

Review

## Heterogeneous Photocatalysis: Recent Advances and Applications

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**Abstract:** Semiconductor heterogeneous photocatalysis, the subject of this review, is a versatile, low-cost and environmentally benign treatment technology for a host of pollutants. These may be of biological, organic and inorganic in origin within water and air. The efficient and successful application of photocatalysis demands that the pollutant, the catalyst and source of illumination are in close proximity or contact with each other. The ability of advanced oxidation technology to remove low levels of persistent organic pollutants as well as microorganisms in water has been widely demonstrated and, progressively, the technology is now being commercialized in many areas of the world including developing nations. This review considers recent developments in the research and application of heterogeneous semiconductor photocatalysis for the treatment of low-level concentrations of pollutants in water and air using titanium dioxide as a “model” semiconductor. The review considers charge transport characteristics on the semiconductor surface, photocatalyst reactor design and organic degradation mechanistic pathways. The effects of photoreactor operating parameters on the photocatalytic process are discussed in addition to mineralization and disinfection kinetics.

**Keywords:** semiconductor; photocatalysis; band gap; illumination; reactor; catalyst; mineralization; degradation

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## 1. Introduction

The field of heterogeneous photocatalysis has expanded rapidly within the last four decades, having undergone various developments especially in relation to energy and the environment. It can be defined as the acceleration of photoreaction in the presence of a catalyst. The two most significant applications of photocatalysis have been in solar water splitting and the purification of air and water containing low concentrations of pollutants. The multidisciplinary nature of the field has also increased significantly and includes semiconductor physics, surface sciences, photo and physical chemistry, materials science and chemical engineering [1].

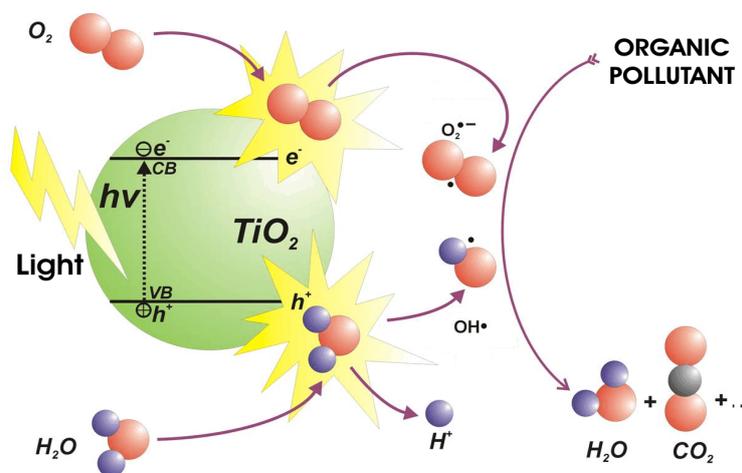
Heterogeneous photocatalysis can be described as the acceleration of photoreaction in the presence of a catalyst. In the contexts of history and research, interest in heterogeneous photocatalysis can be traced back to many decades when Fujishima and Honda discovered in 1972 the photochemical splitting of water into hydrogen and oxygen in the presence of  $\text{TiO}_2$ . From this time, extensive research, much of it published, has been carried out to produce hydrogen from water in oxidation reduction reactions using a variety of semiconductor catalyst materials.

In recent years, interest in photocatalysis has focused on the use of semiconductor materials as photocatalysts for the removal of ambient concentrations of organic and inorganic species from aqueous or gas phase systems in environmental clean-up, drinking water treatment, industrial and health applications. This is because of the ability of  $\text{TiO}_2$  to oxidize organic and inorganic substrates in air and water through redox processes. In this context,  $\text{TiO}_2$  has not only emerged as one of the most fascinating materials in both homogeneous and heterogeneous catalysis, but has also succeeded in engaging the attention of physical chemists, physicists, material scientists and engineers in exploring distinctive semiconducting and catalytic properties.

Inertness to chemical environment and long-term photostability has made  $\text{TiO}_2$  an important material in many practical applications, and, in commercial products ranging from drugs to foods, cosmetics to catalysts, paints to pharmaceuticals, and sunscreens to solar cells in which  $\text{TiO}_2$  is used as a desiccant, brightener, or reactive mediator [2]. The U.S. Food and Drug Administration permits up to 1%  $\text{TiO}_2$  as an inactive ingredient in food products. While there are no known health effects associated with the use of  $\text{TiO}_2$ , a recent study found that 3–6 year old children are the most affected group of people that consume  $\text{TiO}_2$  particles from food products. Many new properties of  $\text{TiO}_2$  have been explored during the past few years [3]. It should be stated that regulatory frame work for the use of  $\text{TiO}_2$  in food products are yet to be firmly established in many countries, especially developing nations. The catalyst itself is unchanged during the process and no consumable chemicals are required. This results in considerable savings and simpler operation of the equipment involved.

Large bandgap semiconductors like  $\text{TiO}_2$  are commonly investigated in the rutile (bandgap 3.0 eV) and anatase (bandgap 3.2 eV) phases and  $\text{TiO}_2$  response to UV light has not only led to photocatalysis research [4–6] but also to an extensive investigation of  $\text{TiO}_2$  superhydrophilicity its use in environmental remediation and solar fuel production. Bandgap excitation of  $\text{TiO}_2$  causes charge separation followed by scavenging of electrons and holes by surface adsorbed species, Figure 1:

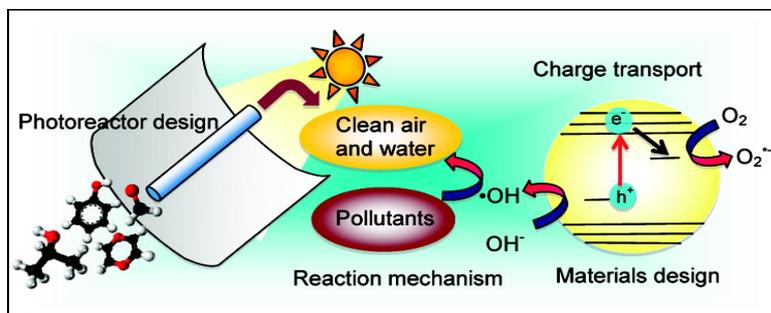
**Figure 1.** Schematic of semiconductor excitation by band gap illumination [4,7] leading to the creation of “electrons” in the conduction band and “holes” in the valance band.



Visible photocatalysis can thus be utilized by doping  $\text{TiO}_2$  with a sensitizing dye or short bandgap semiconductors. By controlling the surface treatment and medium conditions, it is possible to fine-tune the photocatalytic properties of  $\text{TiO}_2$  to desired applications including the effective mineralization of contaminants in air, as self-cleaning glass and ceramic tiles. On the other hand, the practical use of  $\text{TiO}_2$  for remediation of chemical contaminants in wastewater is a challenge because of catalyst poisoning or deactivation. In addition, there remain some challenges with respect to extending the photocatalytic response of  $\text{TiO}_2$  in the visible region [6], an area that merits fundamental research.

In spite of the extensive efforts to dope  $\text{TiO}_2$  with C, N, S and transition metal ions such as Ag, Au, Fe, Ru, photocatalytic activity of  $\text{TiO}_2$  in the visible region has remained quite low, an issue that has been addressed in recent articles highlighting issues and challenges associated with the application of photocatalysis. Generally, two or more phases are involved in a photocatalytic reaction—a light source and a semiconductor material are used to initiate the photoreaction while the catalyst system can simultaneously carry out oxidation and reduction reactions using long wavelength, UV light as well as sunlight. As a method for contaminant control in water and air, Figure 2, heterogeneous photocatalysis using semiconductors such as titanium dioxide is more efficient than conventional methods. This is because as the photocatalytic process gradually breaks down the contaminant molecules, no residue of the original material remains and therefore no sludge requiring disposal to landfill is produced. The catalyst itself is unchanged during the process and no consumable chemicals are required. This results in considerable savings and a simpler operation of the equipment involved. Additionally, because the contaminant is attracted strongly to the surface of the catalyst, the process will continue to work at very low concentrations. Taken together, these advantages mean that the process results in considerable savings in water production cost and keeping the environment clean.

**Figure 2.** Schematic of the interplay of photocatalysis treatment, reactor and material design and photocatalytic reaction mechanism [1]. Note: This figure is reproduced with permission from [1], Copyright © 2012 American Chemical Society.



In order to activate the degradation process, pure TiO<sub>2</sub> requires photo-excitation with light at wavelengths exceeding the band gap of the active anatase phase of 3.2 eV, that is, wavelengths of <387 nm. Indeed, commercially available photocatalytic water treatment plant using artificial UV-light as the energy source is available and can be considered as a developed market.

However, UV in natural sunlight represents only 5%–8% of the solar spectrum at sea level and this provides a limitation and the requirement of artificial illumination of the catalysts in order to achieve degradation of the organic material in times that are practical for water treatment processing. This greatly restricts the application of the technology to areas where abundant electricity supplies are available. The need for more stable, efficient catalysts which can be activated by natural sunlight is now the goal of researchers. In order to achieve significant improvements in catalytic activity using visible light, precise control of the stoichiometry of the catalytic metal oxides and mixed metal oxides, addition of dopants, particle shape and pore topology are all critical factors for catalyst developers.

Advances in the manipulation of matter at the nanoscale are leading to potential solutions for the depollution of water in remote locations. In recent years, the development of nanoscale metal oxides has greatly increased the catalytic activity by virtue of the high specific surface area available for reaction of the smaller particles. In addition, the strategy to alter the band gap of the catalyst is an important approach as this determines the portion of the solar spectrum the catalyst absorbs and, consequently, the amount of energy that is converted to reactive species. Photocatalysts that have high activity using wavelengths of light in the visible spectrum (380 nm <  $\lambda$  < 500 nm) have been demonstrated where potentially greater amounts of energy is available (solar peak energy is around 460 nm). This has been achieved by altering the band gap of, for example, TiO<sub>2</sub>. Doping of TiO<sub>2</sub> with transition metal ions (for example, V, Cr, Mn, Fe and Ni) as well as with Ag, Au and Ru, have been demonstrated to red-shift the TiO<sub>2</sub> absorption band from the UV into the visible region, resulting in a great increase in the efficiency of solar-light photocatalysis.

Many industrial waste streams are not suitable for biological processing due to their inherent toxicity, but their treatment by traditional non-catalytic chemical processes or by incineration is energy intensive [7]. On the other hand, TiO<sub>2</sub> photocatalysts has been shown to decompose organic contaminants in water efficiently because a strong oxidizing ability is generated when the TiO<sub>2</sub> is irradiated by appropriate band gap illumination [8]. Increased attention is being paid to heterogeneous

solution phase catalysis in order to develop an environment-friendly technology to purify polluted air and water without electricity or other energy consuming sources.

Heterogeneous photocatalytic reactions are carried out either in a slurry-type reactor where the catalyst particles are suspended in the contaminated water or in an immobilized-type reactor where the catalyst particles are immobilized onto the surface of various inert substrates of various types and configurations [9–11] and the process can be explained on the basis of the following mechanism.

## 2. Mechanism of Semiconductor Catalysis

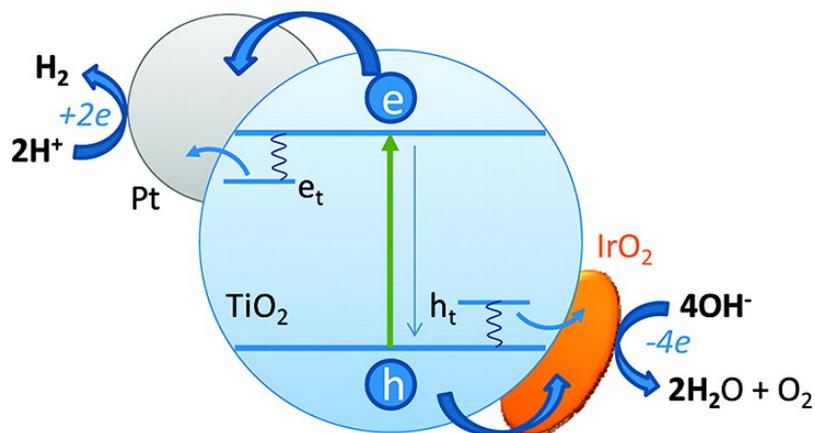
A photocatalyst harnesses UV radiation from sunlight or artificial light and uses the energy to break down different substances including organic materials, organic acids, estrogens, pesticides, dyes, crude oil, microbes (including viruses) and chlorine resistant organisms, inorganic molecules such as nitrous oxides (NO<sub>x</sub>) and, in combination with precipitation or filtration, can also remove metals such as mercury [13–15]. Due to this universal applicability, photocatalysis with nanoparticles as catalysts is used to reduce air pollution, in building materials, for self-cleaning surfaces in addition to water purification. Titanium dioxide (TiO<sub>2</sub>) is the most common photocatalyst and comparably little research has been conducted on zinc oxide, ZnO, which could be a viable alternative for some applications. To avoid free nanoparticles in water, TiO<sub>2</sub> nanoparticles are usually immobilized on a substrate [16] or integrated into thin-films and other materials. For the activation of TiO<sub>2</sub>, UV irradiation from sunlight or artificial light is needed, with UVB more efficient than UVA. To allow activation by visible light, TiO<sub>2</sub> can be modified with a second semiconductor, dyes, nitrogen, carbon or sulphur. For example, TiO<sub>2</sub> doped with nitrogen demonstrated superior photocatalytic activities compared to commonly used unmodified TiO<sub>2</sub> nanoparticles in both chemical compound degradation and bactericidal reactions [17].

With respect to a semiconductor oxide such as TiO<sub>2</sub>, photocatalytic reactions are initiated by the absorption of illumination with energy equal to or greater than the band gap of the semiconductor. This produces electron-hole (e<sup>-</sup>/h<sup>+</sup>) pairs as in Equation (1), Figure 3:



where cb is the conduction band and vb is the valence band. Thus, as a result of irradiation, the TiO<sub>2</sub> particle can behave either as an electron donor or acceptor for molecules in contact with the semiconductor. The electron and hole can recombine, releasing the absorbed light energy as heat, with no chemical reaction taking place. On the other hand, they can participate in redox reactions with adsorbed species as the valence band hole is strongly oxidizing while the conduction band electron is strongly reducing. On the semiconductor surface, the excited electron and the hole can participate in redox reactions with water, hydroxide ion (OH<sup>-</sup>), organic compounds or oxygen leading to mineralization of the pollutant.

**Figure 3.** Schematic of the charge transfer across semiconductor interface. Note: This figure is reproduced with permission from [12], Copyright © 2012 American Chemical Society.



In fact, research shows that the charges can react directly with adsorbed pollutants, but reactions with water are predominant since the water molecules are more abundant than contaminant molecules. Consequently, oxidation of water or  $\text{OH}^-$  by the hole produces the hydroxyl radical ( $\cdot\text{OH}$ ), a powerful oxidant. For the purpose of comparison, it is important to compare the oxidation potential of hydroxyl radical ( $\cdot\text{OH}$ ) which is 2.8 V relative to the normal hydrogen electrode. Apart from electron and their holes, other substances that may be used for water disinfection include ozone (2.07 V),  $\text{H}_2\text{O}_2$  (1.78 V),  $\text{HOCl}$  (1.49 V) and chlorine (1.36 V).  $\text{OH}$  radicals are able to rapidly attack pollutants on the semiconductor surface and, as such, are the most important radicals formed in  $\text{TiO}_2$  photocatalysis. An important reaction of the conduction band electron is reduction of adsorbed oxygen to oxygen radicals and this prevents the electron from recombining with the hole and results in an accumulation of oxygen radicals that can also participate in degrading contaminants in solution [11,18].

Published work indicate that heterogeneous photocatalytic process involves at least five separate reaction steps [19] and include (1) diffusion of reactants to the surface of semiconductor, (2) adsorption of reactants onto the surface of semiconductor, (3) reaction on the surface of semiconductor, (4) desorption of products from the surface of the semiconductor and (5) diffusion of products from the surface of the semiconductor. There are two routes through which  $\text{OH}$  radicals can be formed—the reaction of the valence-band holes with either adsorbed  $\text{H}_2\text{O}$  or with the surface  $\text{OH}$  groups on the  $\text{TiO}_2$  particle. These processes have been summarized using appropriate equations [20].

### 3. Photocatalyst Materials and Supports

Current and past research in photocatalytic materials has investigated several photocatalysts and their properties. Ideally, a photocatalyst should possess the following properties: photoactivity, biological and chemical inertness, stability toward photo-corrosion, suitability for visible or near UV light energy harnessing, low cost and lack of toxicity [21].  $\text{TiO}_2$  as a semiconductor photocatalyst, has excellent pigmentary properties, high ultraviolet absorption and high stability which allow it to be used in different applications such as electro-ceramics, glass and in the photocatalytic degradation of chemicals in water and air. It has been used in the form of a suspension, or a thin film in water

treatment [22,23] and has different crystalline forms, the most common forms being anatase and rutile while the third, brookite, is uncommon, unstable and hence does not feature in discussion of catalyst materials.

Anatase TiO<sub>2</sub>, the most stable form of TiO<sub>2</sub> [24], can be converted to rutile by heating to temperatures above 700 °C. In photocatalytic applications, research has shown that anatase is more efficient than rutile because of its more open structure compared with rutile. Degussa P-25 is the commercially available form of TiO<sub>2</sub> and consists of two forms of approximating 25% rutile and 75% anatase, and has been used in many studies of photocatalytic degradation because of its chemical stability, ready availability, reproducibility and activity as a catalyst for oxidation processes [13,25]. However, studies are being carried out to develop existing or prepare new materials which can be used under solar energy and hence shortening the time needed for degradation.

This development includes increasing the surface area, the active sites, the absorption of photon and reducing the band gap energies of the semiconductor. For industrial applications, high activity, resistance to poisoning and stability for prolonged use at elevated temperatures, mechanical stability, and resistance to attrition, physical and chemical stability in various conditions, are required characteristics of catalysts [21]. In addition, in the degradation of organic compounds, the redox potential of the H<sub>2</sub>O/·OH electrode, OH<sup>-</sup> → ·OH + e<sup>-</sup>; E<sub>0</sub> = -2.8 V, must lie within the band gap of the photocatalyst as illustrated in Figure 1. Nowadays, many semiconductors are used as photocatalysts because of their narrow band gap between the valence and conduction bands and they need to absorb energy equal to or more than this energy gap. This involves the movement of electrons from e<sup>-</sup>/h<sup>+</sup> or negatively charged electrons to positively charged hole pairs [26].

Many semiconductors have enough band-gap energies for the effective catalysis of many chemical reactions and this includes materials such as TiO<sub>2</sub>, WO<sub>3</sub> and ZnO. Though it is well known that metal oxides are usually less active catalysts than noble metals in the majority of applications, metal oxides are more suitable since they are more resistant to poisoning and deactivation. In addition, combining two or more metal oxide catalysts could improve or enhance catalytic activity. TiO<sub>2</sub> is the most frequently used photocatalyst because of its photostability and low cost, combined with its biological and chemical inertness and resistant to photo and chemical corrosion. On the other hand, binary metal sulfide semiconductors such as CdS and PbS are regarded as insufficiently stable for catalysis and are toxic. ZnO is also unstable in illuminated aqueous solutions while WO<sub>3</sub> has been investigated as a potential photocatalyst, but it is generally less active catalytically than TiO<sub>2</sub>. However, these can be combined with other semiconductors including TiO<sub>2</sub> to achieve greater photocatalytic efficiency or stability [27–30].

There are many semiconductor support materials that have been investigated. Usually, semiconductor supports are classified by their chemical nature and these can be organic or inorganic supports. They play an important role in immobilizing active catalyst, increase the surface area of catalytic material, decrease sintering and improve hydrophobicity, thermal, hydrolytic and chemical stability of the catalytic material. Examples include glass, carbon fibers and woven fiber cloths and these have been studied as support materials in groundwater denitrification and in the photocatalytic oxidation of water pollutants as well as in other applications. When fibrous supports are applied, loss of pressure is low and pore diffusion resistance is significantly lower than with pellet shaped catalysts.

Glass possess an advantage as a catalyst support because of its transparency to UV light in photocatalytic applications [30].

Studies by Teoh, Kamat and others [1,9,12,31–33], show that interest in photocatalysis has also centered on ZnO, which has similar energy characteristic to TiO<sub>2</sub>. They report that ZnO however suffers from photo-corrosion problems upon excitation in solution. Hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) on the other hand, which is low cost, abundant and has narrow bandgap for harnessing solar energy, suffers from rapid charge recombination and a short charge carrier diffusion length. As a result of these draw backs, renewed interest in this material has focused on its modification with cationic dopants such as Cr and Mo to improve its charge transport properties [34] or doping with Si to reduce the charge diffusion path length. Other reviews have also talked about Tungsten trioxide WO<sub>3</sub> as another narrow bandgap material, 2.7 eV, and, as such, it has received renewed interest. Like hermatite, Tungsten trioxide, has the disadvantage of a low electron conduction band, although studies claim that coupling with Pt cocatalyst has been observed to be useful in promoting alternative multiple-electron reduction processes with lower reduction potentials. This has increased the use of WO<sub>3</sub> as one of the very few highly visible-light-active single-phase oxide photocatalysts [29–31,34–41].

In many cases, the superiority of other photocatalyst materials over P25 is based on a selection of test reactions or only a single organic substrate and this has its problems as all of the important factors cannot be validated in a single experiment or reaction. An example is the pairing of test substrate degradation mechanistic Langmuir-Hinshelwood kinetic model, direct charge transfer, hydroxyl radicals, and superoxide radicals with many physicochemical characteristics of the photocatalyst such as the crystallinity, hydroxyl group density, size, specific surface area, surface defects, surface energetic and aggregation [12]. Even among flame-made TiO<sub>2</sub> of similar crystallinity, about 80% anatase and 20% rutile, and exact anatase-rutile content, differences in the photocatalytic activity of P25 were observed [42] due mainly to the class of organic substrate [43] used and the materials intrinsic efficiencies for ·OH generation and direct charge transfer, which governed the dominant degradation mechanism for each of the substrate functional groups. In a broader context, Ryu and Choi [44] compared the photocatalytic performance of commercial variants of TiO<sub>2</sub> and observed that one photocatalyst cannot meet all photocatalytic requirements, a fact borne out by several studies [45].

With respect to the synergy between anatase and rutile, the dominant phases of TiO<sub>2</sub> studies [46] have suggested that polymorphic characteristics of these materials was one of the reasons for the high photocatalytic efficiency of P25 and that the heterojunction of anatase-rutile promoted efficient charge separation as evidenced by studies indicating discrete trapping of electrons and holes across the different crystal phases. Any synergistic effect, however, is difficult to measure because of the differences in the physicochemical characteristics of pure anatase and rutile (surface area, crystallite size, defect content, surface hydroxylation, *etc.*), compared with the individual components in the mixture. Ohtani and other studies [46–48] on the other hand, isolated the individual components of P25 by selective acid dissolution and assessed the single components for a range of photocatalytic reactions. The studies concluded, at least for P25, a less probable synergistic effect beyond the photocatalytic activity of the individual components. By carefully synthesizing highly crystalline and physically similar anatase and rutile nanoparticles, Kho [49,50] and other studies demonstrated higher rates of hydrogen evolution from aqueous methanol across a wide range of mixed anatase-rutile compositions. The effect, however, was only observed when a strong inter-particle contact existed

between the anatase and rutile nanocrystals, supporting the view of an efficient charge separation across heterojunctions in these materials [1].

Doping of TiO<sub>2</sub> with fine noble metals such as silver (Ag), gold (Au) and palladium (Pd) has been carried out extensively as a means of enhancing charge separation. Doping has been reported [51] to establish a barrier through equilibration between the photocatalyst and metal deposits and is governed by the difference in work function of the deposits and the electron conduction band of the photocatalyst and does not influence the mechanism of the specific reaction [1]. Previous studies noted differences in the enhancement by Pt and Ag as well as other noble metals, on TiO<sub>2</sub> over a range of organic classes arising from the combination of substrate or functional group specificity and the dark catalytic oxidation effects [12,32,33,51,52]. The latter included the catalytic oxidation of formic acid, oxalic acid, methanol, and the opening of aromatic rings, with each reaction induced by the catalytic properties of the metals. Studies have shown that when a photocatalyst is illuminated, a type of synergistic effect between the catalytic and photocatalytic processes is possible and in fact studies have shown these effects do exist. [33,52,53].

With respect to new materials for use in photocatalytic work, Teoh *et al.* [1] reported in a recent article that a graphene oxide material was demonstrated to act as a mediator for electron transport and for visible-light water splitting in photocatalysis. It has to be stated that prior to this development, electron mediators were largely based on aqueous redox couples such as Fe<sup>2+</sup>/Fe<sup>3+</sup> and CO<sub>2</sub><sup>+</sup>/CO<sub>3</sub><sup>+</sup> as well as Au and Ag. A recent study by Wei and coworkers [54] using hybrid Fe<sub>2</sub>O<sub>3</sub>-Pd nanoparticle photocatalyst grown by epitaxial growth of Fe<sub>2</sub>O<sub>3</sub> on Pd nanoparticles, showed improved photocatalytic efficiency, although this was limited by the presence of organic stabilizers which are difficult to remove. Other materials considered in recent work include ZnS, ZnO, CdSe, Fe<sub>2</sub>O<sub>3</sub> and InP [55]. Some of these materials were reported to show some photocatalytic promise, but with uncertainty over their efficiencies and spectral characteristics [56]. Fe<sub>2</sub>O<sub>3</sub> is particularly interesting because of its stability against photo/chemical corrosion at neutral or basic pH and has band gap energy of about 2.0 to 2.2 eV corresponding to the absorption of 564 to 620 nm light [54].

#### 4. Photocatalytic Test Materials

Investigations of photocatalytic degradation processes including the mechanisms have usually been carried out by using model compounds. This can strongly influence the photocatalytic performance of a material according to Teoh and co-workers [1] because of the effect of the structure of such model compounds and other factors on the degradation process. The study show that, for example, while monitoring the decolorization of dyes in solution using spectroscopic techniques is simple and convenient, using a dye as the model compound can yield unreliable results as this may not represent the intrinsic photocatalytic activity of the semiconductor, especially for visible-light-activated materials for which dyes are a good example and these include methyl orange, congo red, alizarin yellow, *etc.*

Cationic and anionic azo-dyes can undergo photolysis or sensitize the semiconductor and thereby inject an electron into its conduction band [1,12]. In addition, because of their complex structure, dyes have complex photodegradation mechanistic pathways thus making determining accurate photocatalytic efficiencies a very difficult exercise [56]. In addition, studies [1] have indicated that dyes do not necessarily require carbon oxidation for decolorization to occur. Although photocatalysis

can play a significant role in treating dye-polluted systems [57], the choice of a model pollutant substrate should be undertaken with due consideration when assessing a photocatalytic activity under visible illumination. This reviewer has carried out photocatalytic work using azo-dyes as model substrates and would agree with the conclusion reached regarding the use of model compounds activated by visible light to validate photocatalytic degradation mechanisms and efficiency.

## 5. Doping Mechanisms

Research into photocatalyst doping has spanned several decades. Usually doping involves the use of metals or non-metals and is designed to extend the photocatalytic activity of a semiconductor lower energy excitation. Technically, doping is the introduction of foreign elements into the parent photocatalyst without giving rise to a new crystallographic forms, phases or structures and the aims are [1] to enhance the net separation of photogenerated charges and thereby efficiently harness the wide visible-light component of about 43% in the solar spectrum as opposed to the narrow ultraviolet component of 5%. It is thus an area of increasing research activity in photocatalysis.

Although discovered as a modification technique in the early 1980s, doping has become a standard and routine method in the design of water-splitting photocatalysts [12]. Modifying pure photocatalyst materials with metal ions, especially d block metal ions such as  $\text{Fe}^{3+}$  and  $\text{Cr}^{3+}$  results in the insertion of impurity energy levels between the parent conduction and valence bands. In this case, the inserted energy levels provide sub-bandgap irradiation from which electrons can be excited from dopant d-band to conduction band or from valence band to dopant d-band by lower energy photons than are required by the pure photocatalysts. However, there are a number of issues associated with metal ion doping, related to the efficiency of subsequent photocatalytic processes. Whereas the presence of metal dopants was found in some cases to enhance charge separation as well as interfacial charge transfer [58,59] in many other cases, the metal dopants actually resulted in rapid charge recombination through their switchable redox states, for example,  $\text{Fe}^{3+} \leftrightarrow \text{Fe}^{2+}$  and thereby reducing the electron diffusion length and lifetime [1,9,12,60]. This is one of the reasons for the reduced quantum efficiency in many photo response-extended doped photocatalysts.

Several studies have indicated that doping creates structural defects that could be sources for charge recombination and in this sense are potentially negative in their effects. The only exception being doping using high-energy RF and magnetron sputtering, which provide the uncommon existence of tetravalent dopants such as  $\text{Fe}^{4+}$  and  $\text{Cr}^{4+}$  that match the valency of  $\text{Ti}^{4+}$  in  $\text{TiO}_2$  [61]. Co-doping with a conjugate metal cation pair such as  $\text{Rh}^{3+}/\text{Sb}^{5+}$  can preserve charge equality of the doped photocatalysts and result in improved and extended photocatalytic ability. However, this may not necessarily prevent structural defects arising from the differences in cationic radii between dopants and the host photocatalyst. In a recent study, Serpone and co-workers [62] provided a substantiated alternative argument that the extended photo-response instead of arising from d-band insertion, may actually originate from the color centers and oxygen vacancies that arise from the doping [63,64].

Doping involving the use of non metals has also been investigated and studies have reported that the introduction of non-metal such as N, C and S impurity energy levels above the parent photocatalyst valence band has been a popular doping technique and although doping wide bandgap photocatalysts such as  $\text{TiO}_2$  and  $\text{ZrO}_2$  with F [64–69] does not result in coloration, their enhanced photocatalytic efficiencies, even under sub-bandgap excitation, likely results from enhanced stoichiometric defects

and this is useful in photocatalytic processes. Higher photocatalytic activity, stability [28] and nontoxicity of dopant ions are among the advantages of nonmetal over metal dopants and, in general, TiO<sub>2</sub> and several other materials have been studied including the effect of impurity levels in the dopant on photocatalytic efficiency. In addition, results obtained using TiO<sub>2</sub> and oxides such as WO<sub>3</sub>, Ta<sub>2</sub>O<sub>5</sub> and Ba<sub>5</sub>Ta<sub>4</sub>O<sub>15</sub> have been published [69–71]. By studying nitrogen doped TiO<sub>2</sub> using real-time fluorescence imaging, Tachikawa and coworkers [72] confirmed the absence of ·OH under sub-bandgap irradiation but retained the formation of O<sub>2</sub><sup>•-</sup>, which, in turn, became the dominant radicals. Whereas full band gap excitation from the valence to the conduction band may result in the original oxidative potential of the parent photocatalysts, the quantum efficiency is hampered because of the pronounced charge recombination at dopant-induced defect sites [36].

Similar to metal-doping strategies, anionic co-doping, for example involving N/F-TiO<sub>2</sub> or N/F- and C/N-ZnWO<sub>4</sub> [73–75] has been used to lower charge defects, but in many cases, the quantum efficiencies remain unmatched compared with the excited photocatalysts. Many studies, for example [76,77], have also reported that new conduction and valence bands are produced in a semiconductor when significant levels of foreign elements are introduced to the photocatalyst. Research using this band gap engineering approach has been carried out successfully and resulted in the emergence of new photocatalytic materials for water-splitting purposes including Bi<sup>3+</sup>, Ti<sup>4+</sup> and W<sup>6+</sup> [78,79]. From the various studies carried out on doping and the effect of doping, it is obvious that the exploration of new photocatalytic doping materials will continue to be driven mainly by efforts in water splitting reactions although these materials will find relevance in other photocatalytic applications such as PbBi<sub>2</sub>Nb<sub>2</sub>O<sub>9</sub>, for the treatment or remediation of aqueous pollutants, CaBi<sub>2</sub>O<sub>4</sub> for the oxidation of gaseous pollutants and ZnGa<sub>2</sub>O<sub>4</sub> for the reduction of carbon dioxide and similar materials [77,80,81].

## 6. Morphology of Photocatalyst Materials

Generally, for all catalyst materials, a high surface area is an advantage in terms of a greater concentration of active sites per square meter and this generally leads to higher reactivity. The smaller the particle size, the larger the surface area, and the higher the expected activity [81]. This can be explained in terms of an increase in the number of active sites per square meter as well as greater absorbance of the pollutant on the catalyst surface [80]. It has often been reported however that while the activity of the TiO<sub>2</sub> catalyst is affected by its external surface [82], photocatalytic activity is not a function of the surface area alone. For example, while an increase in the extent of heat treatment applied leads to a reduction in the surface area, the impact of this reaction on the photocatalytic activity is not as significant as that of the phase transformation. The increase in crystallite size and changes in the microstructure with a decrease in surface area greatly influence the photocatalytic property of the catalyst [83,84].

One of the ways to increase the efficiency of photocatalytic reaction is to couple semiconductor nanoparticles to noble metal co-catalysts to enhance the quantum yield of the electron transfer processes through improvement in charge separation in the semiconductor, discharging photogenerated electrons across the interface and providing a redox pathway with low over-potential. The interfacial charge transfer processes are influenced by the presence of a metal co-catalyst or surface bound molecular relays. If metal nanoparticles are coupled to the semiconductor nanoparticle, then they

readily accept and shuttle electrons to an acceptor molecule at the interface easily. The discharge capacity of metal nanoparticles plays an important role in dictating Fermi level equilibration between semiconductors and metal nanoparticles [1,9,12].

It follows from these studies that in order to enhance the photoactivity of titanium oxide particles, interfacial charge-transfer reactions need to be enhanced. Improved charge separation and inhibition of charge carrier recombination is essential in improving the overall quantum efficiency for interfacial charge transfer. This can be achieved by modifying the properties of the particles by selective surface treatment and several approaches have been taken to achieve this including surface modification of the semiconductor particles with redox couples or noble metals and the coupling of two semiconductor particles with different electronic energy levels. To this end, catalytic thin films, foams and hybrid nanoparticles of TiO<sub>2</sub> as well as gels have been made and used in various catalytic applications [85–88] as described in this review.

## 7. Semiconductor Films and Foams

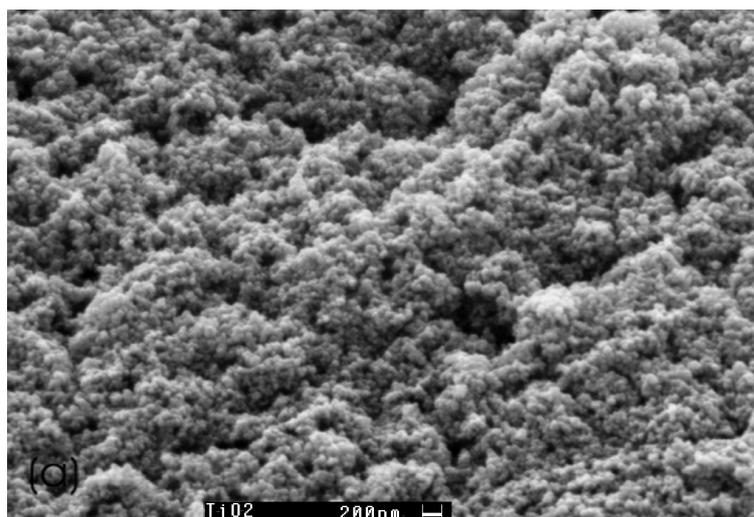
In thin film deposition, a thin layer of material is prepared on a suitable substrate or a previously deposited layer. “Thin” is a relative term, since a film may look operationally thin or thick compared to the wavelength of the light used. Compared to conventional thin film forming processes such as evaporation, or sputtering, sol-gel processing makes it possible to control the microstructure of the deposited film including the pore volume, pore size, and surface area [89] and uses mainly alkoxide, organic/ inorganic salts, metal oxides and other salts in a liquid phase chemical reaction. The method provides excellent chemical homogeneity and the possibility of deriving unique metastable structures at low reaction temperatures [90]. The liquid phase reaction enhances the uniformity of the product produced and the process can be operated under ambient conditions. The reactant concentration, temperature and type of solvent will affect the quality of the final product.

In the production of TiO<sub>2</sub> particles, calcinations at high temperatures are necessary to change the crystalline structure of TiO<sub>2</sub> that possesses photo catalytic activity and the specific surface area, particle size, and other properties of TiO<sub>2</sub> can be altered after calcinations at different temperatures. Thus thin films formed by dipping or spinning, use little raw materials and may be processed quickly without cracking and thus overcoming most of the disadvantages of sol-gel processing. In addition, large substrates may be accommodated and it is possible to uniformly coat both sides of planar and axially symmetric substrates such as pipes, tubes, rods and fibers which are not easily handled by more conventional coating processes.

There are two main ways to synthesize gels at room temperature: spin coating and dip coating. Spin coating is used for applications where relatively flat substrates or objects are coated with thin layers of material. On the other hand, the dip-coating process, involves immersion, start-up, deposition, evaporation and drainage. The substrate is slowly dipped into and withdrawn from a tank containing the sol, with a uniform velocity, in order to obtain a uniform coating. The gel samples are dried at 100 °C and then fired at 450 °C to remove organics from the film pyrolytically. Once the sample has reached the desired thickness through multiple coatings, it is crystallized by heating. The maximum thickness of crack free coatings that can be achieved is 0.5 microns. Sol-gel and “doctor blade” TiO<sub>2</sub> films vary in thickness from 0.2 microns to 0.8 microns.

A foam is a substance that is formed by trapping pockets of gas in a liquid or solid. Particle sizes, porosity differ for various materials depending on the synthetic routes chosen, we have synthesized TiO<sub>2</sub> foams (reported in nano-letters) of 100–500 nm in thickness. TiO<sub>2</sub> films similarly have various thicknesses ranging from a few microns to hundreds or even more depending on the synthetic conditions. We have produced sol-gel and “doctor blade” TiO<sub>2</sub> films varying in thickness from 0.2 microns to 0.8 microns. Generally, the porosity of the foam is larger than that of films (depending on the film and process conditions). Foams usually offer more diffusion pathways than films especially for solution phase degradation. Films on the other hand are usually easier to integrate into structured photocatalytic reactors and light absorption is better than in films. Foams usually get “clogged” at some stage during the photocatalytic process. The synthetic route for TiO<sub>2</sub> foam as reported in the literature [91]. The thickness of the TiO<sub>2</sub> foam produced by this process was 100 nm and it should be pointed out that particle size of 500 nm is possible depending on the synthetic process. The TiO<sub>2</sub> foam offers extended porosity which is important for “light harvesting”, Figure 4.

**Figure 4.** Degradation of Benzene, Toluene and Xylene in contaminated air with TiO<sub>2</sub> Foam [82,86]. The porous structure results in “improved light harvesting” by the catalyst.

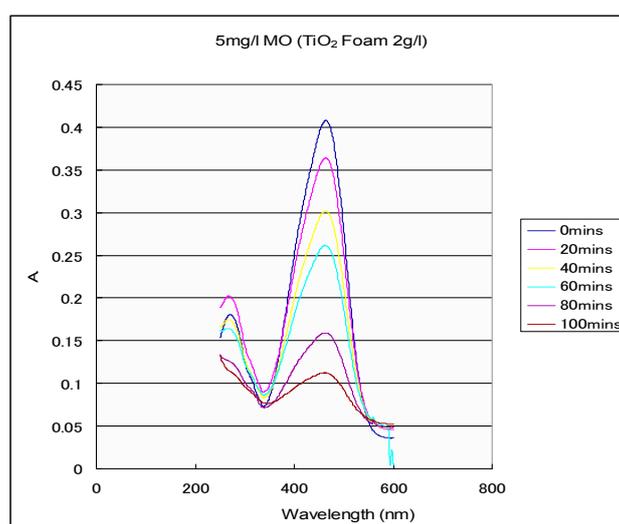


The TiO<sub>2</sub> foams have been used as catalyst materials in the degradation of low concentrations of benzene, toluene and xylene (BTX) in contaminated air. The degradation of anionic and cationic dyes in industrial effluents [8,82,86] as shown in Figure 5, an example given with methyl orange has been undertaken.

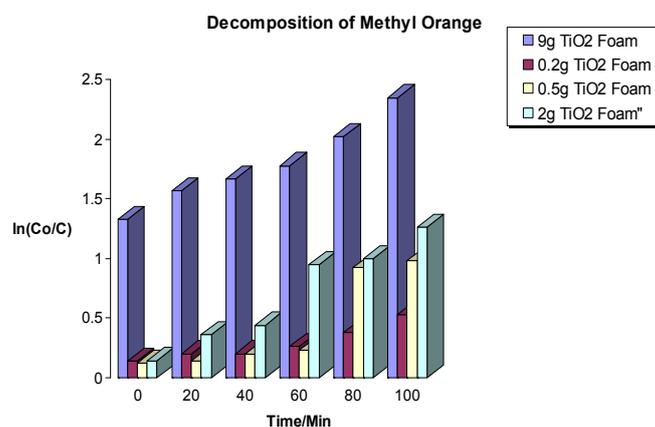
A metal can affect the surface properties of a semiconductor by generating a “barrier” which acts as an electron trap of the metal in contact with the semiconductor surface. Similarly, doping of transition metal ions to semiconductors improves the trapping of electron and inhibits e<sup>-</sup>/h<sup>+</sup> recombination because the relatively low photoactivity of TiO<sub>2</sub> is believed to be due to the fast recombination of photogenerated electrons and holes. In recent years, researchers have focused on the combination of different kinds of metallic oxide particles. Oliviero *et al.* [89] showed that Ru/CeO<sub>2</sub> particle catalysts have very different behavior in the catalytic wet air oxidation of acrylic, succinic and acetic acids depending on the support morphology and the metal/support contact. The use of metal nanoparticles and hybrids has also been researched [92] and the synthetic route for TiO<sub>2</sub>/RuO<sub>2</sub>/SiO<sub>2</sub> nanoparticles is

reported elsewhere [92]. These materials have been used in the degradation of low concentrations of anionic and cationic azo-dyes in industrial effluents, Figure 6.

**Figure 5.** The photocatalytic degradation of an anionic azo-dye in a UV irradiated porous titania foam [8,86]. The decrease in absorption peaks is an evidence of degradation. This evidence cannot however be conclusive (see section 4-on the use model compounds in this review).



**Figure 6.** The photocatalytic activity of TiO<sub>2</sub> foam and surface modified binary oxide nanoparticles [8,86]. As expected, a higher catalyst concentration results in increased photocatalytic efficiency until a maximum catalyst loading is reached.

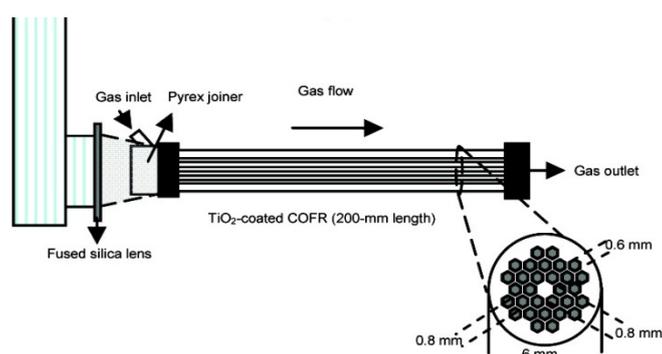


Recent work by Wei *et al.* [54] using hybrid Fe<sub>2</sub>O<sub>3</sub>/Pd nanoparticulate photocatalyst grown by epitaxial growth of Fe<sub>2</sub>O<sub>3</sub> on Pd nanoparticles showed improved photocatalytic efficiency, although this was limited by the presence of organic stabilizers which are difficult to remove. Other materials considered in recent work include ZnS, ZnO, CdSe, Fe<sub>2</sub>O<sub>3</sub> and InP [93]. Some of these materials were reported to show some photocatalytic promise, but with uncertainty over their efficiencies and spectral characteristics. Fe<sub>2</sub>O<sub>3</sub> is particularly interesting because of its stability against photo and chemical corrosion at neutral to basic pH and has a band gap energy of about 2.0 to 2.2 eV corresponding to the absorption of 564 to 620 nm light.

## 8. Photocatalytic Reactor Design

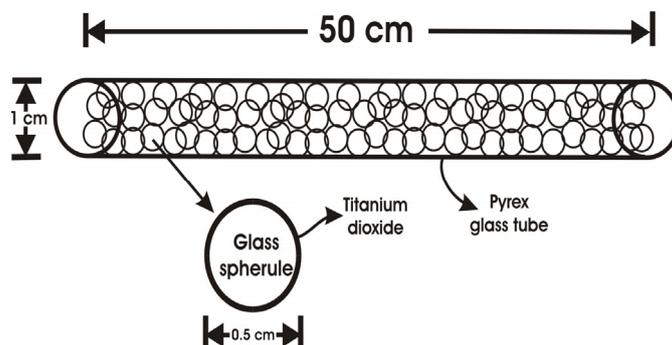
Significant advances have been made in reactor design for various photocatalytic reactions. Published literature contains several types and designs of photocatalytic reactors [1,12,92–94]. Apart from the conventional reactor design parameters, the major challenge in the design of a photocatalytic reactor is the efficient illumination of the catalyst. For a high activity in the reactor, a large area has to be illuminated. Therefore, in immobilized systems the thickness of the supported catalyst layer should be small enough to enable the light to reach all the catalyst. Therefore, one of the most important parameters in design consideration for photocatalytic reactors is light intensity and how the reactor is to be designed to accommodate various light sources. Types of reactors developed include fixed bed and slurry bed. With regard to design considerations, various models have been reported to deal with irradiation of the photocatalyst and how the photocatalyst affects the irradiation—the degree of absorption, scattering, the nature and type of particles, surface of the photocatalyst, *etc.* Light intensity is an important reactor design factor when considering light sources because the major requirement of any photocatalytic process is that the catalyst, pollutant and source of illumination must be in close proximity. This partly because studies have shown that the rate of photocatalytic degradation has a nonlinear dependence on light intensity and is proportional to  $I^{0.5}$  at high intensity and  $I^{1.0}$  at low intensity [93]. It has also been shown that an excess of light promotes a faster electron-hole recombination and the low activation energy of photocatalytic reactions (5–20 kJ/mol), compared with ordinary thermal reactions. In slurry type systems, catalyst loading is an important design parameter for the effective use of reactor space and photocatalyst and a wide range (0.15 to 8 g/L) of optimal catalyst loading in aqueous suspensions has been reported for different photocatalyst systems and reactor configurations [1,12,91–99], Figure 7:

**Figure 7.** Schematic diagram of Channelled Optical Fiber Reactor (COFR) system for gas-phase photocatalytic degradation of volatile organic compounds [1].



Another example of a design that has been used in the degradation of organic in polluted air is shown in Figure 8. This reactor is filled with silica beads coated with titania paste and is externally irradiated by UV irradiation and used in the photocatalytic degradation of organic pollutants in air or water.

**Figure 8.** A photocatalytic reactor filled with silica beads coated with titania paste externally irradiated by UV irradiation [4].

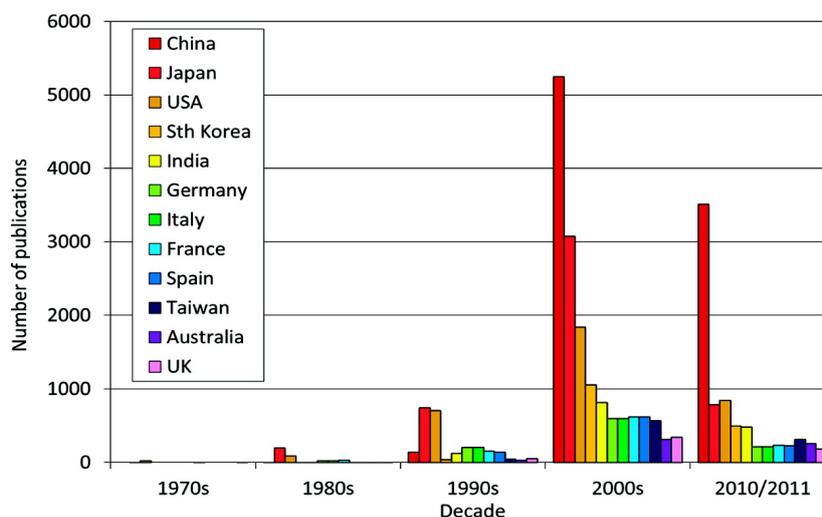


The design and selection of a photocatalytic reactor depends on the experimental conditions and the application and two main types have been extensively researched—reactors that use a catalyst as suspension form and reactors that use a thin film catalyst either coated to the reactor wall or coated in spherical glass beads. Both reactors can be designed as an immersion wall or flat wall. Immersion well photoreactors are normally used at laboratory scale for evaluation purposes and are operated in batch or continuous mode where oxidant flow and temperature can be easily monitored. The light source can be either single or multiple with or without reflectors. Catalyst in these reactors can be used as thin film or as suspension form, with suspension system more preferable as they are more efficient than thin film reactors due to the large surface area in contact with the substrates. This allows more number of photons to hit the catalyst and large adsorption capacity results. Other reactors are flat wall and tubular photoreactors, which are simple and easy to design and generally use solar energy. In tubular reactors, reflectors are used to concentrate the light and enhance the photoreaction.

## 9. Applications of Photocatalysis

Selected applications of photocatalysis are given in Tables 1–3. Heterogeneous photocatalysis has been demonstrated as a low cost and sustainable technology for the treatment of a host of pollutants in air and water including organics and heavy metals, *etc.*, with Japan, USA, India and China as major users of this technology as partly demonstrated by the number of research publications in this area, Figure 9 [1]. Unlike reverse osmosis, nano and ultrafiltration, photocatalysis is a cheap and a potential “stand alone” technology for water treatment. As photocatalysis makes use of sunlight or UV radiation, the technology is inexpensive, environmentally friendly and can be applied worldwide. It requires minimal equipment, is highly deployable and appropriate for developing countries and remote sites with no access to electricity. Photocatalysis has also been used successfully in many developing nations to destroy pathogens [5, 92] and algal blooms in fresh water supplies. Photodisinfection sensitized by  $\text{TiO}_2$  has been used to degrade the green algae, treat humic substances [100] which act as substrates for bacterial growth, inhibit bacterial degradation of impurities in natural water, and aid the transport of metals in the environment and complex with Fe, Pb, Mn, making it harder to remove them. Specific examples of applications are as follows.

**Figure 9.** Number of publications pertaining to photocatalysis since 1970. China, Japan, USA and India have the edge in the number of publications on this Subject. Note: This figure is reproduced with permission from [1], Copyright © 2012 American Chemical Society.



**Table 1.** Selected applications of photocatalysis. Note: this Table is reproduced with permission from [92], Copyright © 2000 Elsevier Science S.A.

Property	Category	Application
Self-cleaning	Materials for residential and office buildings	Exterior tiles, kitchen and bathroom components, interior furnishings, plastic surfaces, aluminum siding, building stone and curtains, paper window blinds
	Indoor and outdoor lamps and related systems	Translucent paper for indoor lamp covers, coatings on fluorescent lamps and highway tunnel lamp cover glass
	Materials for roads	Tunnel wall, soundproofed wall, traffic signs and reflectors
	Others	Tent material, cloth for hospital garments and uniforms and spray coatings for cars
Air cleaning	Indoor air cleaners	Room air cleaner, photocatalyst-equipped air conditioners and interior air cleaner for factories
	Outdoor air purifiers	Concrete for highways, roadways and footpaths, tunnel walls, soundproof walls and building walls
Water purification	Drinking water	River water, ground water, lakes and water-storage tanks
	Others	Fish feeding tanks, drainage water and industrial wastewater
Antitumor activity	Cancer therapy	Endoscopic-like instruments
Self-sterilizingHospital		Tiles to cover the floor and walls of operating rooms, silicone rubber for medical catheters and hospital garments and uniforms
	Others	Public rest rooms, bathrooms and rat breeding rooms

**Table 2.** Applications of super hydrophilic technology. Note: this Table is reproduced with permission from [92], Copyright © 2000 Elsevier Science S.A.

Property	Category	Application
Self-cleaning	Roads	Tunnel lighting, tunnel walls, traffic signs and sound proof walls
	Houses	Tiles on kitchen walls and bathrooms, exterior tiles, roofs and windows
	Buildings	Aluminum panels, tiles, building stone, crystallized glass and glass film
	Agriculture	Plastic and glass greenhouses
	Electrical and electronic equipment	Computer displays and cover glass for solar cells
	Vehicles	Paint work, coatings for exterior surfaces of windows and headlights
	Daily necessities and consumer products	Tableware, kitchenware and spray-on anti-fouling coatings
	Paint	General-purpose paints and coatings
Anti-fogging property	Roads	Road mirrors
	Houses	Mirrors for bathrooms and dressers
	Stores	Refrigerated showcases
	Electrical and electronic equipment	Heat exchangers for air conditioners and high-voltage electric transmission equipment
	Vehicles	Inside surfaces of windows, glass films, rear-view mirrors and windshields
	Daily necessities and consumer products	Spray-on antifogging coatings and films
		Paint
	Optical instruments	Optical lenses
Bio-compatibility	Medical instruments and supplies	Contact lenses and catheters

**Table 3.** Waterborne microbial species known to be inactivated by solar disinfection [5].

Microbe	Species
Bacteria	<i>Campylobacter jejuni</i>
	<i>Enterococcus</i> sp.
	Enteropathogenic <i>E. coli</i>
	<i>Mycobacterium avium</i>
	<i>Mycobacterium intracellulare</i>
	<i>Pseudomonas aeruginosa</i>
	<i>Salmonella typhi</i>
	<i>Salmonella typhimurium</i>
	<i>Shigella dysenteriae</i> type 1
	<i>Shigella flexneri</i>
	<i>Streptococcus faecalis</i>
	<i>Staphylococcus epidermidis</i>
	<i>Vibrio cholerae</i>
<i>Yersinia enterocolitica</i>	

Table 3. Cont.

Viruses	Bacteriophage f2
	Encephalomyocarditis virus
	Polio virus
	Rotavirus
	Coxsackie virus A/B
	Hepatitis A
Protozoa	<i>Acanthamoeba polyphaga</i> (cyst )
	<i>Cryptosporidium parvum</i> (oocyst)
	<i>Entamoeba</i> sp. (cysts)
	<i>Giardia</i> sp. (cysts)
	<i>Naegleria</i> sp.

### 9.1. Water Treatment

Growth in the global population, the diminishing supply of clean water, heightened environmental concerns, and the strong link between water quality and human health require the identification and employment of effective sustainable water treatments to meet the urgent global need for clean water. Advanced oxidation processes (AOPs) have shown tremendous promise in water purification and treatment, including for the destruction of naturally occurring toxins, contaminants of emerging concern, pesticides, and other deleterious contaminants. One of the first references to AOPs was by Glaze in 1987 as processes that involve the generation of hydroxyl radicals in sufficient quantity to affect water purification. The definition and development of AOPs have evolved since the 1990s and include a variety of methods for generating hydroxyl radical and other reactive oxygen species including superoxide anion radical, hydrogen peroxide, and singlet oxygen. However, hydroxyl radical is still the species most commonly tied to the effectiveness of AOPs. Most organic compounds react with hydroxyl radical by addition or hydrogen abstraction pathways to form a carbon-centered radical. The resulting carbon-centred radical reacts with molecular oxygen to form a peroxy radical that undergoes subsequent reactions, ultimately producing a host of oxidation products such as ketones, aldehydes and alcohols [21].

Hydroxyl radical can also abstract an electron from electron-rich substrates to form a radical cation, which in aqueous media, is readily hydrolyzed, ultimately leading to an oxidized product. The oxidation products are often less toxic and more susceptible to bioremediation. AOPs include UV/O<sub>3</sub>, UV/H<sub>2</sub>O<sub>2</sub>, Fenton, photo-Fenton, non-thermal plasmas, sonolysis, photocatalysis, radiolysis and supercritical water oxidation processes. Problematic substances in wastewater can include organic matter and/or different trace contaminants and industrial wastewater may also contain heavy loads of metals or organic compounds and these cannot be treated by disinfection. In drinking water production microbe contamination is a problem especially in developing countries and remote locations without access to a centralized drinking water supply.

In Europe, conventional technologies for wastewater treatment are in most cases able to meet the current water quality standards. The chances and potential fields of application of photocatalytic systems with artificial UV-sources include new water treatment plants or plants where conventional

methods need to be replaced and the treatment of water contaminated with trace contaminants such as estrogens, the treatment of industrial wastewater contaminated with high loads of organic compounds or metals as well as small scale systems, for example, for the disinfection of swimming pools [92,100].

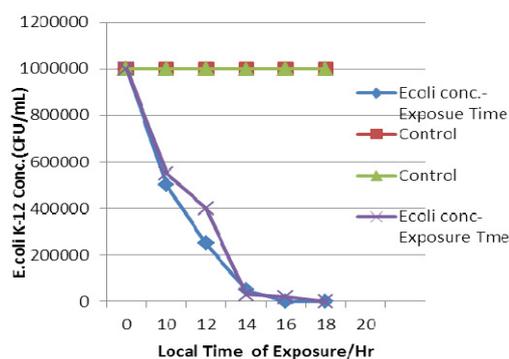
Globally, 1 billion people lack access to safe water supplies and 2.6 billion are without access to basic sanitation [5]. This is especially true for the least developed regions of Asia, Central and South America, and Africa, innovative methods for water treatment are needed urgently. In the most developed markets such as the USA, Canada, Japan, and most of Western Europe, the success of a new water treatment method is mainly based on its ability to improve the quality of drinking water and/or to reduce water contamination. The beneficial effects of clean water are obvious. Most importantly, the improvement of water supply, sanitation, hygiene, and management of water resources could prevent almost one-tenth of all diseases worldwide. Nanotechnology is one of the most promising emerging technologies for efficient, economical and environmentally friendly water and waste water treatment offering great potential for manufacturers in Europe.

The demand for water treatment products globally reached \$44.6 billion in 2008 and it is predicted, by Freedonia Group Inc., to increase annually by 5.7% reaching \$59 billion by 2013 [5]. The fastest annual growth was predicted to be in large developing countries like China and India due to rapid industrialization and increased efforts to expand access to safe water supplies and adequate sanitation facilities especially in rural areas. The worldwide turnover of nanotechnological applications in water and wastewater treatment reached \$1.6 billion in 2007 and was predicted to increase to \$6.6 billion in 2015. In 2015 the leading countries in water treatment with nanoparticle-based methods are the USA, Germany, Japan, and China [101]. Disinfection is one of the fastest growing market segments with broad applications and benefits; photocatalysis with nano-catalysts is a promising method for disinfection. In addition, photocatalysts combined with filtration membranes can reduce membrane fouling and thus enhance water cleaning efficiency significantly. Small-scale photocatalytic systems with artificial UV-light have already been on the market for several years whereas solar photocatalytic water treatment plants are at a demonstration phase and pilot projects for drinking water purification in developing countries have only just started.

Recently, humic substance was also decomposed both in highly saline and natural seawater using different photocatalytic materials. The decomposition rate of humic substances in seawater was slow compared with pure water media and no toxic byproducts were detected during the decomposition. Minero and other workers [29,100,102–104] studied the decomposition of dodecane and toluene in crude oil in seawater media and found that no chlorinated compounds were detected during the irradiation. Complete decomposition was achieved after a few hours of irradiation. Another study conducted on the decomposition of seawater-soluble crude-oil fractions found that it can be decomposed under illumination of nanoparticles of  $\text{TiO}_2$  using artificial light [47].

Photocatalysis can also be used to destroy bacteria and viruses [92,100,105]. The increasing incidence of algal blooms in fresh water supplies and the consequent possibility of cyanobacterial microcystin contamination of potable water *Microcystin toxins* are also degraded on immobilized titanium dioxide catalyst. Photodisinfection sensitized by  $\text{TiO}_2$  had some effect on the degradation of the green algae which has a thick cell wall. This is being used to great advantage in many developed and developing nations to treat water especially in remote and disaster areas without portable water supply or electricity, as shown in Figure 10.

**Figure 10.** Inactivation of bacteria Ecoli K-12 in drinking water exposed to solar irradiation. Adapted from EU Contract Number INCO-DEV 031650 (2006) [5].



Specific successful applications have been in the following areas, amongst others.

### 9.2. Removal of Trace Metals

Trace metal such as mercury (Hg), chromium (Cr), lead (Pb) and others metals are considered to be highly health hazardous. Thus, removing these toxic metals is essentially important for human health and water quality. The environmental applications of heterogeneous photocatalysis include removing heavy metals such as (Hg), chromium (Cr), lead (Pb), Cadmium (Cd), lead (Pb), Arsenic (As), nickel (Ni) copper (Cu). The photoreducing ability of photocatalysis has been used to recover expensive metals from industrial effluent, such as gold (Au), platinum (Pt) and silver (Au) [22].

### 9.3. Destruction of Organics

Photocatalysis has been used for the destruction of organic compounds such as alcohols, carboxylic acids, phenolic derivatives, or chlorinated aromatics, into harmless products, for example, carbon dioxide, water, and simple mineral acids. Water contaminated by oil can be treated efficiently by photocatalytic reaction. Herbicides and pesticides that may contaminate water such as 2,4,5 trichlorophenoxyacetic acid, 2,4,5 trichlorophenol, *S*-triazine herbicides and 1,1,1-trichloro-2,2-di(4-chlorophenyl)ethane (DDT) have also been successfully degraded [22].

### 9.4. Removal of Inorganic Compounds

In addition to organic compounds, wide ranges of inorganic compounds are sensitive to photochemical transformation on the catalyst surfaces. Inorganic species such as bromate, or chlorate, azide, halide ions, nitric oxide, palladium and rhodium species, and sulfur species can be decomposed. Metal salts such as  $\text{AgNO}_3$ ,  $\text{HgCl}$  and organometallic compound (e.g.,  $\text{CH}_3\text{HgCl}$ ) can be removed from water as well as cyanide, thiocyanate, ammonia, nitrates and nitrites [22].

### 9.5. Degradation of Natural Organic Matter

Humic substances have also been degraded photochemically. Humic are naturally occurring biogenic heterogeneous organic substances characterized as being yellow brown and having high molecular weights They can also be described as the fraction of filtered water that adsorbs on

non-ionic polymeric adsorbent at pH 2. They are the main constituents of the dissolved organic carbon pool in surface and ground waters, imparting a yellowish-brown color to the water system. The concentration of humic substances varies from place to place, the values in seawater being normally from 2–3 mg/L. Humic substances affect the behaviour of some pollutants in natural environments, such as trace metal speciation and toxicity, solubilization and adsorption of hydrophobic pollutants. They act as substrates for bacterial growth; inhibit the bacterial degradation of impurities in natural water, complex with heavy metals such as Fe, Pb, Mn making it harder to remove them. Advanced oxidation has been used to decrease the organic content in water including humic acid [100] and it has the advantage of not leaving any toxic byproducts or sludge.

Bekbolet and Ozkosemen [103] investigated the photocatalytic degradation using humic acid as a model and observed that after 1 h irradiation and in the presence of 1.0 g/L TiO<sub>2</sub> (P25), 40% TOC and 75% of the colour (400 nm) were removed. On the other hand, Eggins and coworkers found the suspension of TiO<sub>2</sub> (P25) irradiated by a mercury lamp showed a very efficient reduction of humic acid concentration of about 50% in 12 min. Heterogeneous photocatalysis has also been coupled with other physical methods in order to increase the degradation rate of organic molecules including humic substances [100,103].

### 9.6. Medical Applications

Application in TiO<sub>2</sub> Fabrics is a major and important application of TiO<sub>2</sub> photocatalysis. The ability of TiO<sub>2</sub> to disinfect microbes, viruses and bacteria has been put into good use by Japanese researchers. Hospital garments worn by doctors and nurses have “doses” of TiO<sub>2</sub> added to the fabric during processing operations and the fabric are used to make hospital garments that are worn to control hospital infections, including MRSA. Many lives have been lost because of methicillin resistant *Staphylococcus* (MRSA) and research is concentrating efforts on “TiO<sub>2</sub> fabrics” as well as the use of antimicrobial photodynamic therapy (APDT) to decolonize MRSA from patients [92].

### 9.7. Application Photodynamic Therapy

Targeting cancer such as colon or kidney cancer (tumor therapy) in an organism with a source of irradiation is easy. However, tumors in rats have shown to respond to PDT treatment. Basically, TiO<sub>2</sub> is introduced in the site of the cancer and illuminated by and is photo sensitized using an optic fiber cable to introduce the illumination [92]. The activation of the photo sensitizer on illumination creates reactive oxygen species that kill the surrounding cells of the tumor.

### 9.8. Applications in Construction

TiO<sub>2</sub> cement (“pellite cement”) containing TiO<sub>2</sub> has been used in road construction (tunnels) in some European countries to control exhaust emissions due principally to NO and NO<sub>2</sub>. These are especially severe in summer months especially in dense and large urban cities with high traffic levels. This application however, is not new to the market [106].

## 10. Societal Impact of Photocatalysis

The widespread application of nanoparticle  $\text{TiO}_2$  should, in theory, have beneficial impacts on the health of the general public and thus on the quality of life [3]. Since nanoparticle  $\text{TiO}_2$  particles are inexpensive and may be integrated into different materials, photocatalytic systems and surfaces, they are not limited to large-scale applications in water treatment facilities. They may also be applied in homes, hospitals, or offices for disinfection or the degradation of water and air pollutants [6,9–11]. The use of nanoparticle  $\text{TiO}_2$  for water treatment and disinfection is expected to have a positive effect on the environment, as it can replace more toxic substances such as organic biocides. This has a significant implication for developing nations. It can also improve the quality of the water released from water treatment plants by assisting traditional treatment methods to target more substances and thereby obtain a higher efficiency of the whole process [14–16].

## 11. Outlook and Challenges

$\text{TiO}_2$  has been extensively studied worldwide resulting in more than 13,600 publications between 2010 and 2011. Opportunities for  $\text{TiO}_2$  now lie in areas such as energy conversion and storage.  $\text{TiO}_2$  nanostructures have shown promise in designing Li-ion and Na-ion storage batteries and shape- and size-controlled  $\text{TiO}_2$  nanostructures will continue to provide the base architecture to construct light-harvesting assemblies and facilitate photo-induced charge separation processes. As stated earlier in this review, pure nanoparticle  $\text{TiO}_2$  is only activated by UV-light and this means that for indoor applications it is important to develop a  $\text{TiO}_2$  based catalysts that can absorb visible wavelengths. Furthermore, the most efficient system set-up and substrate materials have to be determined for different applications in private and public facilities to assure maximal longevity, efficiency, and functionality of the photo-catalyst. A significant problem that still needs to be addressed is suppressing charge recombination in semiconductor materials. Studies have shown that manipulation of interfacial charge transfer can assist in improving photocatalytic and solar cell conversion efficiency. This may be achieved by surface modification surface modification and/or with a co-catalyst [12].

Another major challenge is that nanoparticle  $\text{TiO}_2$  does not only destroy all organic materials but also the organic matrix in which the nanoparticles are embedded. This limits its application to inorganic environments. Nanoparticle  $\text{TiO}_2$  is expected to have minimal negative effect both on human health and the environment since it is usually immobilized in/on a substrate material, for example, metals, tiles, or glass beads. However, nanoparticle  $\text{TiO}_2$  can accumulate if its use is widespread and could potentially have health impacts for workers exposed to nanoparticle  $\text{TiO}_2$  dust. There are currently no regulations related to the use of nanoparticle  $\text{TiO}_2$  for water treatment, but standards on test methods for photocatalytic water purification are under development. Stricter water treatments standards would require new treatment methods and could thus further the application of photocatalytic systems with nanomaterials.

## 12. Conclusion

This review covered mainly TiO<sub>2</sub> semiconductor as well as RuO<sub>2</sub> and SnO<sub>2</sub>. The principles and methods covered in this review apply to all photocatalyst materials in general. It is now possible to tailor catalysts to specific applications and there are ways of enhancing photocatalyst activity and improving performance. As well as destruction of viruses and bacteria, heterogeneous photocatalysis has been used to decompose natural organic matter, volatile organic compounds in water, air and soil and there are applications in consumer goods, food and medicine. Extending the wavelength for TiO<sub>2</sub> application is an area of increasing research. One of the ways of doing this is by doping, as already described in this review and this merits continuing research efforts.

## Conflict of Interest

The authors declare no conflict of interest.

## References

1. Teoh, W.Y.; Amal, R.; Scott, J. Progress in heterogenous photocatalysis: From classical radical chemistry to engineering nanomaterials and solar reactors. *J. Phys. Chem. Lett.* **2012**, *3*, 629–639.
2. Kamat, P. TiO<sub>2</sub> nanostructures: Recent physical chemistry advances. *J. Phys. Chem. Lett.* **2012**, *116*, 11849–11851.
3. Weir, A.; Westerhoff, P.; Fabricus, L.; Hristovski, K.; von Goetz, N. Titanium dioxide nanoparticles in food and personal care products. *Environ. Sci. Technol.* **2012**, *46*, 2242–2250.
4. Ibhaddon, A.O. Multifunctional TiO<sub>2</sub> Catalysis and Applications. In *Proceedings of Green Chemistry and Engineering International Conference*, Washington, DC, USA, 24–26 June 2008.
5. Sodis Water Project. Available online: <http://cordis.europa.eu/documents/documentlibrary/122807461EN6.pdf> (accessed on 20 February 2013).
6. Cho, M.; Chung, H.; Choi, W.; Yoon, J. Linear correlation between inactivation of *E. coli* and OH radical concentration in TiO<sub>2</sub> photocatalytic disinfection. *Water Res.* **2004**, *38*, 1069–1077.
7. Fujishima, A.; Zhang, X.; Tryk, D.A. TiO<sub>2</sub> photocatalysis and related surface phenomena. *Surf. Sci. Rep.* **2008**, *63*, 515–582.
8. Ibhaddon, A.O.; Yue, Y.; Greenway, G.M. The photocatalytic activity of surface modified TiO<sub>2</sub>/RuO<sub>2</sub>/SiO<sub>2</sub> nanoparticles for azo-dye degradation. *Catal. Commun.* **2008**, *9*, 153–157.
9. Kamat, P.V. Manipulation of charge transfer across semiconductor Interface. *J. Phys. Chem. Lett.* **2012**, *3*, 663–672.
10. Chen, D.; Ray, A.K. Removal of toxic metal ions from wastewater by semiconductor photocatalysis. *Chem. Eng. Sci.* **2001**, *56*, 1561–1570.
11. Bhatkhande, D.S.; Pangarkar, V.G.; Beenackers, A.A.C.M. Photocatalytic degradation for environmental applications—A review. *J. Chem. Technol. Biotechnol.* **2001**, *77*, 102–116.
12. Kamat, P.V. Graphene-based nanoarchitectures. Anchoring semiconductor and metal nanoparticles on a two-dimensional carbon support. *J. Phys. Chem. Lett.* **2010**, *1*, 520–527.

13. Blake, D.M. *Bibliography of Work on the Heterogeneous Photocatalytic Removal of Hazardous Compounds from Water and Air*; National Renewable Energy Laboratory: Denver, CO, USA, 2001; pp. 1–158.
14. Schmitt-Kopplin, P.; Hertkorn, N.K.A. Structural changes in dissolved soil humic matter during photochemical degradation processes under nitrogen and oxygen atmospheres. *Environ. Sci. Technol.* **1998**, *32*, 2531–2541.
15. Paleologou, A.; Marakas, H.; Xekoukoulotakis, N.P.; Moya, A.; Vergara, Y.; Kalogerakis, N.; Gikas, P.; Mantzavinou, D. Disinfection of water and wastewater by TiO<sub>2</sub> photocatalysis, sonolysis and UV-C irradiation. *Catal. Today* **2007**, *129*, 136–142.
16. Sunada, K.; Watanabe, T.; Hashimoto, K. Studies on photo-killing of bacteria on TiO<sub>2</sub> thin film. *J. Photochem. Photobiol. A* **2003**, *156*, 227–233.
17. Daneshvar, N.; Niaei, A.; Akbari, S.; Aber, S.; Kazemian, N. Photocatalytic disinfection of water polluted with *Pseudomonas aeruginosa*. *Glob. Nest J.* **2007**, *9*, 132–136.
18. Pirkanniemi, K.; Sillanpa, M. Heterogeneous water phase catalysis as an environmental application: A review. *Chemosphere* **2002**, *48*, 1047–1060.
19. Huang, A.; Cao, L.; Chen, J.; Spiess, F.J.; Suib, S.L.; Obee, T.N.; Hay, S.O.; Freihaut, J.D. Photocatalytic degradation of triethylamine on titanium dioxide thin films. *J. Catal.* **1999**, *188*, 40–47.
20. Arabatzis, I.M.; Antonaraki, S.; Stergiopoulos, T.; Hiskia, A.; Papaconstantinou, E.; Bernard, M.C.; Falaras, P. Enhanced performance of dye-sensitized solar cells via plasmonic sandwiched structure. *J. Photochem. Photobiol. A* **2002**, *149*, 237–245.
21. Al-Rasheed, R.A. Water Treatment by Heterogeneous Photocatalysis: An Review. In *Proceedings of the 4th SWCC Acquired Experience Symposium*, Jeddah, Saudi Arabia, 7 May 2005.
22. Bekbolet, M.; Boyacioglu, Z.; Ozkaraova, B. The influence of solution matrix on the photocatalytic removal of color from natural waters. *Water Sci. Technol.* **1998**, *38*, 155–162.
23. Mills, A.; Belghazi, A.; Rodman, D. Bromate removal from water by semiconductor photocatalysis. *Water Res.* **1996**, *3*, 1973–1978.
24. Kokorin, A.I.; Bahnemann, D.W. *Chemical Physics of Nanostructured Semiconductors*; VSP: Boston, MA, USA, 2003.
25. Mills, A.; Leunte, S. An overview of semiconductor photocatalysis. *Chem. Soc. Rev.* **1997**, *22*, 417–425.
26. Gerischer, H. Electrochemical behaviour of semiconductors under illumination. *J. Electrochem. Soc.* **1966**, *113*, 1174–1182.
27. Minero, C.; Pelizzatti, E.; Sega, M.; Friberg, S.E.; Sjoblom, J. The role of humic substances in photocatalytic degradation of water contaminants. *J. Dispersion. Sci. Technol.* **1999**, *20*, 643–661.
28. Cherepy, N.J.; Liston, D.B.; Lovejoy, J.A.; Deng, H.; Zhang, J.Z. Ultrafast studies of photoexcited electron dynamics in  $\gamma$ - and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> semiconductor nanoparticles. *J. Phys. Chem. B* **1998**, *102*, 770–776.
29. Eggleston, C.M. Toward new uses for hematite. *Science* **2008**, *320*, 184–185.

30. Kleiman-Shwarsctein, A.; Hu, Y.S.; Forman, A.J.; Stucky, G.D.; McFarland, E. Electrodeposition of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> doped with Mo or Cr as photoanodes for photocatalytic water splitting. *J. Phys. Chem. C* **2008**, *112*, 15900–15907.
31. Teoh, W.Y.; Denny, F.; Amal, R.; Friedmann, D.; Mädler, L.; Pratsinis, S.E. Photocatalytic mineralisation of organic compounds: A comparison of flame-made TiO<sub>2</sub> catalysts top. *Catalysis* **2007**, *44*, 489–497.
32. Teoh, W.Y.; Mädler, L.; Amal, R. Inter-relationship between Pt oxidation states on TiO<sub>2</sub> and the photocatalytic mineralisation of organic matter. *J. Catal.* **2007**, *251*, 271–280.
33. Teoh, W.Y.; Mädler, L.; Beydoun, D.; Pratsinis, S.E.; Amal, R. Direct (one-step) synthesis of TiO<sub>2</sub> and Pt/TiO<sub>2</sub> nanoparticles for photocatalytic mineralisation of sucrose. *Chem. Eng. Sci.* **2005**, *60*, 5852–5861.
34. Tran, H.; Chiang, K.; Scott, J.; Amal, R. Understanding selective enhancement by silver during photocatalytic oxidation. *Photochem. Photobiol. Sci.* **2005**, *4*, 565–567.
35. Cesar, I.; Kay, A.; Gonzalez-Martinez, J.A.; Grätzel, M. Translucent thin film Fe<sub>2</sub>O<sub>3</sub> photoanodes for efficient water splitting by sunlight: Nanostructure-directing effect of Si-doping. *J. Am. Chem. Soc.* **2006**, *128*, 4582–4583.
36. Abe, R.; Takami, H.; Murakami, N.; Ohtani, B. Pristine simple oxides as visible light driven photocatalysts: Highly efficient decomposition of organic compounds over platinum-loaded tungsten oxide. *J. Am. Chem. Soc.* **2008**, *130*, 7780–7781.
37. Tada, H.; Mitsui, T.; Kiyonaga, T.; Akita, T.; Tanaka, K. All-solid-state Z-scheme in CdS-Au-TiO<sub>2</sub> three-component nano-junction system. *Nat. Mater.* **2006**, *5*, 782–786.
38. Bickley, R.I.; Gonzalez-Carreno, T.; Lees, J.S.; Palmisano, R.L.; Tilley, J.D. A structural investigation of titanium dioxide photocatalysts. *J. Solid State Chem.* **1991**, *92*, 178–190.
39. Gaffney, J.S.; Marley, N.A.; Clark, S.B. Humic and Fulvic Acids and Organic Colloidal Material in the Environment. In *Humic and Fulvic Acids: Isolation, Structure, and Environmental Role*; American Chemical Society: Washington, DC, USA, 1996.
40. Ohno, T.; Sarukawa, K.; Matsumura, M. Photocatalytic activities of pure rutile particles isolated from TiO<sub>2</sub> powder by dissolving the anatase component in HF solution. *J. Phys. Chem. B* **2001**, *105*, 2417–2420.
41. Hurum, D.C.; Agrios, A.G.; Gray, K.A.; Rajh, T.; Thurnauer, M.C. Explaining the enhanced photocatalytic activity of degussa P25 mixed-phase TiO<sub>2</sub> using EPR. *J. Phys. Chem. B* **2003**, *107*, 4545–4549.
42. Li, G.; Chen, L.; Graham, M.E.; Gray, K.A. A comparison of mixed phase titania photocatalysts prepared by physical and chemical methods: The importance of the solid-solid interface. *J. Mol. Catal. A* **2007**, *275*, 30–35.
43. Ohtani, B.; Prieto-Mahaney, O.O.; Lia, D.; Abe, R. What is degussa (evonik) P25? Crystalline composition analysis, reconstruction from isolated pure particles and photocatalytic activity test. *J. Photochem. Photobiol. A* **2010**, *218*, 179–182.
44. Ryu, J.; Choi, W. Substrate specific photocatalytic activities of TiO<sub>2</sub> and multiactivity test for water treatment application. *Environ. Sci. Technol.* **2008**, *42*, 294–300.
45. Tanka, S.; Oba, K.; Fukushima, M.; Nakayasu, K.; Hasebe, K. Water solubility enhancement of pyrene in the presence of humic substances. *Anal. Chim. Acta* **1997**, *337*, 351–357.

46. Ohtani, B. Preparing articles on photocatalysis—Beyond the illusions, misconceptions, and speculation. *Chem. Lett.* **2008**, *37*, 217–229.
47. Memming, R. *Applications in Semiconductor Electrochemistry*; Wiley-VCH: Weinheim, Germany, 2007.
48. Coleman, H.M.; Chiang, K.; Amal, R. Effects of Ag and Pt on photocatalytic degradation of endocrine disrupting chemicals in water. *Chem. Eng. J.* **2005**, *113*, 65–72.
49. Kho, Y.K.; Teoh, W.Y.; Mädler, L.; Amal, R. Dopant-free, polymorphic design of TiO<sub>2</sub> nanocrystals by flame aerosol synthesis. *Chem. Eng. Sci.* **2011**, *66*, 2409–2416.
50. Denny, F.; Scott, J.; Chiang, K.; Teoh, W.Y.; Amal, R. Insight towards the role of platinum in the photocatalytic mineralisation of organic compounds. *J. Mol. Catal. A* **2007**, *263*, 93–102.
51. Kudo, A. Z-scheme photocatalyst systems for water splitting under visible light irradiation. *MRS Bull.* **2011**, *36*, 32–38.
52. Young, C.; Lim, T.M.; Chiang, K.; Scott, J.; Amal, R. Photocatalytic oxidation of toluene and trichloroethylene in the gas-phase by metallised (Pt, Ag) titanium dioxide. *Appl. Catal. B Environ.* **2008**, *78*, 1–10.
53. Lee, J.; Choi, W. Photocatalytic reactivity of surface platinized TiO<sub>2</sub>: Substrate specificity and the effect of Pt oxidation state. *J. Phys. Chem. B* **2005**, *109*, 7399–7406.
54. Wei, Y.; Han, S.; Walker, D.A.; Warren, S.C.; Grzybowski, B.A. Enhanced photocatalytic activity of hybrid Fe<sub>2</sub>O<sub>3</sub>-Pd nanoparticle catalyst. *Chem. Sci.* **2012**, *3*, 1090–1094.
55. Xu, Q.C.; Ng, Y.H.; Zhang, Y.; Loo, J.S.C.; Amal, R.; Tan, T.T.Y. A three-way synergy of triple-modified Bi<sub>2</sub>WO<sub>6</sub>/Ag/N-TiO<sub>2</sub> nanojunction film for enhanced photogenerated charges utilization. *Chem. Commun.* **2011**, *47*, 8641–8643.
56. Anpo, M.; Takeuchi, M. The design and development of highly reactive titanium oxide photocatalysts operating under visible light irradiation. *J. Catal.* **2003**, *216*, 505–516.
57. Rajeshwar, K.; Osugi, M.E.; Chanmanee, W.; Chethanmarakshan, C.R.; Zaroni, M.V.B.; Kajitvichyanukul, P.; Krishnan-Ayer, R. Heterogeneous photocatalytic treatment of organic dyes in air and aqueous media. *J. Photochem. Photobiol. C* **2008**, *9*, 171–192.
58. Nah, Y.C.; Paramasivam, I.; Hahn, R.; Shrestha, N.K.; Schmuki, P. Nitrogen doping of nanoporous WO<sub>3</sub> layers by NH<sub>3</sub> treatment for increased visible light photoresponse. *Nanotechnology* **2010**, *21*, 105704.
59. Lam, S.W.; Chiang, K.; Lim, T.M.; Amal, R.; Low, G.K.C. The effect of platinum and silver deposits in the photocatalytic oxidation of resorcinol. *Appl. Catal. B* **2007**, *72*, 363–372.
60. Di Paolo, A.; Marci, G.; Palmisano, L.; Schiavello, M.; Uosaki, K.; Ikeda, S.; Ohtani, B. Preparation of polycrystalline TiO<sub>2</sub> photocatalysts impregnated with various transition metal ions: Characterization and photocatalytic activity for the degradation of 4-nitrophenol. *J. Phys. Chem. B* **2009**, *106*, 637–645.
61. Teoh, W.Y.; Amal, R.; Mädler, L.; Pratsinis, S.E. Flame sprayed visible light-active Fe-TiO<sub>2</sub> for photomineralisation of oxalic acid. *Catal. Today* **2007**, *120*, 203–213.
62. Serpone, N. Is the band gap of pristine TiO<sub>2</sub> narrowed by anion- and cation-doping of titanium dioxide in second-generation photocatalysts? *J. Phys. Chem. B* **2006**, *110*, 24287–24293.

63. Murase, T.; Irie, H.; Hashimoto, K. Visible light sensitive photocatalysts, nitrogen-doped Ta<sub>2</sub>O<sub>5</sub> powders. *J. Phys. Chem. B* **2004**, *108*, 15803–15807.
64. Emeline, A.V.; Sheremetyeva, N.V.; Khomchenko, N.V.; Kuzmin, G.N.; Ryabchuk, V.K.; Teoh, W.Y.; Amal, R. Spectroscopic studies of pristine and fluorinated nano-ZrO<sub>2</sub> in photostimulated heterogeneous processes. *J. Phys. Chem. C* **2009**, *113*, 4566–4574.
65. Asahi, R.; Morikawa, T.; Ohwaki, T.; Aoki, K.; Taga, Y. Visible-light photocatalysis in nitrogen-doped titanium oxides. *Science* **2001**, *293*, 269–271.
66. Sakthivel, S.; Kisch, H. Daylight photocatalysis by carbon-modified titanium dioxide. *Angew. Chem. Int. Ed.* **2003**, *42*, 4908–4911.
67. Umabayashi, T.; Yamaki, T.; Itoh, H.; Asai, K. Band gap narrowing of titanium dioxide by sulfur doping. *Appl. Phys. Lett.* **2002**, *81*, 454.
68. Wang, L.; Mukheji, A.; Lu, G.Q.; Sun, C.; Smith, S.C. Photocatalytic hydrogen production from water using N-doped Ba<sub>5</sub>Ta<sub>4</sub>O<sub>15</sub> under solar irradiation. *J. Phys. Chem. C* **2011**, *115*, 15674–15678.
69. Yu, J.C.; Yu, J.; Ho, W.; Jiang, Z.; Zhang, L. Effects of F-doping on the photocatalytic activity and microstructures of nanocrystalline TiO<sub>2</sub> powders. *Chem. Mater.* **2002**, *14*, 3808–3816.
70. Carp, O.; Huisman, C.L.; Reller, A. Photoinduced reactivity of titanium dioxide. *Prog. Solid State Chem.* **2004**, *32*, 33–177.
71. Li, D.; Haneda, H.; Hishita, S.; Ohashi, N. Visible-light-driven N-F-codoped TiO<sub>2</sub> photocatalysts. 2. Optical characterization, photocatalysis, and potential application to air purification. *Chem. Mater.* **2005**, *17*, 2596–2602.
72. Tachikawa, T.; Fujitsuka, M.; Majima, T. Mechanistic insight into the TiO<sub>2</sub> photocatalytic reactions: Design of new photocatalysts. *J. Phys. Chem. C* **2007**, *111*, 5259–5275.
73. Sun, L.; Zhao, X.; Sun, H.; Li, Y.; Li, P.; Fan, W.; Cheng, X. Evaluating the C, N and F pairwise codoping effect on the enhanced photoactivity of ZnWO<sub>4</sub>: The charge compensation mechanism in donor-acceptor pairs. *J. Phys. Chem. C* **2011**, *115*, 15516–15524.
74. Yamakata, A.; Ishibashi, T.; Kato, H.; Kudo, A.; Onishi, H. Photodynamics of NaTaO<sub>3</sub> catalysts for efficient water splitting. *J. Phys. Chem. B* **2003**, *107*, 14383–14387.
75. Kudo, A.; Miseki, Y. Heterogeneous photocatalyst materials for water splitting. *Chem. Soc. Rev.* **2009**, *38*, 253–278.
76. Maeda, K.; Domen, K. Photocatalytic water splitting: Recent progress and future challenges. *J. Phys. Chem. Lett.* **2010**, *1*, 2655–2661.
77. Tang, J.; Zou, Z.; Ye, J. Efficient photocatalytic decomposition of organic contaminants over CaBi<sub>2</sub>O<sub>4</sub> under visible-light irradiation. *Angew. Chem. Int. Ed.* **2004**, *43*, 4463–4466.
78. Maeda, K.; Teramura, K.; Lu, D.; Takata, T.; Saito, N.; Inoue, Y.; Domen, K. Photocatalyst releasing hydrogen from water. *Nature* **2006**, *440*, 295.
79. Kim, H.G.; Hwang, D.W.; Lee, J.S. An undoped, single-phase oxide photocatalyst working under visible light. *J. Am. Chem. Soc.* **2004**, *126*, 8912–8913.
80. Yan, S.C.; Ouyang, S.X.; Gao, J.; Yang, M.; Feng, J.Y.; Fan, X.X.; Wan, L.J.; Li, Z.S.; Ye, J.H.; Zhou, Y.; *et al.* A room-temperature reactive-template route to mesoporous ZnGa<sub>2</sub>O<sub>4</sub> with improved photocatalytic activity in reduction of CO<sub>2</sub>. *Angew. Chem. Int. Ed.* **2010**, *122*, 6544–6548.

81. Chang, H.T.; Wu, N.M.; Zhu, F. A kinetic model for photocatalytic degradation of organic contaminants in a thin-film TiO<sub>2</sub> catalyst. *Water Res.* **2000**, *34*, 407–416.
82. Arabatzis, M.I.; Falaras, P. Synthesis of TiO<sub>2</sub> foam. *Nano Lett.* **2003**, *3*, 249–251.
83. Chen, X.; Mao, S.S. Titanium dioxide nanomaterials: Synthesis, properties, modifications and applications. *Chem. Rev.* **2007**, *107*, 2891–2959.
84. Joanna, G.; Maciej, H.; Antoni, W.M. Photocatalytic decomposition of oil in water. *Water Res.* **2000**, *34*, 1638–1644.
85. Henderson, M.A. A surface science perspective on TiO<sub>2</sub> photocatalysis. *Surf. Sci. Rep.* **2011**, *66*, 185–297.
86. Ibhaddon, A.O.; Yue, Y.; Greenway, G.M.; Falaras, P.; Tsoukleris, D. The photocatalytic activity of TiO<sub>2</sub> foam and surface modified binary oxide nanoparticles. *J. Photochem. Photobiol. A* **2008**, *197*, 321–328.
87. Yang, H.G.; Sun, C.H.; Qiao, S.Z.; Zou, J.; Liu, G.; Smith, S.C.; Cheng, H.M.; Lu, G.Q. Anatase TiO<sub>2</sub> single crystals with a large percentage of reactive facets. *Nature* **2008**, *453*, 638–641.
88. Kontos, A.G.; Pelaez, M.; Likodimos, V.; Vaenas, N.; Dionysiou, D.D.; Falaras, P. Visible light induced wetting of nanostructured *N-F* co-doped titania films. *Photochem. Photobiol. Sci.* **2011**, doi:10.1039/c0pp00159g/.
89. Legrini, O.; Oliveros, E.; Braun, A.M. Photochemical processes for water treatment. *Chem. Rev.* **1993**, *93*, 671–698.
90. Ibhaddon, A.O.; Yue, Y.; Greenway, G. Design and synthesis of polymetallic nanoparticles and their catalytic applications. *Mater. Lett.* **2011**, *65*, 602–605.
91. Prieto-Mahaney, O.O.; Murakami, N.; Abe, R.; Ohtani, B. Correlation between photocatalytic activities and structural and physical properties of titanium dioxide powders. *Chem. Lett.* **2009**, *38*, 238–239.
92. Akira, F.; Rao, T.; Tryk, D. Titanium dioxide photocatalysis. *J. Photochem. Photobiol. C* **2000**, *1*, 1–21.
93. Denny, F.; Scott, J.; Peng, G.D.; Amal, R. Channelled optical fibre photoreactor for improved air quality control. *Chem. Eng. Sci.* **2010**, *65*, 882–889.
94. Xu, N.; Shi, Z.; Fam, Y.; Dong, J.; Shi, J.; Hu, M.Z.C. Effects of particle size of TiO<sub>2</sub> on photocatalytic degradation of methylene blue in aqueous suspensions. *Ind. Eng. Chem. Res.* **1999**, *38*, 373–379.
95. Fang, W.Q.; Gong, X.Q.; Yang, H.G. On the unusual properties of anatase TiO<sub>2</sub> exposed by highly reactive facets. *J. Phys. Chem. Lett.* **2011**, *2*, 725–734.
96. Hsien, Y.H.; Chang, C.F.; Chen, Y.H.; Cheng, S. Photodegradation of aromatic pollutants in water over TiO<sub>2</sub> supported on molecular sieves. *Appl. Catal. B* **2001**, *31*, 241–249.
97. Al-Rasheed, R.; Cardin, D.J. Photocatalytic degradation of humic acid in saline waters. Part 2. Effect of various photocatalytic materials. *Appl. Catal. A* **2003**, *246*, 39–48.
98. Herrmann, J.M. Fundamentals and misconceptions in photocatalysis. *J. Photochem. Photobiol. A* **2010**, *216*, 85–93.
99. Ibhaddon, A.O.; Falaras, P.; Tsoukleris, D.S.; Arabatzis, I.M. The design and photoreaction kinetic modeling of a gas-phase titania foam packed bed reactor. *Chem. Eng. J.* **2007**, *133*, 317–323.

100. Eggins, B.R.; Palmer, F.L.; Bryne, J.A. Photocatalytic treatment of humic substances in drinking water. *Water Res.* **1997**, *31*, 1223–1226.
101. Kerc, A.; Bekbolet, M.; Saatci, A.M. Effect of partial oxidation by ozonation on the photocatalytic degradation of humic acids. *Int. J. Photoenergy* **2003**, *5*, 75–80.
102. Matatov, M.Y.I.; Sheintuch, M. Catalytic abatement of water pollutants. *Ind. Eng. Chem. Res.* **1998**, *37*, 309–326.
103. Bekbolet, M.; Ozkosemen, G. A preliminary investigation on the photocatalytic degradation of a model humic acid. *Water Sci. Technol.* **1996**, *33*, 189–194.
104. Praire, M.R.; Stange, B.M.; Evans, I.R. *Photocatalytic Purification and Treatment of Water and Air*; Ollis, D.F., Al-Ekabi, H., Eds.; Elsevier Science Publishers: Amsterdam, The Netherlands, 1993; pp. 353–363.
105. Fukushima, M.; Tatsumi, K.; Moimoto, K. Influence of Fe (III) and humic acid on the photodegradation of pentachlorophenol. *Environ. Toxicol. Chem.* **2000**, *19*, 1711–1716.
106. Ohama, Y.; van Gemert, D. *Application of Titanium Dioxide Photocatalysis to Construction Materials*; Springer: London, UK, 2011; pp. 15–33.

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