irradiation:

- Anti fungal or bactericidal activities of nanostructured fabrics and cellulose membranes grafted with RB[96]
- Inactivation of *Escherichia coli* and *Enterococcus faecalis* by Ru(II) complexes immobilized on porous silicone polymers in Compound Parabolic collectors (CPC) solar reactors. [50,102,103]
- Strong dual antibacterial effect under day light of anion exchange polystyrene nanofibers bearing sulfonatoporphyrin derivatives when iodine ion where co-adsorbed on the fibers.[28]
- Antibacterial nanofibers from various polymers including TPP displayed bactericidal activity depending on oxygen permeabilitu/diffusion coefficient and on fibers diameter.[197]
- Significant increase in the photooxidation of polar substrates and of the bactericidal efficiency by increasing surface wettability of polystyrene nanofibers encapsulating tetraphenylprophyrin.[161,178]
- Inactivation of *Gram-positive* and *–negative* bacteria, as well as fungi, and suppression of biofilms with TPP embedded in silicon polymer.[198]
- Inactivation of *Gram-positive* pathogens with a hydrophobic Si(IV) phthalocyanine in a layered nanoclay[155] or of *S. Aureus* and *E. Coli* with phthalocyanines embedded in polymer nanofibers. [28,29,125,145]
- Grafting of a silicon phthalocyanine in zeolites for designing a new nano-architecture containing fluorescence labelling, photosensitizing ability and cellular adhesion[199]
- Photosensitizing polymer,[200] siloxane,[201] keratin,[202] containing the phenothiazinium chromophore exhibited measurable levels of singlet oxygen. The corresponding films were photobactericial against *Staphylococcus epidermidis* or *Escherichia coli*.[131] Polysiloxane polymers containing embedded MB and gold nanoparticles were also shown to have a significant activity against *Staphylococcus aureus* and *Escherichia coli*, and the presence of gold nanoparticles enhanced the bactericidal effect.[201]
- Silicon polymer doped with Methylene Blue for inactivation of *Staphylococcus epidermidis* via type I and Type II mechanisms.[203]

- Inactivation of MS2 bacteriophage in water with C_{60} immobilized on polystyrene or silica.[172]
- Photodynamic action of a photoactive polymer comprising covalently bound anthraquinone used for immobilizing micro-organisms on the surface and for producing singlet oxygen inactivating a broad spectrum of microbes on the substrate surface.[204]
- Anthraquinone cotton fabrics successfully used or selective oxidation of sulfides to sulfoxides and deactivation of *Pseudomonas fluorescens* [205,206]

4.1.3. Photodynamic therapy

PDT involves the systemic administration of a photosensitizer, its accumulation in the tumor and irradiation of the tumor with a light well absorbed by the PS. The photo-produced ROS (mainly $^1O_2$ and $O_2^{\bullet -}$) are capable of oxidizing biomolecules and ultimately induce tumor cell death. Three main issues are currently relevant: optimization of the spectral and photophysical properties of the PS in the therapeutic window, targeting of the PS (often lipophilic) by incorporation into nanoparticulate drug delivery systems to ensure compatibility with plasma and facilitate selective targeting, co-encapsulation of adjuvant therapeutics or diagnostic/imaging agents into the drug delivery system.[207,208,209] Accordingly numerous papers were recently devoted to the grafting or encapsulation of various PSs inside nanoparticles for *potential* applications to PDT.

Once again, only selected examples will be given here:

- RB in porous monolithic polymers [210] or mesostructured silica nanoparticles[211]
- Ru complexes encapsulated in biocompatible poly($_{\text{D,L}}$-lactide-co-glycolide)nanoparticles studied in vitro on C6 glyoma cells.[105]
- Mesochlorin e_6, a derivative of porphyrin, grafted on a N-(2-hydroxypropyl)methacrylamide copolymer through a disulfide bond demonstrated a time-dependant increase of singlet oxygen generation and in photodynamic efficiency on exposure to the reductive agent, dithiothreitol.[212]
- Phthalocyanines loaded in adamantane modified nanochannels of mesoporous silica nanoparticles,[150] in layered double hydroxides.[156]
- Nanoparticles containing MB (silica coated magnetic particles,[213] silica,[214,] aptamer-silica,[215] phosphonate-terminated silica,[216] calcium phosphate coated with polymer[217] or gold containing polymers,[218] …) demonstrated efficient singlet oxygen production. Photodynamic damage against various cancer cell lines was observed *in vitro* with all these materials. Noteworthy, the singlet oxygen production of MB in silica nanoparticles could be controlled by the aggregation state of the dye in the host.[214]

4.1.4. Water persistent or emerging pollutants

For real water containing natural organic matter and phosphates or for waste-water treatment, it should be emphasized that $HO^{\bullet}$ radicals are much more susceptible to hindrance by background matrices, while singlet oxygen is only slightly inhibited.[219] This is confirmed by the numerous data on the degradation of organic pollutants in water by photosensitizing materials.

Significant degradation of pharmaceuticals under visible light (λ>400 nm) by tin porphyrin on silica and amino-C_{60} on silica was compared with conventional TiO_2 photocatalyst in real wastewater effluents. It was shown that photosensitized singlet oxygenation was efficiently achieved in the presence of background organic matters, while significant interference was observed for photocatalyzed oxidation involving non-selective $HO^{\bullet}$ radical.[220]

4-chlorophenoxyacetic acid was more efficiently oxidized with TPP^+ in zeolites than with TiO_2 under visible light owing to appropriate absorption spectrum of TPP^+, favorable thermodynamics of the electron transfer pathway and co-operative contribution of the zeolite host.[78] Similarly, oxidation of cinnamic acid derivatives was achieved under solar light with TPP^+ in zeoliteY.[221]

Phototransformation of model micropollutants (ibuprofen, bisphenolA, paracetamol) in water samples was achieved with tris(4,7-diphenyl-1,10-phenanthroline)ruthenium(II)chloride or RDP^{2+}, immobilized in a porous poly(dimethylsiloxane) inert support.[30]

Silicagel beads covalently modified with metal-free mono-pyridyltriphenylporphyryneporphyrin (PyTPP) were introduced into polymer microchannel chips and were successfully used for phenol oxidation under continuous flow conditions.[123]

Parabens photodegradation occurred under visible light with polyurethane nanofibers incorporating TPP via singlet oxygen formation, even if the multiple use of the fibers still needed improvements.[134]

Phenol oxidation in water was obtained under solution-flow conditions with polymer microchannel chips accommodated with PyTPP-SiO$_2$ particle (metal-free monopyridyltriphenylporphyrin PyTPP) with better conversion than with bare PyTPP-SiO$_2$ suspension. The evolution of the material after use was assessed by UV spectroscopy.[123]

Degradation by selective oxidation of pesticides (fenamiphos to sulfoxide/sulfone and pentachlorophenols to tetrachlorohydroquinone) was described with three Zn-phthalocyanines incorporated in an ordered mesoporous oxide Al-MCM-41.[222]

Photooxidation of trimethylamine was observed under sunlight in a one-pass flow reactor containing 24 layers of Nafion films containing metal-free phthalocyanine and a perylene-bisbenzimidazole as PSs. The turnover frequency of the catalyst was determined.[223]

Photosensitized degradation of pharmaceuticals under visible light was described with magnetic C$_{60}$-functionalized mesoporous silica encapsulating magnetites nanoparticles for convenient separation from water[174] or by C$_{60}$ derivatized silica.[171,173]

A novel application of core–shell poly-methylmethacrylate nanoparticle as inert, polymeric nano-support for the immobilization of charged ionic sulfonato-porphyrins disclosed a mild, inexpensive, and sustainable procedure for the recovery of the resulting nanocatalyst from aqueous colloids. The NP separation technique, named membrane-mediated electrocoagulation (EC), was based on a new variant of electrocoagulation, which was achieved through water electrolysis and mediated by an ion-permeable membrane. Formation of singlet oxygen in aqueous media was demonstrated by continuous flow sulfoxidation of a model sulfide.[224]

4.1.5. Solvent-free oxygenation

Due to the extended lifetimes of singlet oxygen in air[69] and at the solid-air interface,[179] solvent-free photooxygenation of electron-rich reactants like sulfide is easily carried out. This is an actual green process, only using visible (or solar light) and air as reactants. For instance, when DCA or DBTP were adsorbed on silica beads[115,225] or included or grafted in silica monoliths prepared by the sol-gel method,[117,226] solvent-free photoinduced oxygenation of gaseous dimethylsulfide to sulfoxides (and sulfone in minor amounts) could be easily performed. Since the oxygenated products are efficiently absorbed on silica, the outlet gas phase in a one-pass reactor may be totally free of any sulfide for prolonged periods of time. The absorbed polar products may be removed by washing in suitable solvents.

Similarly, surface decontamination of chemical-warfare agent simulants (demeton-S, malathion, aryl chloroalkyl sulfides) by polymer (hydrothane and polycarbonate) films and fibers containing Zn-octaphenoxyphthalocyanine (ZnOPPc) occurred in solution as well as within polymer matrices.[227] Anthraquinone-2-carboxylic acid, grafted on commercial silica beads or on nanostructured mesoporous silica thin films, led to solvent-free photosensitized oxygenation of dimethylsulfide in a one-pass flow reactor.[26,228] Evidence for type I reaction with radicals formation was obtained by comparison with other singlet oxygen producing materials.

Polystyrene beads loaded with TPP or with grafted TPP, swollen in an appropriate organic solvent, successfully oxidized various substrates directly in Petri dishes where they were introduced.[229] Solvent-free photooxygenation of ethylbenzene mainly to acetophenone and hydroperoxide by Hyflon membranes embedding a fluorous-tagged decatungstate also proceeded by radical mechanisms. Determination of the turnover number (TON) was determined as well as the PS released in hydrocarbon media after irradiation.[188]

5. Supported photocatalysts based on TiO_2

Photocatalytic semi-conductor materials are often commercialized in the form of powders or colloidal suspensions, with well-defined particle size (nanoparticles or aggregates), surface area, cristallinity and surface properties. They can also be lab-prepared by sol-gel process and may thus be obtained as thin films and coatings on various types of surfaces. A comprehensive review of the numerous contributions to the field of photocatalytic materials is not aimed in this short review. Some reference papers on these topics will instead be referred to, as for instance the broadening of the absorption spectrum of TiO_2 towards the visible,[36,35,230,231] or the general properties of TiO_2.[5,232,233,234] Among the thousands of papers dealing with visible light TiO_2, Asahi *et al.*[231] highlighted the significance of N-doped or co-doped TiO_2, which, depending on its preparation method, had sufficient power for mineralization of acetaldehyde in air despite the lower oxidative power of visible-light induced holes. In air, the important role of the conduction band electrons and the possible formation of $HO^{\bullet}$ radicals mediated by superoxide and H_2O_2 (see Eq. 7 and 8) are assumed although the detailed origin of photocatalysis over visible-light-activated N-doped-TiO_2 is still under debate. Likewise, the bactericidal and hydrophilic properties as well as practical applications (textiles, indoor passive materials, tooth bleaching, air purification systems and water treatment systems) of visible-light TiO_2 are extensively discussed in this review[231] and will not be recalled here.

For an easy handling of photocatalysts and a cost-effective separation of it from the systems, the immobilization of TiO_2 nanoparticles on solid supports was investigated from the late 1980s. Various solid supports such as non-woven fabric, ceramic foams, porous metallic Ni or Ti mesh are now available.[1] The supported photocatalyst has to minimize the intrinsic drawbacks issued from the immobilization of TiO_2 on a macroscopic support, namely *i*) low exposed surface-area to volume ratio, *ii*) possible mass transfer limitations, *iii*) increase of pressure drop inside the photocatalytic reactor, *iv*) complexity in providing the light to the photocatalyst, *v)* possible catalyst washout or fouling due to poor photocatalyst adherence.[235]

5.1. Applications of TiO_2 materials

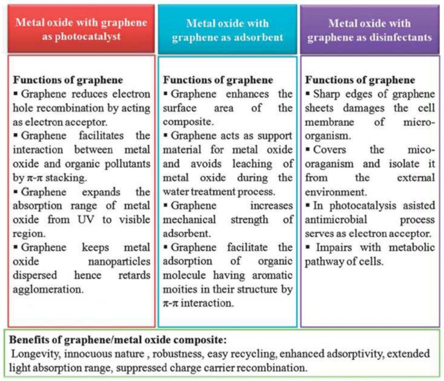
Among the already cited review papers on TiO_2 photocatalysis,[1,5,36,35,230,231,232,233,234] the perspective paper by Teoh and al.[236] provides contemporary views on heterogeneous photochemical conversion, encompassing charge transport characteristics, radical chemistry and organic degradation mechanisms, photocatalyst design and photoreactor engineering. In the following, after the section devoted to water treatment, solid-gas oxidation will be treated according to its application. For *active* air-purifying devices and HVAC (Heating, Ventilation and Air-Conditioning) systems used for indoor air remediation, the photocatalytic media is permeable (monoliths, foams, mesh, non-woven fabrics, fiber mats, ..). On the other hand, gas impermeable *passive materials* (such as films, coatings, paints, glasses, cements, concretes, pavements, ceramics,…) mainly used for self-cleaning properties and sometimes for air purification (mainly oxidation of Volatile Organic Compounds or VOCs indoor and of nitrogen oxides or NO_x outdoor), will be dealt with in section 5.1.3 Photocatalytic passive materials. Self-cleaning and superhydrophilicity properties of TiO_2 based photocatalytic glasses and surfaces will not be considered here.

5.1.1. Water treatment

Chong *and al.*[9] summarized several key scientific and technical requirements for an effective photocatalytic water purification: (i) catalyst improvement for a high photo-efficiency that can utilize wider solar spectra; (ii) catalyst immobilization strategy to provide a cost-effective solid-liquid separation; (iii) improvement in the photocatalytic operation for wider pH range and to minimize the addition of oxidant additives; (iv) new integrated or coupling system for enhanced photomineralization or photo-disinfection kinetics and (v) effective design of photocatalytic reactor system or parabolic solar collector for higher utilization of solar energy to reduce the electricity costs. Since slurry-type catalysts require an additional separation process, the most suitable immobilization strategies are membranes: TiO_2/Al_2O_3 composite, TiO_2 supported or embedded in polymer and metallic membranes, ceramic membranes. The main issues remain membrane structure deterioration, low photocatalytic activity and loss of TiO_2 over time.[9] β-SiC foams are also promising supports with low pressure drop, induced static mixer effect and good light penetration.[237]

Malato *et al.* extensively discussed the use of sunlight to produce $HO^{\bullet}$ radicals by photocatalysis and photo-Fenton process[13] and the treatment of pharmaceutical wastes in water by heterogeneous photocatalysis was recently reviewed.[37,39] Tutorial reviews reported on the different numeration methods for evaluating the efficiency of the photocatalytic action on microorganisms.[238,239]

The application of metal oxide/graphene composites in water treatment and their role as photocatalyst, adsorbent and disinfectant in water remediation was highlighted:[240] other than limiting the electron hole recombination, graphene oxide derivatives also prevent the corrosion and leaching of the metal oxide nanoparticles into the water thereby enhancing the longevity of the photocatalyst. Moreover the formation of π–π stacking between aromatic rings of graphene and organic pollutants also facilitates their adsorption on the photocatalyst thereby enhancing their quenching. Solar photocatalytic disinfection of water using TiO_2/graphene oxide composites was very fast under UV, but also under visible light, evidencing possible singlet oxygen formation.[241]



Metal oxide with graphene as photocatalyst	Metal oxide with graphene as adsorbent	Metal oxide with graphene as disinfectants
Functions of graphene ▪ Graphene reduces electron hole recombination by acting as electron acceptor. ▪ Graphene facilitates the interaction between metal oxide and organic pollutants by π-π stacking. ▪ Graphene expands the absorption range of metal oxide from UV to visible region. ▪ Graphene keeps metal oxide nanoparticles dispersed hence retards agglomeration.	**Functions of graphene** ▪ Graphene enhances the surface area of the composite. ▪ Graphene acts as support material for metal oxide and avoids leaching of metal oxide during the water treatment process. ▪ Graphene increases mechanical strength of adsorbent. ▪ Graphene facilitate the adsorption of organic molecule having aromatic moities in their structure by π-π interaction.	**Functions of graphene** ▪ Sharp edges of graphene sheets damages the cell membrane of micro-organism. ▪ Covers the mico-oraganism and isolate it from the external environment. ▪ In photocatalysis asisted antimicrobial process serves as electron acceptor. ▪ Impairs with metabolic pathway of cells.

Benefits of graphene/metal oxide composite:
Longevity, innocuous nature , robustness, easy recycling, enhanced adsorptivity, extended light absorption range, suppressed charge carrier recombination.

Figure 18 : Roles of graphene in improving photocatalytic activity, adsorptivity and antimicrobial activity of the metal oxide/graphene composite and its possible benefit. From [240] with permission of the copyright owners.

5.1.2. *Active photocatalytic air treatment*

Photocatalytic treatment of VOCs in indoor air is extensively investigated to-day. Mo *et al.* reviewed the various photocatalyst used for that purpose, their preparation, their use as coatings and deactivation, as well as the kinetic models and VOCs successfully oxidated.[3] Based on patents analysis, Paz identified several challenges associated with using photocatalysis for indoor air treatment:[10] *i)* mass transport on the photocatalytic surface; *ii)* adsorption of pollutants; *iii)* contact time; *iv)* degradation of VOCs with minimum emission of by-products: *v)* deactivation of the catalyst, *vi)* optimizing the utilization of photons; *vii)* adhesion of photocatalysts to substrates. According to Hay *et al.,* both catalyst lifetime and by-products formation are still barriers for implementing this technology.[42] Some efforts towards the photocatalytic elimination of biological air pollution were also described.[12,242,243]

Non-woven photocatalytic fabrics are light, flexible and inexpensive and some of them were or are commercial (media 1048 from Ahlstrom®, Quartzel® from Saint-Gobain Quartz,…..). However they are often not mechanically stable and may release TiO_2 nanoparticles when handled. An annular plug-flow reactor coated with such a media was used for ammonia and butyric acid degradation.[244] A prototype air cleaner provided with flat or pleated photocatalytic Quartzel® media, was operated in a 20 m^3 recirculated environmental chamber. The use of pleated media was shown to increase significantly the system performance by increasing the dwelling time of pollutants on the irradiated photocatalytic surface.[245] Pure TiO_2 microfibers, prepared by a sol-gel process followed by wet spinning, injection and coagulation of fiber material dispersed in a liquid were used in specially designed recirculation batch reactors for the mineralization of several VOCs.[246],[247] With the thinner fibers (17 x 40 μm) arranged as a loose mat, the kinetics of mineralization of acetone, heptane and toluene were compared with that obtained with a Quartzel® mat under strictly similar conditions, specially regarding light absorption. The lab-made pure TiO_2 fibers proved to be less efficient than commercial material for acetone and heptane mineralization at 20% relative humidity (RH), but performed as well at 60 % RH. However the pure TiO_2 fibers were more efficient for toluene mineralization, probably due to their improved micro/mesoporosity.[248] A TiO_2-coated polyester photocatalyst was also used for the gas-phase degradation of gaseous methanol in a single-pass reactor.[249] In addition to the previous supports, polymer-supported TiO_2, which have ability to maximize utilization of sunlight, might also be useful.[250]

Porous or multichannel support materials such as honeycomb- or square monoliths combine a good contact between the photocatalyst and air and may stand high flow rates with low pressure drop. However they suffer poor irradiation distribution and a limited penetration of light inside the monolith,[251] except with organic polymers with high transmittance in the UVA range.[252]

TiO_2-immobilized porous ceramic foams are one of the most useful photocatalytic filter for commercial air-purifiers designed for indoor-air remediation.[253] They present a high heat-resistivity for TiO_2 immobilization via sintering of a titania-based xerogel. Their highly open porous structure with large surface area provides excellent properties for optimizing gas flow with a low pressure drop and a good surface contact.[1] Besides the most often used metallic (mainly made of nickel or aluminium) and ceramic foams (mainly made of alumina or cordierite), polymeric and carbon foams are less used.[235] Alternatively β-SiC foams with medium specific surface area and large mean cell size recently demonstrated very interesting properties for methylethylketone oxidation at low flow rate and concentration both in a single-pass or recirculation mode.[254] A new miniaturized LEDs/β-SiC foams reactor was designed, which showed improved performances with 392 nm LEDS using a visible light responsive Pt chloride modified rutile TiO_2 (MPT623 from Ishihara Sangyo Kaisha) for coating the β-SiC foams. Another approach based on titanium mesh impregnated photocatalyst TMiP™ was developed by Ochiai *et al.* and successfully used for acetaldehyde decomposition in batch mode.[255]

5.1.3. Photocatalytic passive materials

Surface-photocatalysed reactions on pollutant-removing building products are often claimed by companies' homepage. The basic concept is to use large area objects (walls, roofs, tiles, pavements, buildings, bridges,…) as platforms for air decontamination and improvement of the quality of ambient air. The photocatalyst can be applied in various forms including cementitious blocks, concrete objects or over-coated thin-layers, often referred to as "self-cleaning" coatings. Once again the main issues to overcome are mass transport, adsorption of contaminants, deactivation of the catalyst, optimizing the utilization of photons and adhesion of photocatalysts to the substrates.[10]

For indoor air, the efficiency of several coatings and paints under artificial lighting or UV light for pollutants removal and by-products formation,[256,257] or antimicrobial effect[258] was addressed in various papers. For instance, the ability of four samples of tiles, including photocatalytic ones, for removing formaldehyde and several VOCs was investigated in chamber experiments according to standard ISO 16000-9 under artificial light. Secondary emissions, including formaldehyde, were identified and were generated by cleavage, hydrolysis, rearrangement or radical reactions.[256] The ability for decomposition of formaldehyde and of a mixture of 5 VOCs of six photocatalytic indoor-paints with TiO_2 embedded in different binder systems such as lime, polyorganic siloxane, silica sol-gel and organic binders, was studied in an environmental 27 L test chamber in a static batch mode with either office or UVA light. Binders and additives decomposed to aldehydes (including formaldehyde) and ketones, while formaldehyde removal was not detected and side-products were higher under UVA light than under normal light. The VOCs introduced into the chamber were not decomposed.[257] Conversely, photocatalytic paints were shown to quickly oxidize NO and NO_2 mainly to nitric acid/nitrates with near to unity yield in a single-pass flow tube reactor.[45] Photocatalytic mortars containing TiO_2, initially prepared for self-cleaning applications, successfully oxidized gaseous formaldehyde in a specially designed single-pass reactor.[259] The significance of adsorption of molecules to be oxidized on the kinetics of the photoreaction was modeled.[260]

For outdoor air under solar irradiation, the main purpose of these passive photocatalytic materials, besides self-cleaning, is the oxidation of nitrogen oxides.[44,43] Even if numerous laboratory experiments actually demonstrated the efficiency of these materials,[45] real life studies (tunnel under artificial UV) are more balanced owing to severe de-activation of the catalyst and strong influence of relative humidity and wind speed.[261,262]

Other applications include the use of photocatalytic polymer films for miscellaneous pollutant oxidation. Polymer films containing embedded TiO_2 were successfully used for the gas-phase oxidation of ethanol in a single-pass annular reactor where the walls were coated with the polymer. Even if the films appeared stable on the experiment time-scale, polymer degradation occurred to some extent.[263] Industrial photocatalytic virtually impermeable films (VIF), made of polyethylene embedding TiO_2 and polyamide layers were prepared at an industrial scale for degrading dimethyldisulfide (DMDS) used as fumigant, in order to decrease the DMDS concentration in the air space between the treated soil and the film. Large chamber batch reactors designed to reproduce the large fields solar experiments led to the determination of the optimum composition of the films (number of layers, thickness and TiO_2 concentration) by studying the degradation kinetics of acetone and DMDS.[264]

It should be mentioned that mesoporous TiO_2 or mixed SiO_2/TiO_2, although intensely investigated, were only scarcely used for gas-phase environmental applications, but rather for energy applications (water splitting, solar cells, lithium-ion batteries,…).[265] The high photocatalytic efficiency of mesoporous films of TiO_2 prepared by a template-assisted procedure and used for nitrogen oxide oxidation was assigned to a local increase of NO pressure in the nanopores of the mesoporous film close to the photocatalytic sites.[266] Likewise, macrostructured mesoporous TiO_2 materials prepared using a micelle-templated method and containing anatase TiO_2 presented a much higher efficiency for ethylene oxidation than commercial anatase-rutile TiO_2 due to their sponge-like structure favoring ethylene intradiffusion and photoabsorption.[267] Mesoporous titanosilicates with worm-like 3D-mesoporosity were highly efficient for propylene photooxidation due to the three-dimension mesoporosity, large mesopores and enhanced hydrophobicity arising from silylation of the material.[268]

6. Concusion

This perspective paper intends to give a general view of the compared properties, for environmental and health applications only, of inert materials containing photosensitizers (PSs) by comparison with TiO_2-based photocatalytic materials. As far as possible, review papers on these highly investigated topics are recalled and selected non-exhaustive references presented.

The main interest in PS-containing materials is their activation mostly under visible light with possible tuning of the absorption wavelength, hydrophilicity/hydrophobicity, porosity, adsorptive ability and aggregation state of the PS for optimized performances. A particular feature is the possible modulation of the PS properties with its confinement inside porous micro- or meso-structured materials. Singlet oxygen is generally the main produced ROS with only scarce PS examples evidencing type I mechanisms (TPP^+, anthraquinone, Ru(II) salts).

These PS-containing materials are complementary to TiO_2-based materials: no mineralization of organic pollutants is expected as with TiO_2. However a better selectivity towards electron-rich substrates in complex matrices make them highly attractive for the oxidation of emerging organic pollutants in wastewater. Solvent-free oxygenation of electron-rich substrates is also easily achieved. Their efficiency against microbes, viruses and fungi is quite significant due to the production and enhanced lifetime of singlet oxygen, which is able to diffuse through cellular membranes. Another potential application is photodynamic therapy, for which recent efforts are devoted to the selective targeting of tumor cells and to the optimization of the photophysical properties of the PS in the therapeutic window.

The main drawback of these PS-containing materials is the possible leaching of the organic content to the solution (if used as suspensions in a liquid phase), which has to be addressed in the dark and under irradiation. According to the review on numerous papers in the field, the material photostability is sometimes (but not so often) addressed by recycling experiments and should be more carefully considered for the application of these materials under real conditions, with for example a systematic determination of the turnover number (TON).

TiO_2-based materials are much more extensively studied and their applications in the environmental domain are completely different. Visible-light responsive photocatalytic materials appear very appealing, but they have not yet found large market applications. This is possibly due to the fact that photocatalytic reaction rates and quantum yields are still low under visible light and that the exact reaction mechanisms are not completely understood.

A comparison of the advantages-drawbacks, especially from a mechanistic and economic point of view, of visible-light TiO_2 relative to PS-containing materials could be worth. However, for a useful comparison, in both cases the accurate description of the irradiance of the light source is necessary, and if possible the determination of the quantum efficiency of the material, since the determination of quantum yields in these highly diffusing media remains a challenge.

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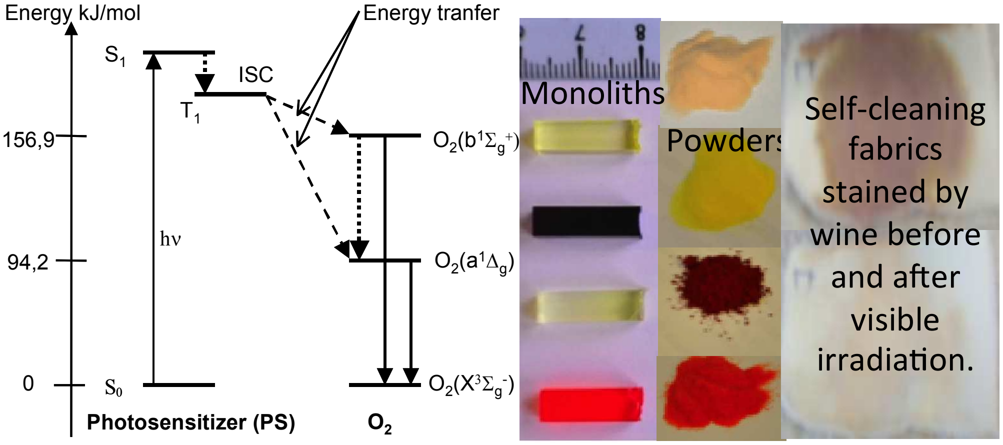

Photosensitizing materials made of organic dyes embedded in various supports are compared to usual supportd TiO_2-based photocatalysts.