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State of the art and perspectives on materials and applications of photocatalysis over TiO_2

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1. Introduction

We present a short review of some recent trends, accomplishments, and problems pertaining to photocatalysis over TiO_2 and related semiconductors. We have focused in particular on developments in TiO_2-based materials, and on applications including continuing progress in longstanding uses such as photocatalytic water or air treatment as well as more recent ones such as self-cleaning surfaces and, finally, new applications. This article will not consider the topics of degradation mechanisms or reactor design, each of which would merit a lengthy review itself. Furthermore, the references cited are not intended to be comprehensive (for that we refer the reader to an extensive bibliography [1]), but to provide some highlights and examples regarding recent research and basic knowledge.

Photon absorption by TiO_2 results in the promotion of an electron from the valence band to the conduction band of the titania, leaving behind a "hole" (i.e, electron vacancy) in the valence band, provided the photon has an energy at least equal to that of the bandgap of the photocatalyst. The bandgaps for anatase and rutile being 3.2 and 3.0 eV, corresponding to wavelengths = 385 and 410 nm, respectively, ultraviolet light is needed for photoexcitation. The electron–hole pairs can either recombine or participate in chemical reactions with surface/adsorbed species (Scheme 1).

Oxidation of water/hydroxide ion by the valence-band hole (h^+_{VB}) can produce the hydroxyl radical, °OH. The conduction-band electron (e^-_{CB}) can react with molecular oxygen to form the superoxide radical-anion, $O_2{}^{\circ -}$, which can be involved in further reactions (Scheme 1). In addition, h^+_{VB} and e^-_{CB} can react directly with adsorbed pollutants (Scheme 1). The radicals thus formed, dioxygen and water can participate in further reactions, resulting ultimately in mineralization of the organic pollutants.

2. Improving TiO_2 activity (Scheme 2)

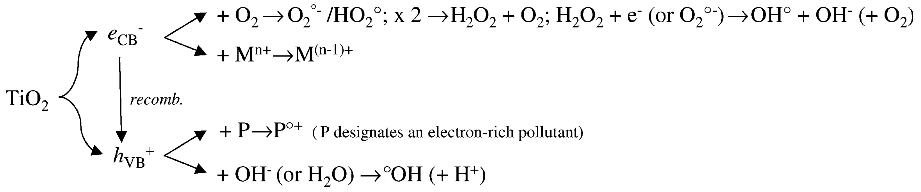
Photocatalytic activity enhancement induced by derivatizing the TiO_2 surface with organic substances is not considered here as it been recently reviewed elsewhere [2].

2.1. *Novel preparations of TiO_2*

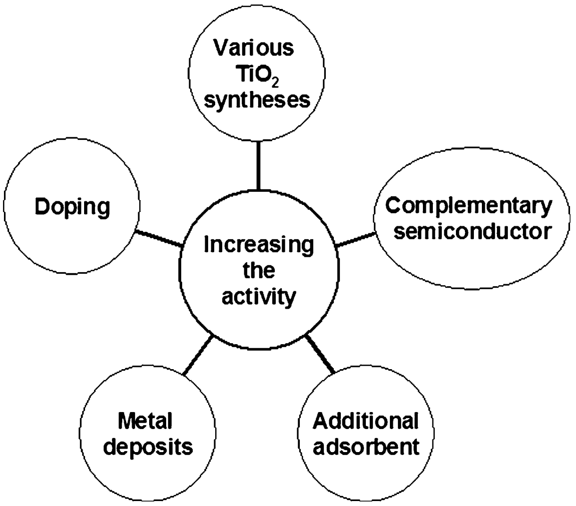
TiO_2 can be synthesized via a variety of techniques, but sol–gel methods have become the most widely used. The ability to alter a number of variables – e.g., pH, the choice of Ti salt, temperature, and reaction times and sequence – to dry in a supercritical fluid [3] and to add other reactants offer great flexibility in the method. We briefly mention here studies regarding mixed-phase TiO_2 samples.

A new method for synthesizing coupled anatase–rutile TiO_2 nanoparticles relies on partially dissolving rutile in sulfuric acid, then reprecipitating the aqueous Ti^{4+} by adding NH_3(aq) [4]. Mixed-phase catalysts outperform either pure anatase or pure rutile, in agreement with earlier reports. However, the authors' optimal preparation had only 0.5 wt% anatase; it outperformed Degussa P25 (about 80% anatase) by 35% with respect to gas-phase removal of acetaldehyde. TiO_2 samples with anatase–rutile ratios similar to that of P25 performed poorly, as did a physical mixture of rutile and 0.5% anatase. This supports the view that processes occurring at the anatase–rutile interface are key to the high activity of mixed-phase titania preparations [5, 6].

One recent trend has been increased attention focused on brookite, the oft-neglected phase of TiO_2. Formerly encountered in trace amounts in largely rutile and/or anatase preparations of TiO_2, brookite has been synthesized in pure nanoparticles by sol–gel methods [7]. Cyclic voltammetry shows a slightly higher electrochemical activity for the brookite nanoparticles than for pure anatase. Brookite also has a slightly higher bandgap than anatase, which would reduce the spectral breadth of its photoresponse. Brookite nanoparticles have been further examined with a view to use in a dye-sensitized solar cell [8], but they have not yet been assessed photocatalytically. Pulsed laser deposition has produced a film consisting of roughly 45% brookite, 35% anatase, and 20% rutile, although it too has not been photocatalytically tested [9].



Scheme 1. Reactive species and chemical equations that are thought to be at the basis of photocatalytic transformations over TiO_2 in the presence of O_2.



Scheme 2. Ways of improving TiO_2 photocatalytic activity.

Furthermore, the role of trace amounts of brookite formed during sol–gel synthesis has been examined [10]. It appears that the presence of brookite, formed during the initial TiO_2 particle formation, reduces the anatase-to-rutile conversion temperature in the sintering step. This is explained in terms of pressure exerted on anatase particles by brookite during heating [11] and the formation of rutile nucleation sites at the anatase–brookite interface. Further investigation is needed on the relationships between photocatalytic performance and phase composition.

2.2. *Combining TiO_2 with another semiconductor oxide*

It was suggested years ago that transferring conduction-band electrons from TiO_2 to another semiconductor could be a good means of decreasing the recombination rate of charges in photoexcited TiO_2. Indeed, this phenomenon was found to occur as evidenced by photoelectrochemical measurements. On this basis, TiO_2 has been combined with several semiconductor oxides among which are ZrO_2 [9, 10, 12, 13], SnO_2 [14], MoO_3 [15], WO_3 [15], In_2O_3 [16] and Nb_2O_5 [17]. Sulfides or even other chalcogenides have also been used but, in general, they are not as stable and/or cost-effective as oxides. Coupled semiconductors that do not include TiO_2 have also been proposed as, for instance, WS_2–WO_3 [18]. Curiously, for most TiO_2–semiconductor oxide couples, the maximum increase in photocatalytic activity for the degradation of various compounds in water and air is between 1.5 and 3 with respect to TiO_2 alone. It is obvious that the surface of the grains or films is modified by the added semiconductor. In that regard, increased surface acidity, as well as textural/structural modifications – especially in the surface layers – have been invoked to contribute to the augmented photocatalytic activity. Not surprisingly, the preparation method and the proportion of the added semiconductor play a great role. In most of the above mentioned studies the authors have tried to sort out the origins of the differences produced by these parameters.

The future of these materials depends on their cost balanced against the increase in photocatalytic activity. Added elements are rarer than Ti and therefore more expensive. Also, changes in the mechanical and optical properties, durability, etc. must be determined in regard to the envisaged utilization.

2.3. *Combinations of TiO_2 and other adsorbents*

The photocatalytic degradation of dilute pollutants can be enhanced by the addition of high-surface area adsorbent materials, in particular activated carbon [19–22] and zeolites [21, 23]. The desired result is a system where the two materials do not perform their respective tasks – adsorption and photocatalytic degradation – independently, but interact synergistically. This can take the form of the migration of pollutant molecules from the adsorbent material to the catalyst surface or degradation of pollutants on the adsorbent by reactive species generated at the TiO_2 surface. Indeed, gas- and aqueous-phase experiments did show increases in reaction rates in the case of various methods of depositing TiO_2 on or mixing TiO_2 with different adsorbents. The optimal adsorbent/TiO_2 ratio is that which yields the maximum interfacial area. In that respect, the use of carbon nanofibers to support TiO_2 could be of interest [Keller et al., unpublished results].

Along with activated C and zeolites, clays have also been used as the additional adsorbent [24, 25]. In that case, TiO_2 can be intercalated and form separated pillar-like structures between the clay layers. For the photocatalytic removal of monochlorophenols in water, the TiO_2-pillared clays were less active than Degussa P-25 TiO_2 when equal masses of both solids were employed [25]. By contrast, some TiO_2-pillared clay samples were more active than Degussa P-25 for the stationary-state removal of methanol in an air stream [25], suggesting that transfers between the clay and TiO_2 were easier in the absence of liquid water.

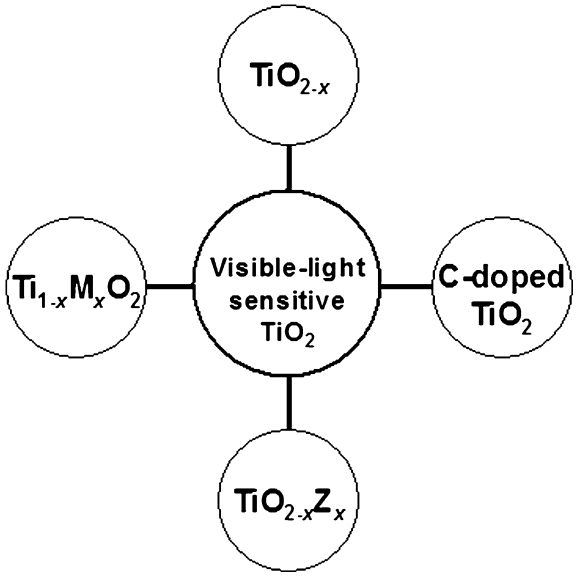
Such results from applied studies have been bolstered by more fundamental research on well-defined structures of stripes or islands of TiO_2 on Si, which showed that pollutants can diffuse from Si sites to TiO_2 sites over distances as long as 20 μm [26]. Migration of active species generated by photoexcitation of TiO_2 has also been demonstrated by experiments in which soot deposited on a partially TiO_2-coated glass plate by *n*-hexane combustion was oxidized into CO_2 even when the soot and TiO_2 were separated by distances as high as 80 μm [27]. The oxidizing species are also supposed to be able to diffuse via air [28].

2.4. *Methods for extending the TiO_2 photocatalytic activity to the visible spectral range (Scheme 3)*

Driven by the need to use solar light more completely, many investigations have been performed to make TiO_2 photocatalytically active beyond its absorption threshold of 400 nm. The goal is to create energy levels within the band gap or to shift adequately the conduction band and/or the valence band, so that photons of lower energy are able to excite electrons.

Substitution of Ti^{4+} cations by other cations having about the same size is one of the means. However, the use of Cr^{3+} cations, for example, was found unsuccessful even for a content of 0.85 at.% when the substitution was homogeneous within the TiO_2 lattice because of the use of a flame reactor to prepare the samples. Moreover, the photocatalytic activity in the UV spectral region was dramatically decreased. This effect was attributed to electron–hole recombination at the foreign cations [29].

However, the introduction of foreign cations by the sol–gel method was sometimes found to be favorable [30]. For example, substitutionally disordered TiO_2 containing an optimum doping of ca. 20 at.% W was four times more active than undoped TiO_2, prepared otherwise identically, for the stationary-state removal of toluene in wet O_2 under simulated-sunlight irradiation for the same mass of photocatalyst. The W 5d orbitals were assumed to increase the width of the Ti 3d conduction band toward lower energies; also, the contraction of the lattice due to the introduction of tungsten was supposed to broaden both the valence band and the conduction band, thus diminishing the band gap [31].



Scheme 3. Routes to TiO_2 active under visible light irradiation.

It has been observed that TiO_2 can be sensitized to visible light by implanting V, Cr, Mn and Fe with a high voltage accelerator [32]. In that case, the cations are deeply implanted, while the first layers of TiO_2 remain free of foreign cations. From XANES spectra it has been deduced that V^{3+}, V^{4+} and Cr^{3+} cations in these implanted samples were isolated and in octahedral positions, whereas chemically doped Cr–TiO_2 contains aggregates of Cr^{6+} and Cr^{3+} cations in tetrahedral coordination. The mixture of the Ti 3d orbitals and the orbitals of the other cation was supposed to be the origin of the decrease in the band gap, but it was not clear why the coordination state and isolation of the implanted cations was essential.

In 1986, TiO_2 prepared from titanium hydroxide – itself made from $TiCl_4$ hydrolysis using NH_4OH – was found to be visible-light active, unlike TiO_2 prepared without using NH_4OH, and the activation was tentatively attributed to a NO_x impurity level [33]. However, it is only recently that anion doping of TiO_2 has been thoroughly investigated [34–36]. The sensitization of $TiO_{2-x}N_x$ to ca. 550 nm has been attributed to a mix of N 2p orbitals with O 2p orbitals giving rise to an energy level above the valence band. The increase in photocatalytic activity depends very much on both the N content and the method of preparation. One of the drawbacks is the possible creation of Ti–O–N bands or the introduction of interstitial N. That may lead to energy states below the conduction band enhancing the recombination rate of the charge carriers [35].

S-doping of TiO_2 has been achieved by using either thiourea (mixed with titanium isopropoxide) as the source of the S element [37] or by annealing TiS_2 [38, 39]. In the first case, S was found to be introduced as S^{6+} cations, according to the interpretation of XPS spectra, and the resulting distortion of the TiO_2 lattice was suggested to be probably the origin of the sensitization to ca. 600 nm; however, the activity at 350 nm for methylene blue in water was decreased by a factor of about 1.7. For the samples produced from TiS_2 [38, 39], the sensitization to ca. 500 nm was proposed to arise from substitution of O by S in the lattice, resulting in a broader valence band due to the S 3p states. No comparison of UV generated photocatalytic activity with a similar undoped TiO_2 could be made, because of the particular preparation mode.

Introducing 0.5–3 at.% of C in TiO_2 – as carbonate according to IR spectra – reduced the band gap by a maximum of 0.14 eV, and the samples were 30–60 times more active than unmodified TiO_2 for the removal of 4-chlorophenol in water under irradiation at 455 nm [40]. No indication was provided about the relative activities under UV-irradiation. C "incorporation" in TiO_2 is presently the subject of many investigations. The chemical state of carbon in TiO_2 is not yet clear.

It is known that TiO_{2-x} can be more sensitive beyond 400 nm than TiO_2. However, for any practical use, this defect in stoichiometry must be irreversible, which is generally not the case if a thermal treatment in a reducing atmosphere is employed to produce the defect. By contrast, irreversible oxygen vacancies have been found to be created by RF plasma as inferred from an EPR signal attributed to an electron trapped at these vacancies [41, 42]. Sensitivity up to 600 nm was observed and assumed to correspond to energy states situated at 0.75–1.18 eV below the conduction band. The sample irradiated at 450 nm allowed the removal of NO in air, unlike non-plasma-treated TiO_2, and the activity under UV-A irradiation was not changed. It is obvious that TiO_2 sensitive in the visible spectral range is colored, at least slightly. Consequently, one should be aware that the color can hinder some uses, e.g., for certain self-cleaning materials.

In conclusion, the photocatalytic activity of TiO_2 in both the visible and UV spectral regions is highly dependent on the preparation method and the content of the foreign element if any. Nevertheless, activity dependence upon these factors is very often found in the case of catalysts used thermally in industry, so it should not be prohibitive for applications. Methods such as ion-sputtering, ion implantation, and plasma treatment can be readily industrialized. Whether it is cost-effective is obviously determined by the increase in activity under visible-light irradiation and by the use of TiO_2 thus modified. Reproducibility of the other methods, stability of the samples obtained, and applicability on a large scale require further research and development. Ongoing investigations aim at better determining the origin(s) of the change in sensitivity in both the visible and UV spectral regions, which obviously involves excellent characterizations of the samples.

3. Ongoing applications

3.1. *Supported TiO_2*

TiO_2 immobilization is essential in most applications. Recent years have seen significant progress in expanding the repertoire of methods for coating TiO_2 onto fixed supports. The goals are to obtain films that are highly active, stable, and easy and inexpensive to produce, and that can be fabricated on a variety of surfaces. Whereas early TiO_2 films were cast mainly on glass, or sometimes metal, there is intense interest in designing coating methods compatible with organic substrates. This would allow the fabrication of photocatalytically active flexible plastics or membranes. The two principle challenges in coating TiO_2 on organics are (1) the limited thermal tolerance of organic surfaces precludes the sintering temperatures used on glass or metals to better anchor the TiO_2 layer, and (2) the substrates themselves are prone to photocatalytic degradation [43].

The first problem has been addressed via work toward the development of low-temperature sol–gel synthesis techniques. One approach is to seek sols that can form well-crystallized TiO_2 at mild temperatures [44, 45]. Another approach has been "cold sintering", where high pressure is applied at room temperature to cause crystallites to fuse together [46–49]. Cold-sintered films, on flexible plastic substrates, are suitable for use in dye-sensitized solar cells (although with reduced efficiency) but have not been tested photocatalytically.

The second concern is often approached by placing some intermediate layer between the organic substrate and the TiO_2. But this raises the difficulties of finding a material that has sufficient affinity for both the organic substrate and the inorganic photocatalyst while satisfying other necessary properties. Methods involving multiple layers which progress from organic to inorganic character add to the difficulty and expense of manufacture.

But it is possible that intermediate layers may be avoided altogether by casting TiO_2 films from sols containing a protective polymer. Using a TiO_2 sol containing poly(dimethylsiloxane) (PDMS), a film was cast on a poly(methyl methylacrylate) (PMMA) substrate [50]. The TiO_2 was well crystallized after heat treatment at only 373 K. The Si–O–Si backbone of the PDMS polymer is resistant to photocatalytic attack and provides some protection to the underlying substrate. The addition of PDMS reduces the photocatalytic activity. However, for practical and economical interests, this can be balanced against the protection of the organic substrate. For example, the addition of 20 wt% PDMS to a titania sol reduces the photoactivity of the resulting film by 17% (with respect to the degradation of a coating of methylene blue), while reducing the degradation of the PMMA support by 81%, compared to a PDMS-free sol [50].

3.2. *Self-cleaning surfaces*

3.2.1. *Hydrophilicity*

Under UV-irradiation TiO_2-coatings become hydrophilic. This is of great interest for a number of applications such as, for example, rear-view mirrors. The water contact angle thus obtained and the duration of the phenomenon in the dark depend on the coating, e.g. roughness has been found to be favorable [51].

According to various experiments, hydrophilicity appears to be related to the density in surface OH groups. This density increases under UV-irradiation. Water molecules are prone to be hydrogen-bound to the OH groups, which explains why rainwater forms films instead of depositing as droplets [52].

The most recent interpretation advanced by the discoverers of UV-induced TiO_2 hydrophilicity is based on the existence, before UV-irradiation, of Ti–O(H)–Ti surface species [52]. As a result of photonic excitation a hole is located on the O atom of some of these species, thus weakening the Ti–O bonds. Subsequent dissociative adsorption of a water molecule, acting as a nucleophilic agent, gives rise to two Ti–OH surface species and the release of a proton. This dissociative adsorption competes with the hole-induced formation of a hydroxyl radical from a water molecule. Assuming that two neighboring Ti–OH species are less stable than one Ti–O(H)–Ti species, a gradual decrease in surface OH groups – and hence in the hydrophilicity – occurs in the dark [52]. However, this reversibility would imply, in ambient air, desorption of O_2 and formation of water or formation of H_2O_2. It is expected that establishing the mechanism could lead to materials having a more stable hydrophilicity in the dark.

TiO_2 films are used to render surfaces self-cleaning. This property is due in part to the fact that irradiated TiO_2 films are not just hydrophilic but ampiphilic: the surface contains both hydrophilic and hydrophobic microdomains, which attract drops of polar or nonpolar liquids, respectively. This allows a water rinse to flush away an oily coating [53].

3.2.2. *Degradation of organic deposits*

Organics are also photocatalytically degraded on the same coatings [54–58]. Frequently, this is tested against fatty acids (e.g., octadecanoic (stearic) acid [55], hexadecanoic (palmitic) acid [56, 58]), which are solid at room temperature and resemble real-world oily deposits, for example, those deposited following the erosion and transport of the waxy surface layers of tree leaves. Although efficiencies for degradation are often low, the rates have been calculated to be, for instance, sufficient to degrade human daily bioeffluents given reasonable assumptions for window surface area and solar irradiation [55] or to remove oily finger prints very rapidly [58].

Self-cleaning glass is sold by various companies including Pilkington, PPG, Saint-Gobain, Toto, etc. A TiO_2-based material can be applied to existing window panes using simple rollers (Toto). In Japan, several building façades include TiO_2-coated stainless steel or aluminum. TiO_2 can also be incorporated into the top layers of cementitious materials used as the finishing coverage in buildings, houses, etc. [59]. Examples include, in Europe, the "Dives in Misericordia" church near Rome and "l'Ecole de Musique" in Chambéry, France (CTG/Italcementi).

3.3. *Air purification and deodorization*

3.3.1. *Indoor air*

A priori, photocatalysis appears well suited to the purification and deodorization of ambient air. First, this technology transforms all categories of organic pollutants and oxidizes NO, NO_2 and SO_2. Second, the concentrations of the pollutants are low, so that for a well-designed treatment unit no saturation of the TiO_2 surface is expected.

Nevertheless, several characteristics of photocatalytic reactions and indoor air composition and conditioning have to be considered to achieve proper purification. First, comparison of the photocatalytic transformation rate r with the usual rate of air exchange between indoors and outdoors shows that, for a photocatalytic purifier of reasonable size, the concentrations of CO and CH_4 cannot be expected to be significantly decreased because they reach a few ppmv in ambient air; on the other hand, for a pollutant at a concentration C below one ppbv, r (which is proportional to C) can be so low that the decreases in C might also not be significant. Second, r depends on the chemical stability of the pollutants; therefore, pollutants containing the benzene ring will slowly yield products corresponding to ring opening, so that partially oxidized benzene derivatives may cover the TiO_2 surface; a sufficient amount of TiO_2-coated material must be employed in any photocatalytic unit to avoid this problem [60]. Third, NO, NO_2 and SO_2 are photocatalytically oxidized to nitrate and sulfate anions, which form solid deposits on TiO_2; periodic replacement of the TiO_2-coated material must be made [60] and the customer must be instructed appropriately [60]. Fourth, pollutants containing several C atoms cannot be expected to be completely mineralized after a single pass in the photocatalytic purifier, given the high air flow rates (required to homogenize the air adequately) and the finite number of TiO_2-coated sheets used in the purifier [61, 62]. In general, oxidation displaces the equilibrium from the gas phase to the absorbed phase, but cleavage of C–C bonds increases the volatility. Consequently, low molar-mass carbonyls are released into the air; they are progressively mineralized only because of multiple passes in the purifier. Carboxyl acids are less volatile and more readily adsorbed and mineralized, so that they are not of concern compared with carbonyls. Testing photocatalytic purifiers for their effect on the concentrations of low molar-mass carbonyls under the conditions of their use is indispensable [62]. On the basis of this test, the maximum air volume that can be treated by the purifier should be communicated to the individual customer or to the institutions in charge of air conditioning in buildings.

3.3.2. *Outdoor air*

It has been claimed that TiO_2-coated cimentitious materials used to cover façades or to pave roads can significantly improve air quality in certain locations [63]. In fact, as photocatalytic transformations are restricted to pollutants that are adsorbed, only an extremely small fraction of air pollutants can be photocatalytically eliminated in open spaces. The effect of TiO_2-coated materials may be noticeable only in confined spaces, such as canyon streets. In such situations, it is expected that the rate of clean air delivery from TiO_2 is higher than the sum of the emission rates of pollutants by vehicles (and other sources) within the space considered and the rate of influx of pollutants from outside the space considered. Recent field experiments concerning NO_x are encouraging [Italcementi group, unpublished results]. However, further measurements are necessary regarding total hydrocarbons, BTEX and low molar-mass carbonyls (as mentioned for indoor air). The acidity generated by photocatalytic oxidation of NO_x and SO_x to nitrate and sulfate ions is, in principle, avoided in the case of cementitious materials because of their basic constituents [59].

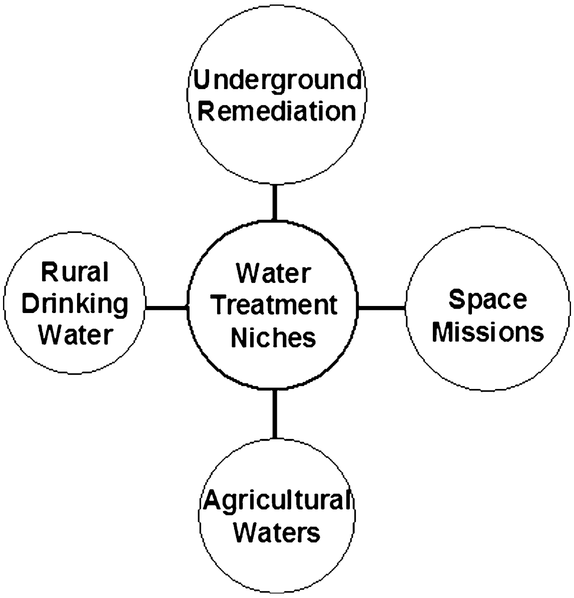
3.3.3. *Air effluents*

Possibility of efficiently treating air effluents as well as aqueous effluents (Section 3.4.) depends on the case. Photocatalysis is impeded by low removal rates and the associated need for long contact times. An improvement may result from the use of planar waveguides which transmit light in an attenuated total reflection mode and thereby can achieve a better light distribution to TiO_2 [64]. In addition, plastic waveguides can be used as monoliths [65, 66] to minimize the pressure drop.

Adding ozone to either dioxygen or air is also an excellent means of increasing the photocatalytic rates [61, 67]. It may be applicable in some cases.

3.4. *Water purification*

Applications of photocatalysis in this domain are obviously determined by the quality and quantity (or flow rate) of the water to be treated and the requirements regarding the treated water, as is also the case for gaseous effluents (indoor air being a particular case with no equivalent for water). Given the low photocatalytic rates of degradation/mineralization of pollutants and the difficulties in increasing them markedly (see Section 2), applications are limited to niches, but there are a variety of niches (Scheme 4).



Scheme 4. Niche applications of photocatalytic water treatment.

Some of them take advantage of the fact that photocatalytic treatment does not involve liquid and gaseous reactants, can be automated and, accordingly, does not need attendance, which is particularly appropriate for isolated locations. A Canadian firm [68] has demonstrated that photocatalysis can be used successfully for the remediation of underground water containing diverse pollutants at abandoned industrial sites. Mobile units can be used. Photocatalytic treatment has been found to be more economical than adsorption on activated carbon, at least in certain cases. However, laboratory-scale trials are needed each time to evaluate the potential results. Prior chemical precipitations can be necessary to remove substances detrimental to the photocatalytic rates.

NASA is interested in photocatalysis to provide drinkable water in space shuttles [68]. The reuse of water after photocatalytic cleaning is considered in the semiconductor industry. A common characteristic of both applications is the daily treatment of very small or relatively small quantities of water with low pollutant levels.

Other niche applications are based on the use of solar light if the low and variable UV radiant flux allows it [69, 70]. Experiments at various scales have shown that solar photocatalysis can be used in agriculture to treat water used to rinse vessels that had contained pesticides [69–71]. A field experiment has assessed the capability of a solar photocatalytic device including a photovoltaic-driven pump to be used on the side of a vineyard to purify the rinse waters from tractor cisterns; in that case, favorable factors are the 12-day interval between two pest control treatments, as well as the sunny region and season [71]. Of course, photocatalysis cannot eliminate toxic ions, such as Cu^+ and Zn^{2+}, that are present in the rinse waters either free or combined with the organic constituents. The use of solar photocatalysis to clean waters from textile industry has been investigated in view of reusing them and/or discarding less-polluted waters [72]. As it is capable of inactivating bacteria, solar photocatalysis could be a well-adapted technology to provide drinkable water to isolated communities. Again, preliminary trials are indispensable, and the photocatalytic apparatus must be greatly over-sized as a precaution.

The future of photocatalysis to purify waters lies in (i) field experiments for the particular cases identified as relevant for this technique, and, possibly, in combination with another technique as a pre- or post-treatment, and (ii) improving the photocatalytic rates by synthesizing more photocatalytically active materials as for the other applications (see Section 2). Present fundamental knowledge appears sufficient to select the particular applications, and to choose the conditions for photocatalytic purification, even though some aspects of the basic mechanisms and degradation pathways are debated.

3.5. *Water splitting*

Many attempts have been made to split water. Recently, there has been renewed interest in this area. The challenges are significant. The semiconductor must be able to oxidize water to O_2 and to reduce H^+ to H_2, without being itself decomposed. In addition, sensitivity in the visible spectral region is often looked for. A variety of perovskites [73, 74] and spinels [75] have been prepared among which are, not only oxides, but also oxynitrides [76] and oxysulfides [77]. Catalysts, such as Pt, NiO or RuO_2, have sometimes been added, as well as a sacrificial electron donor or acceptor.

Indeed, active samples have been prepared, some of them sensitive to about 600 nm. However, as they have been synthesized by reaction between solids, that is, at temperatures of the order of 1273 K, their surface area was very low and therefore their activity per photocatalyst mass unit was also very low. It is difficult to predict whether this obstacle, inherent to the preparation method, can be surmounted. Otherwise, the research in this field presents a great interest from the viewpoint of the understanding of the physics and chemistry of semiconductors, and new applications may emerge from these elegant investigations.

4. More recent applications

4.1. *Cooling buildings*

It has been proposed to cover buildings with TiO_2-coated hydrophilic materials and to pour water from the building top along the façades in order to cool them and thereby to decrease the average temperature in city centers with a high density of elevated buildings. Field studies demonstrated a 1.5 K indoor temperature drop using this technique [78].

An alternate means of cooling with TiO_2 is the use of “smart windows”, which can be darkened by sunlight or an applied voltage, thereby reducing the solar flux into a building. Three different designs are as follows. In the first [79], a window consists of a layer of WO_3 electrically connected to a layer of dye-sensitized TiO_2, with an electrolyte solution in between. Solar activation of the dye injects a charge into TiO_2, which is relayed to the WO_3 and trapped, giving a stable blue color. When irradiation is ceased, the WO_3 is discharged and the glass becomes transparent again. Colorization or decolorization is complete within a few minutes. In the second design [80], an applied voltage transfers charge from the TiO_2 (onto which a non-sensitizing donor molecule is adsorbed) to WO_3, which then becomes blue. And in the third scheme [81], a layer of TiO_2 is coated with a molecular dyad: a sensitizer coupled with an electron donor in a single molecule. Irradiation results in charge transfer from the sensitizer to the TiO_2, which is compensated by charge transfer from the donor, which becomes colored upon oxidation.

4.2. *Corrosion protection*

TiO_2 coatings have been used to provide reductive protection against corrosion. A TiO_2 coating on stainless steel reduces the corrosion potential under UV irradiation [82]. A composite TiO–WO_3 film stores photogenerated electrons in the WO_3 particles, resulting in corrosion protection that persists for a few hours after irradiation is ceased [83].

4.3. *Potential medical applications*

The capability of TiO_2 photocatalysis for degrading organic matter might be used to treat cancer [84, 85]. Indeed, human bladder cancer cells deposited on TiO_2-coated glass have been shown to be killed under UV irradiation; the hindering effect of photoexcited TiO_2 particles upon the growth of these cells developed on the backs of mice has been demonstrated; and TiO_2 was found to reduce the formation of pyrimidine dimers (believed to cause skin cancer) upon UV-C irradiation of human cells *in vitro* and mouse skin *in vivo* [86]. These anti-tumor properties are further investigated by use of TiO_2-coated gold particles implanted in mouse tumors and irradiated by UV light.

Other medical applications of photocatalysis include a silicone catheter internally and externally coated with TiO_2; sufficient light penetrates to render the catheter self-sterilizing and self-cleaning throughout [87]. After use, the catheter is sterilized in a small box containing a UV lamp.

5. Conclusions

The commercial potential of different applications of photocatalysis appears to be as follows, in descending order. Self-cleaning surfaces are attracting significant industrial interest and are already well on their way toward widespread commercialization. Indoor air treatment also seems to be a promising application, but the efficiency and the effect on the concentrations of low molar-mass carbonyl compounds need to be further evaluated in order to commercialize appliances appropriate to their respective use. Conventional pollution treatment of aqueous or air effluents must be evaluated on a case-by-case basis. Remediation of underground water at polluted sites has been claimed to be successful.

The factor driving this ranking is the slow rates of photocatalytic degradation. Photocatalysis succeeds where pollutant concentrations are low and the slow kinetics are acceptable. In self-cleaning applications, light is plentiful and free, and the efficiency is sufficient as long as the organic dirt is relatively uniformly deposited with low daily rates, whereas photocatalytic removal of thick stains of chemically stable matter intentionally or accidentally deposited is unlikely to be fast enough. For indoor air treatment, the time scale appears sufficient to degrade, within a finite space, a low total amount of pollutants (not including CO and CH_4). But in treating a waste stream, either in water or in air, photocatalytic rates can be overwhelmed by high flow rates and/or pollutant concentrations.

Improving the activity of TiO_2 and TiO_2-based materials remains an active area of research. Until now, the best improvements in activity have been by roughly a factor of 3 relative to a benchmark such as Degussa P25. The applicability of these improvements will depend on the balance between the increase in activity and the increase in cost.

There have been advances in the methods of affixing TiO_2 to surfaces. Photocatalytically active TiO_2 coatings may be used in direct (cleaning the coated surface) or indirect (cleaning air or water passed through a filter, for example) applications. Expanding the commercial applications for photocatalysis as a polluted effluent treatment technique will require further significant improvements in the activity of such films. However, for TiO_2 photocatalysis there are numerous niche possibilities (see Section 4) whose interest merits further assessment.

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