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TiO₂: A Semiconductor Photocatalyst

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Abstract

Titanium dioxide (TiO₂) is considered as an inert and safe material and has been used in many applications for decades. TiO₂ have been widely studied, due to its interesting general properties in a wide range of fields including catalysis, antibacterial agents, in civil as nano-paint (self-cleaning) and especially photocatalysis, and that affect the quality of life. Thus, the development of nanotechnologies TiO₂ nanoparticles, with numerous novel and useful properties, are increasingly manufactured and used. TiO₂ doped with noble metal are good candidates in the performance these applications. The fascinating physical and chemical features of TiO₂ depend on the crystal phase, size and shape of particles. For example, varying phases of crystalline TiO₂ have different band gaps that rutile TiO₂ of 3.0 eV and anatase TiO₂ of 3.2 eV, determine the photocatalytic performance of TiO₂. This chapter explains basic information on TiO₂ and theoretical concepts of nanostructure of TiO₂ nanoparticles as a semiconductor photocatalyst.

Keywords: TiO₂, nanoparticles, semiconductor, photocatalyst

1. Introduction

An ideal photocatalyst should possess following nature: biologically and chemically inert, inexpensive, nontoxic, stable towards photocorrosion and certainly highly active and suitable towards the visible/UV light photoreaction. An additional criterion for such ideal photocatalyst is better redox potential of the H₂O/[•]OH couple (EOP = 2.80 V) [1]. Among the available semiconductors, TiO₂, ZnO, ZnS and WO₃ have gap energies sufficient for catalyzing a wide range of chemical reactions [2].

Binary metal sulphide semiconductors such as CdS, CdSe or PbS are regarded as unstable photocatalyst due to easy photoanodic corrosion property and their toxic nature [2, 3]. Furthermore, the iron oxide semiconductors are not suitable as they readily perform the photocathodic reaction and finally produced corrosive materials [1]. ZnO on the other hand is known to have the similar quality of band gap energy like TiO₂ (3.0 eV) but it is highly unstable towards pH condition, where precipitate of Zn (OH)₂ is formed on the particle surface and resulted in photocatalyst deactivation [2].

Of these, titanium dioxide (TiO₂) is the most ideal semiconductor for photocatalytic destruction of organic compounds [2, 4]. It also provides an excellent conciliation between catalytic performance and stabilization in aqueous media [5].

2. Titanium dioxide (TiO₂)

The strong oxidation and reduction power of photoexcited TiO₂ was successfully discovered by Honda-Fujishima [6, 7]. Since its innovation, extensive efforts have been made in the development of TiO₂ photocatalyst owing to its potential application in the removal of various types of organics and in both aqueous and air phase [8, 9]. It resulted in flexible applicability either in the form of a suspension, or immobilization [10–13].

Regardless the high superior photocatalytic efficiency of TiO₂, it is popular for its unique wider applications as electroceramic, antifogging agent and as therapy for cancer [14, 15]. Moreover, it also acts as an antibacterial agent due to its strong oxidation activity and superhydrophilicity and was employed for electrolysis of water (H₂O) to produce H₂ and for harvesting solar energy as dye-sensitized solar cells [16]. Additionally, it possesses superior pigmentary property, UV light absorption capability and durability [17]. The high refractive indices of rutile and anatase phase of TiO₂ laid a pathway for its versatility nature.

In general, the crystallinity, impurities, specific surface area and density of the surface hydroxy groups are the physical parameters that have influence over the photocatalytic activity of TiO₂. Apart from that the band gap energy, charge-carrier and recombination as well play a crucial role for photoactivation [18, 19]. Among the available phases the anatase is the most stable form with 8–12 kJ/mol. This describes the quantity of energy transferred during phase transformation. The rest phases such as brookite is very uncommon [14, 20–21].

In the terms of density, rutile is greater than anatase, i.e., 4.26 and 3.90 g/mL respectively. However, in terms of utilization and ability, anatase phase is more efficient due to its open structure [14]. The anatase phase remains as most active photocatalyst with greater stability after repeated catalytic cycles illuminated under a photon energy between 300 nm < λ < 390 nm [22]. In addition, it is also chemically stable in aqueous media and in broad range of pH (0 < pH < 14) [23]. Hence TiO₂ with its major anatase phase had more applicability as photocatalyst [24]. Furthermore, it also exhibits relatively high reactivity and chemical stability only under UV light (λ < 387 nm) [7]. Thus, its limited utilization of the activation energy becomes a major drawback. Therefore, to overcome this limitation of TiO₂, an extensive research needs to be emphasized to develop a titania based photocatalyst that can exhibit high reactivity under visible light spectrum (λ > 400 nm) and can persuades the utilization of solar spectrum, even under poor luminance of interior lighting [7].

The reduction in energy gap between the CB and VB further leads to the easy recombination of the formed electrons and holes. This recombination further decreases the interfacial charge-carrier transfer. The size of the TiO₂ further causes difficulties in separating them from the waste's stream. All these issues stress the reseachers to find a suitable composition/dopant for its modification [25].

3. Modification of TiO₂ photocatalyst

The photoactivity of TiO₂ is hindered by the narrow UV wavelength spectrum for photoactivation under ambient conditions. The generation of this UV requires additional power source, which shoots the activation cost of the photocatalyst. Therefore, the utilization of renewable energy source could be a better sustainable choice for the photoactivation [26].

Type	Remark	Reference
Chromium (Cr)	This is a study on the effect of the photoreduction of dinitrogen in a gas–solid regime using Cr as a dopant for phenol degradation. The prepared Cr-TiO ₂ showed an enhanced activity and displacement of the Fermi level at the TiO ₂ interface. But the presence of Cr as donor ion did not favor the charge separation with respect to pure TiO ₂ .	[34]
Iron (Fe)	Fe ³⁺ ion has a unique half-filled electronic structure which resulted in enhanced activity compared to Fe ⁴⁺ and Fe ²⁺ . The stable Fe ³⁺ ion detrapped the electron and hole to adsorbed oxygen and surface hydroxyl group, thereby suppressed the electron–hole recombinations.	[35]
	This study is about the effect of Fe doping into TiO ₂ for the degradation of chloroform (CHCl ₃). It observed that Fe provided shallow trapping sites for the charge-carriers and increase the photocatalytic efficiency. It also found that Fe can act as trap for both electron and hole, at high dopant concentration.	[36]
	This study is about the Fe-doped with TiO ₂ for the degradation of 1, 2-dichloroethane. The study proved that Fe ³⁺ alleviates the surface phenomenon and act as both electron–hole traps.	[37]
	The effect of Fe doping for the inactivation of <i>E. coli</i> was studied. The Fe-doped TiO ₂ proved the enhancement in the inactivation of <i>E. coli</i> . Fe played as a source for the inhibition of the anatase crystal growth.	[38]
Molybdenum (Mo)	The Mo as a cationic dopant was studied in 2009. The dopant increased the surface acidity of TiO ₂ and accelerated the interfacial charge transfer process. Thus, prepared doped photocatalyst degraded the cationic dyes, rhodamine B (RhB) and methylene blue (MB) and anionic dyes, methyl orange (MO) and congo red (CR) at both alkaline and acidic pH.	[39]
Zinc (Zn)	Similarly, the same group studied the effect of Zn as a dopant in 2010 and applied the prepared photocatalyst for the degradation of CR. They produced a small crystallite size and stable filled electronic configuration of Zn ²⁺ -TiO ₂ . Moreover, this photocatalyst provided a shallow trap for the charge-carriers contributing to the overall activity.	[40]
Manganese (Mn)	They further extended their study with Mn as a potential cationic dopant in 2011. From the study, it showed that Mn ²⁺ intimate contact between the mixed anatase and rutile phase of TiO ₂ . Moreover, this dopant has synergistic effects in the bicrystalline framework of anatase and rutile. The unquked half-filled electronic structure of Mn ²⁺ served as a shallow trap for the charge-carrier contributed for the appreciable degradation of both Indigo carmine dye and 4-chlorophenol.	[41]
Cobalt (Co)	Amadelli et al., 2008 studied the effect of Co-doping. They prepared the photocatalyst by incipient impregnation method and cobalt acetate as a precursor. Co addition brings about conspicuous changes in the point of zero charge and in surface polarity. They found that Co-doped TiO ₂ is more active compared to TiO ₂ . The best photocatalytic result of the prepared photocatalyst is obtained for heat treatment at 400°C for 30 min.	[42]
Thorium (Th)	Thorium a naturally occurring radioactive element was studied as a dopant in 2009. It observed that Th can contributed well for the BET surface area of photocatalyst. Moreover, the presence of two absorption edges at 460 and 482 nm in visible region enabled the photocatalyst to utilize more visible light. They reported that the strong adsorption of the pollutant was due to the complex formation between the vacant f orbital of Th ⁴⁺ . Besides, they observed that Th induced the oxygen vacancies which served as shallow traps. But thorium could further contribute for radioactive pollution.	[39]

Table 1.
Literature review of selected metal dopant/hybrid on TiO₂.

Type	Remark	Reference
Nitrogen (N)	In 2001, researchers prepared $\text{TiO}_{2-x}\text{N}_x$ by sputtering the TiO_2 selectively on N_2 (40%)/Ar gas mixture for degradation of MB and acetaldehyde (CH_3CHO) under UV/visible light.	[43]
	Researchers prepared a narrow band gap N-TiO ₂ with oxygen vacancies. Thus, prepared N-TiO ₂ failed to oxidize formate and $\text{NH}_3\text{-OH}^+$ under visible light illumination. Their preparation method resulted the N as a weak anion donor.	[44]
	This is the study about the preparation of N-TiO ₂ by thermal decomposition of the Ti^{4+} -bipyridine complex and had moderately better removal of NO_x under artificial visible light.	[45]
	The researchers prepared $\text{TiO}_{2-x}\text{N}_x$ by solvothermal route, produced violet color of particles and further calcination between 200 and 800°C produced weak violet, bright yellow, weak yellow and gray; no white color of particles. Their findings proved the thermal stability of Ti-N bonding with $\text{TiO}_{2-x}\text{N}_x$.	[46]
	N-TiO ₂ was prepared using Ti-melamine and Ti-salen complex as precursors and reported a higher photoactivity was obtained for the Ti-melamine by degrading MB degradation. The reasoned for the low photoactivity of the Ti-salen complex was due to the low amount of N doping and smaller Ti-N bonds.	[47]
	N-doped layered titanates ($\text{Cs}_{0.68}\text{Ti}_{1.83}\text{O}_{4-x}\text{N}_x$ and $\text{H}_{0.68}\text{Ti}_{1.83}\text{O}_{4-x}\text{N}_x$) with lecitroate structure was prepared and achieved better photoactivity by degrading RhB under visible light illumination. The unique layered structure of titanates and homogeneous distribution of N dopant contributed for the mobility of the charge-carrier further contributed for the faster and better photoactivity.	[48]
	Multitype N-TiO ₂ containing both substitutional (N-Ti-O and Ti-N-O) and interstitial NO characteristics was prepared. The substitutional and interstitial technique resulted in intraband states at 0.14 and 0.73 eV above the VB resulting in faster visible light driven photodegradation of gas phase toluene.	[49]
Carbon (C)	A carbonaceous coke-like species embedded in the TiO_2 matrix was obtained by pyrolysis of alcohol in the sol-gel titania processing and calcined at 250 and 400°C. The resulted C-TiO ₂ calcined at 250°C exhibited a maximum photoactivity for degradation of 4-chlorophenol (4-CP) under visible light than that the later. Further calcination to the higher temperature caused the elimination of carbon from the titania matrix. Thus, showed significance of the calcination temperature.	[50]
	A rutile TiO_2 doped with carbon was prepared by a pyrolysis method using combustion products namely CO_2 and H_2O and used for water splitting reaction. Their doping method resulted in a band gap of 2.32 eV against 3.0 eV and showed the supremacy of the preparation method.	[51]
	$\text{TiO}_2\text{-G}$ (titania-glycine) was successfully prepared through solution combustion route by glycine (G), hexemethylene (H) and oxalyldihydrazide (O) as fuel. The precursors employed contributed for the carbide ion and thus reduced band gap energy and resulted in a superior photoactivity, crystallinity and surface area. The photoactivity was successfully experimented by degrading aqueous phase MB under solar irradiation.	[52]
	$\text{TiO}_2\text{-C}$ was prepared through a simple carbon sources, which is tetrabutylammonium hydroxide ($\text{C}_{16}\text{H}_{37}\text{NO}$) and glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) as precursors. The adopted precursors contributed in two visible absorption edges in their band gap namely 2.78 and 1.45 eV, respectively.	[53]
	Park et al., 2009 showed the importance of optimum calcination temperature like Lettmann and coworkers in 2001.	[54]

Type	Remark	Reference
Fluorine (F)	The researchers chose F as an anionic dopant and obtained F-TiO ₂ via spray hydrolysis from fluorotitanic acid (H ₂ TiF ₆) precursor. Their work showed that F can excited under visible light but does not contributed for the intrinsic absorption properties rather that the extrinsic properties of TiO ₂ absorption.	[55]
Boron (B)	Boron was selected as a potential anion dopant and obtained B-TiO ₂ which resulted in wider band gap energy, larger thermodynamic and faster charge-carrier transfer.	[56]
Phosphorus (P)	Phosphorus as dopant was experimented via phosphoric acid (H ₃ PO ₄) and had higher photooxidation of <i>n</i> -pentane in air. It was due to the formation of Ti ions in tetrahedral coordination of TiO ₂ .	[57]

Table 2.
Literature review of selected non-metal dopant/hybrid on TiO₂.

Attempt to shift the optical response of TiO₂ from the UV to the visible spectrum will have a profound positive effect on the photocatalytic efficiency [27]. The visible light reception potential of these photocatalysts is either highly unstable under their illumination (e.g. CdS and CdSe) or have limited photoactivity (e.g. WO₃ and Fe₂O₃) [26]. Therefore, doping/hybridizing TiO₂ with transition metals like Fe, Co, Ni, etc. [28], non-metals like N, O, C, B, etc. [29], noble metals like Ag, Pt, Au or its metal ions incorporation [30], incorporating carbon nanotubes [31] and dyed sensitizers [32] have been proposed to improve its photocatalytic efficiency under solar light.

These modifications either by doping or hybridization are based on the concept of balancing both the half-reaction rates of the photocatalytic reaction by adding electron acceptor, or modifying the photocatalyst structure and composition [26]. The enhancement shown by doped ions is by providing charge trapping sites which leads to the reduction of electron–hole recombination [33]. In addition, the excited electron is expelled by the electron acceptors and hence hinders the recombination of electron–hole pairs [26].

In general, parameters such as types of doping/hybrid, its concentration, synthesizing technique and physico-chemical characteristics of the photocatalyst will have control over the photocatalytic activity. It was observed that the formation of both free •OH and active O₂ species is improved with the increase in charge separation efficiency [26]. The detailed literature reviews of these metals and non-metals dopant/hybrid are tabulated in **Tables 1** and **2** respectively.

4. Modification of TiO₂ with graphene oxide

The incorporation of highly conductive carbon materials can also enhance the electron–hole pair separation of the photocatalyst. Graphene oxide commonly known as GO, is one such high conductive carbon materials that can be employed as a dopant/hybrid. Graphene can be regarded as the origin of all graphitic forms and can be curled, rolled or stacked to shape buckyball fullerenes, carbon nanotubes or graphite [58–60]. With free-standing 2-dimensional (2D) crystal and one-atom thickness properties, it has emerged with wide applications in several fields but employed mostly in nanotechnology for the improvisation of materials chemistry [61]. The unique single atom-thick planar sheet of sp² hybridized carbon atoms contribute to efficient storing and shuttling of electrons [61]. Moreover, it attracted the scientific community tremendously because of its distinctive electronic properties, superior chemical stability and soaring specific surface area [61].

The exfoliated graphene sheets employ a theoretical surface area of around 2600 m²/g, and as a result graphene appears as an attractive high-surface area 2D photocatalyst support [62]. Besides it has potential ideal electron sinks or electron transfer bridges [63]. This was attributed to its exceptional structure that allow ballistic transport, in which electrons can travel without scattering at mobilities exceedingly approximately 15,000 m²/V/s at room temperature [63]. They are also foremost responsive for chemical doping, adsorbed or bound species and structure distortion [64]. Further incorporation of inorganic materials with modified graphene enormously improves their electronic, electrocatalytic and photocatalytic characteristics [32]. Thus, it proves the potential to enhance the fast electron transfer that highly benefits photocatalysis [32].

Recently modifying TiO₂ surface with carbonaceous materials propounded to induce visible-light responsive property. Few types of carbonaceous materials such as graphitic or coke-like carbon [50, 65], or carbonate structural fragments bonding with titanium were employed for this purpose. Graphene oxide supported TiO₂ is expected to create synergistic effect that enhances the solar photocatalytic activity. The synergistic effect attributes to its unique separation efficiency of electrons and holes between TiO₂ and graphene oxide [32, 66]. The photo-reductions initiated in the transformation of graphene oxide to graphene lays a platform for continuous electron conducting network through cross-surface charge percolation and permitted graphene to act as an efficient exciton sink [66].

Nguyen-Phan et al., [32] adopted a simple one-step colloidal blending method as an environmentally friendly that preserves the TiO₂ properties and combines the advantages of graphene oxide. The prepared composites showed superior adsorptivity and photocatalytic activity under both UV and visible light [32]. This was proved through a photocatalytic degradation study by adopting MB as model pollutant excited under artificial solar energy. The study indicated that graphene oxide acted as an adsorbent, electron acceptor and photosensitizer in the process of accelerating photodecomposition [32].

Recently Hu et al., 2012 also reported that graphene oxide/TiO₂ hybrid (GOT) demonstrated an excellent adsorption and photocatalysis performance under visible radiation by degrading MB dye under solar irradiation. The phenomenon was due to the electron sink in GOT that contributed for the photoactivity [67].

5. Noble metal deposited TiO₂ photocatalyst

Apart from these metals, non-metals and graphene oxide as dopant/hybrid, few reseachers have also utilized the noble metals like platinum (Pt), gold (Au) and silver (Ag) as a potential source of dopant. The expensive Pt deposition on both rutile and anatase TiO₂ was performed by Scalfani et al., 1998, Kim et al., 2002, Sun et al., 2003, Bosc and coworkers, 2006 and Hidalgo and coworkers, 2007. All their study showed that Pt had beneficial effects for the photocatalytic oxidation. The Pt as a dopant/hybrid has increased the electron mobility rate of TiO₂. This mobility has contributed for the electron transfer to the adsorbed oxygen (O⁻_{ads}) especially in rutile TiO₂. A negligible such effect was observed in the anatase phase [68–72].

Owing to the versatile potential of the Au, it was also chosen as a dopant by the reseachers [73, 74]. The study by reseachers showed that Au can behaves like a semiconductor rather than metallic. The size of Au plays a major role in the interfacial electron transfer to adsorbed oxygen (O⁻_{ads}). The Fermi level of the Au particle will

be lowered than that of adsorbed oxygen (O^-_{ads}) in TiO_2 and this depends on the particle size of Au. The Au also contributed for the hindering effect of the surface recombination. Thus, they exhibited an improvised visible light photoactivity.

Finally, the influence of Ag as a dopant/hybrid was studied by Szabo et al., 2003 and Christopher et al., 2010. Their study showed that Ag as a dopant contributed for the uniform morphology of the TiO_2 and increased the probability function of excited oxygen atoms via electron transfer from adsorbed oxygen (O^-_{ads}) produced from O_2^{2-} to the hole. The Ag also further exhibited a unique Surface Plasmon Resonance (SPR) property. Thus, exhibited SPR lowered the electron-hole recombination rate. All these potentially improvised the photoactivity of TiO_2 with a better degradation of the pollutants either under natural or artificial visible light illumination [30, 75].

6. Magnetic particles deposited TiO_2 photocatalyst

Though these noble metals dopant/hybrid had a significant contribution on the photocatalytic mechanism of TiO_2 , they are highly expensive and further increasing the cost of the prepared photocatalyst. Most of the modification techniques solve the issues of photocatalytic efficiency however, leaving behind the separation difficulty. Such separation could make them reuse and contribute for economy of the treatment cost. Most commonly these photocatalysts are nanoparticles and requires high speed centrifugation or membrane filtration. However, adopting these techniques further burdens the economy of the treatment. Hence doping/hybridizing the photocatalyst with a ferromagnetic material could be a best alternative.

Hence coating the photocatalyst with magnetic particles emerges to be a promising method to separate the photocatalyst from treated stream [76]. Nanoparticles combine with magnetic core and photoactive shell using magnetic granules and semiconductor photocatalyst is reported to possess magnetic property and separation could be achieved easily by applying simple magnetic field [77]. For these purpose magnetic cores such as magnetite (Fe_3O_4), maghemite (Fe_2O_3), nickel ferrite ($NiFe_2O_4$), etc. were chosen. Though separation of photocatalysts was achieved their photocatalytic activity was found to decrease than that of pure TiO_2 [8, 78, 79].

Beydoun et al. prepared the magnetic photocatalyst by coating TiO_2 particles onto Fe_3O_4 particles. They observed that the magnetic core was easily oxidized and suppressed the photoactivity of the TiO_2 [76, 80, 81]. Alternatively, Chen et al., 2001 prepared the magnetically separable photocatalyst by coating TiO_2 particles onto $\gamma-Fe_2O_3$ particles. Their preparation method transformed ferromagnetic $\gamma-Fe_2O_3$ to $\alpha-Fe_2O_3$ paramagnetic material and resulted in poor separation efficiency [79]. Such phase transformation from $\gamma-Fe_2O_3$ to $\alpha-Fe_2O_3$ was triggered by annealing temperature. Therefore, difficulties arise to synthesize TiO_2 coated particles with high photoactivity without loss of magnetic property by an iron oxide phase transition, as well as of high crystallinity without agglomeration, or formation of impurities by solid diffusion [9].

Chung et al., 2004 reported a TiO_2 -coated $NiFe_2O_4$ photocatalyst by multi-step ultrasonic spray pyrolysis method. Their complicated synthesise method resulted the photocatalyst in micron size. Owing to the micron size of the photocatalyst the activity and the separation efficiency declined drastically [4]. Similarly, Xu et al., 2007 prepared a magnetically separable nitrogen-doped photocatalyst, $TiO_{2-x}N_x/SiO_2/NiFe_2O_4$ (TSN) by a simple method, which consists of a $NiFe_2O_4$ as magnetic core, a SiO_2 as magnetic barrier and nitrogen as visible-light-active dopant. Their

prepared TSN was found to possess a great photocatalytic activity by removing MO in the presence of artificial UV and visible light illumination [9].

In recent years the M type hexaferrites, $MFe_{12}O_{19}$ ($M = Ba, Sr, Pb$, etc) gained interest over the spinel ferrite ($NiFe_2O_4$), since the magnetic properties of M type hexaferrites allow them to serve as highly stable permanent magnet. One such M type hexaferrites, strontium ferrite ($SrFe_{12}O_{19}$), is regarded as an excellent magnetic material [82]. There was so far no report discussed about nanoscale hexaferrites as carriers for magnetic photocatalyst before Fu et al., 2006 synthesized $TiO_2/SrFe_{12}O_{19}$ composite nanoparticles with core-shell structure. Despite the fact that the photocatalytic activity of the composite is slightly lower than that of Degussa P25, the separation of composite particles was well achieved with an external magnetic field, thus proved the separation incapability of commercial photocatalyst Degussa P25 [82].

Researches on protective layer-coated permanent magnets nanoparticles have been studied for both fundamental magnetic investigations and practical engineering applications. In such investigations, coated nanoparticles attracted the attention as the coating hinders the nanocomposites from coarsening and agglomeration. In practical engineering applications, coating works well in magnetic applications as an insulate phase to achieve high electric resistivity and behaves as a binder to ease the consolidation of the nanoparticles [18, 19].

Coating magnetic nanoparticles with silica (SiO_2) is becoming a significant topic in the research of magnetic nanocomposites. The formation of SiO_2 interlayer on the surface of magnetic nanoparticles helps to screen the magnetic dipolar attraction between magnetic nanoparticles. It also protects from leaching of the core magnetic materials during the dispersion in the aqueous phase. Moreover, SiO_2 coating could be easily activated to provide its surface with various functional groups due to the presence of abundant silanol groups in it. Finally, SiO_2 interlayer plays a very significant role in providing a chemically inert surface for magnetic layer. Hence inclusion of a protective SiO_2 coating will suppress the electron-hole recombination rate that occurs in the photocatalyst and benefits both the photo and magnetic activity.

7. Doped/hybrid TiO_2 photocatalytic mechanism

The basic mechanism of TiO_2 photocatalyst is described based on **Figure 1**, which initiated by the absorption of the photon $h\nu_1$ with energy equal to the band gap of anatase TiO_2 (3.20 eV). Electron-hole pair is produced on the surface of titania as schematized. As known, the electron from the CB is promoted and produced positive hole in VB. The excited state electrons and holes get trap in the metastable states as well as dissipate energy as heat. Besides, they also can react with the electron donor or acceptor adsorbed on its surface. Therefore, the $\cdot OH$ is produced with high oxidation potential which plays an important role in photocatalysis [1, 17].

The interstitial metal doped TiO_2 on the other hand beneficially produced the new energy level in the band gap of TiO_2 by the dispersion of metal nanoparticles in titania matrix. As shown in **Figure 1**, electron from the CB can be excited from the defect state by photon energy equals to $h\nu_2$. The improvement of the electrons trapping to inhibit the electron-hole recombination during its photoactivation as well described the additional advantageous of the metal ion doping. Thus, decreasing in the charge-carrier recombination resulted in enhanced photoactivity of the photocatalyst.

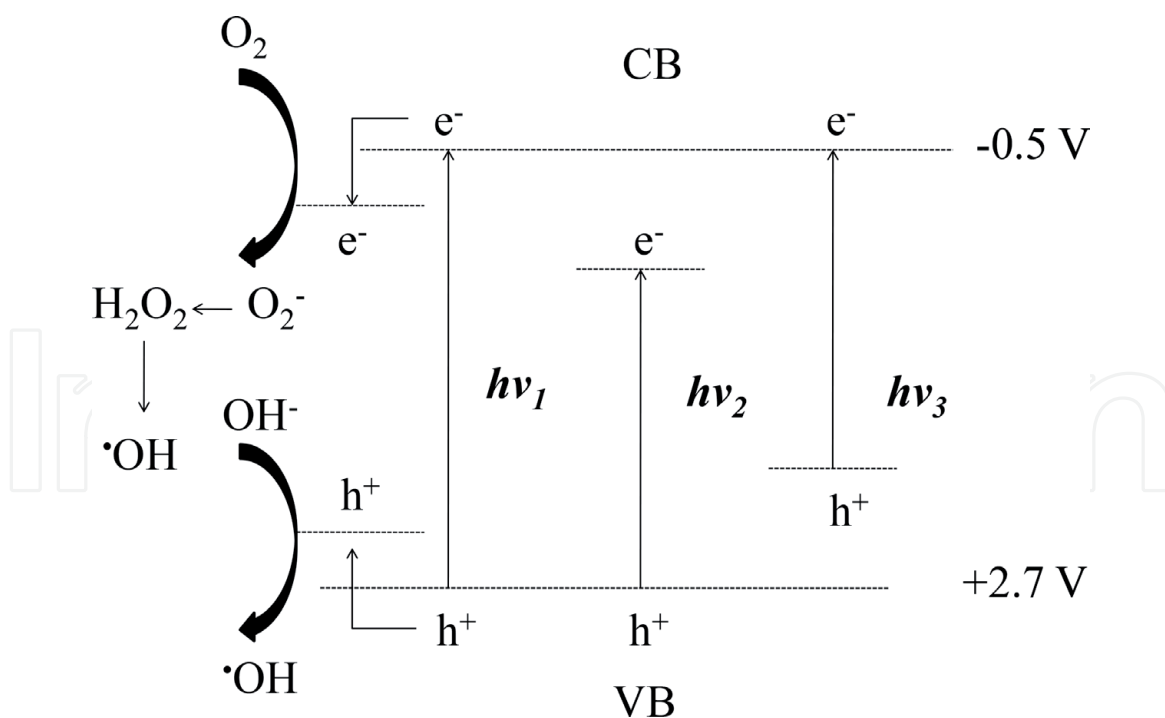


Figure 1.
 Mechanism of TiO₂ photocatalysts: $h\nu_1$: Pure TiO₂; $h\nu_2$: Metal doped TiO₂ and $h\nu_3$: Non-metal doped TiO₂ [7].

The modification of TiO₂ with the non-metal ion doping provides four main opinions regarding the changes in the nature mechanism of photocatalyst as described below [7]:

1. Band gap narrowing: Asahi et al., 2001 found that the energies of the CB and VB are very narrow during the absorption of visible light. The N 2p state hybrids with the O 2p state in anatase TiO₂ doped with nitrogen, narrowed the band gap of N-TiO₂ [43].
2. Impurity energy level: Irie et al., 2003 reported that substitutional doping of nitrogen ion into TiO₂ forms an isolated impurity energy level above the VB. Thus, obtained impurity energy level benefits the visible light driven photocatalysis as the visible light only excites electrons in the impurity energy level [83].
3. Oxygen vacancies: Ihara et al., 2003 showed the importance of oxygen deficient sites which act as a blocker for reoxidation. These sites are produced in the grain boundaries in order to emerge visible light activity.
4. Shallowing the acceptor states: Zhao & Liu, 2008 studied the shallowing effect by substitutional doping of nitrogen into TiO₂ [84].

All these obtained modification in the mechanism will contribute for the better and sustainable treatment of the organic pollutants.

8. Conclusions

Though various studies have been carried out to find an ideal semiconductor photocatalyst, TiO₂ however remains as a benchmark and active photocatalyst

among them and was proved in both laboratory and pilot studies. Other oxides such as ZrO_2 , SnO_2 , WO_2 and MoO_3 do not have the similar application prospects as TiO_2 due to the fact that these oxides are much less active, chemically and biologically instable. Several commercial TiO_2 photocatalysts are produced worldwide. Among them Degussa P25®, an amorphous TiO_2 , emerged as the best photocatalyst due to its better utilization of the UV light. It has a phase ratio of 25:75 (rutile:anatase). It is also considered as standard photocatalyst for environmental applications. The wider band gap, greater recombination of electron-hole pair and low interfacial charger carrier transfer, limit the visible light or sustainable solar energy utilization of TiO_2 photocatalyst. The limitations were successfully achieved by synthesizing a new and modified TiO_2 -based composite nanophotocatalysts through a series of simple preparation processes. The nano-size morphology of the composite photocatalysts well created the quantum effect that improved the photocatalytic properties.

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