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Photocatalytic Applications of Titanium Dioxide (TiO$_2$)

Atta ul Haq, Muhammad Saeed, Samreen Gul Khan and Muhammad Ibrahim

Abstract

Water pollution is one the fundamental problems that have got the serious concerns of the researchers. Water poluution arises due to a number of reasons including domestic, industrial, agricultural, scinec and technology. The textile industry is the main industry that releases the dyes contaminated wastewater to the environment. A varities of protocols have been attempeted for the removal of dyes from aqueous body. Photocatalysis is one of the effective techniques which offer opportunities to overcome the aqueous pollution caused by rapid industrialization and urbanization. The semiconductor metal oxides used as photocatalysts are capable to provide a sustainable and clean ecosystem due to the tunable physiochemical characteristics of semiconductor metal oxides. Titanium dioxide (TiO$_2$) is one of the metal oxides that can be effectively employed as a photocatalyst in the abatement of aqueous pollution due to organic compounds. The catalytic performance of titanium dioxide depends on several parameters like its crystallinity, surface area, and morphology. Titanium dioxide has shown good performance in the different photocatalytic systems, however, the characteristics like wide band gap and low conductivity limit the photocatalytic performance of titanium dioxide. Various attempts have been made to improve the photocatalytic performance of titanium dioxide. Herein, we summarize the various attempts to improve the photocatalytic performance of titanium dioxide in the abatement of aqueous pollution. The attempts made for the improvement of photocatalytic performance of titanium dioxide include modifications in composition, doping of other metal, and formation of heterojunctions with other metal oxides.

Keywords: Titanium dioxide, Photocatalysis, Photodegradation, Wastewater

1. Introduction

Water pollution is one the fundamental problems that have got the serious concerns of the researchers. Water poluution arises due to a number of reasons including domestic, industrial, agricultural, scinec and technology. The contribution of industrial sector in water pollution is significant. A number of industries like textile industry, leather industry, food industry, pharmaceutical industry, printing industries etc. release their wastewater to the environment. These wastewater of these industries contain a variety of organic and inorganic pollutants. Hence, the wastewater released from these induries cause water pollution. The water pollution due to dyes is very serious issue. The textile industry is the main industry that

releases the dyes contaminated wastewater to the environment. Textile industry uses a huge amount of dyes annualy. It is estimated that about 700000 tons of the various dyes are produced annualy around the world. These dyes have been classifies as azo dyes, basic dyes, direct dyes, vat dyes, reactive dyes etc. More than 15% of the globally produced dyes are released to the environment in wastewater from textile and other industries. These dyes released in aqueous system are highly toxic and carcinogeneic in nature. These dyes badly affect the living organisms. Dyes are highly colored substances that impart intense color to the aqueous body when dyes contaminated wastewater is released into it. Due to intense color of aqueous body, the sunlight is inhibited by penetration into the interior of the aqueous body. As a result of non-penetration of sunlight, the aqueous ecosysytem is badly affected by dyes [1–6].

A varities of protocols have been attempeted for the removal of dyes from aqueous body. Techniques like biological degradation technique, membrane filteration technique, adsorption atechniques, sedimentation technique, physical coagulation technique and chemical coagulation technique has been attempted for the elimination of dyes from aqueous medium. However, these techniques are not successful in the removal of dyes. As these techniques do not degrade the dyes molecules, therefore, these techniques fail to remove the dyes from aqueous medium. These techniques only transform the dyes pollutants from one form to another form. Furthermore, these techniques give rise secondary pollution [7–10]. Hence, there is an urgent need to develop effective techniques for the removal of these dyes and other organic pollutants from aqueous medium.

The advanced oxidation processes are considered as effective alternative technique for the removal of dyes from aqueous medium. Advanced oxidation processes are chemical processes which are based on production of hydroxyl radicals. These hydroxyl radicals are highly reactive spectices. These species take part in complete degradation of organic pollutants molecules. The advanced oxidation processes include heterogeneous photocatalysis, electrochemical oxidation and Fenon reactions. **Table 1** shows various advanced oxidation processes. The advanced oxidation processes have many advantages compared to conventional techniques as follows [11–13].

1. The pollutants molecules are directly converted to simple inorganic molecules like water and carbon dioxide by advanced oxidation processes.

2. The advanced oxidation processes can degradade a wide range of organic pollutant with out any selectivity.

3. There is no formation of hazardous products in advanced oxidation process as the organic pollutants are converted into simple inorganic molecules like water and carbon dioxide.

Due to the above mentioned merits of advanced oxidation processes, the advanced oxidation processes have got considerable interest of the scientists. The photocatalysis using heterogeneous metal oxide semicondutors as photocatalyst in the presence of ultra violet or visible light is one of the techniques of advanced oxidation proesses. The photocatalytic treatment of organic pollutants has got significant attention of the researchers recently. The photocatalytic technique doesnot need any extra ordinary energy requirement. Furthermore, there is no formation of hazardous by-products in photocatalysis. A large number of reports are available of photocatalytic degradation of dyes in aqueous medium. **Figure 1** shows the total number of photocatalytic reports for various dyes reported during 2000–2017.

No	AOP	Oxidatant	Benifits	Drawbacks
1	Fenton's reaction	$\cdot O_2^-$ $\cdot OH$	No formation of bromate. No off-gas treatment. Less energy-intensive than ozone and UV alone.	Maintenance costs. Works in low pH only. Requirement of Iron extraction system.
2	Photocatalyst	UV $\cdot O_2^-$ $\cdot OH$ $\cdot HO_2$	Low energy requirement than other AOPs. No formation of bromate. Use of solar irradiation. No off-gas treatment.	Requirement of pre-treatment. Loss of catalytic activity with time. Sensitivity to pH.
3	H_2O_2/O_3	UV O_3 $\cdot O_2^-$ $\cdot OH$	Higher generation of OH. More effective than O3 or UV alone. Supplementary disinfectant.	Requirement of high cost and energy. Formation of bromate. Inhibition to penetration of UV light due to turbidity. Contamination due to failure of the UV lamp.
4	O_3	O_3 $\cdot OH$	The established technique for the treatment of wastewater. Supplementary disinfectant.	Requirement ozone off-gas treatment.
5	Electron beam	e_{aq} H_2O_2 $\cdot OH$ $\cdot H$	No formation of bromate. Minimal effect of turbidity. No off-gas treatment. Can help in disinfection.	Requirement of skilled professionals. Not scalable for practical application. Energy and cost intensive.
6	Cavitation	$\cdot H$ $\cdot OH$	Less energy consumption. No formation of bromate. Low maintenance cost. No off-gas treatment.	Not scalable for practical application. Efficiency is low.
7	O_3/UV	O_3 UV $\cdot O_2^-$ $\cdot OH$	Higher production of OH than H_2O_2/UV. More effective than UV or O_3 alone.	Inhibition to penetration of UV light due to turbidity. Contamination due to failure of UV lamp. Formation of bromate. Comparatively costly.
8	H_2O_2/UV	H_2O_2 UV $\cdot O_2^-$ $\cdot OH$	No formation of bromate. No off-gas treatment is required. Can oxidize more MTBE compared to H_2O_2 or UV alone.	Inhibition to penetration of UV light due to turbidity. Contamination due to failure of the UV lamp. Absorption of UV by interfering compounds.

Table 1.
Various advanced oxidation processes.

Figure 2 shows the total number, percentage and number of reports under visible and ultra violet radiation for various dyes.

The data given in **Figure 2** shows that researchers have studidied the tiazine dyes mostly. The xanthenes dyes are at second position in the mostly investigated dyes in the subject of photocatalytic degradation.

The applications and fundamentals of photocatalysis developed tremendously during the last four decades. Photocatalysis can be defined as a reaction induced by irradiation of light in the presence of a substance called a catalyst. The photocatalytic reactions are initiated by the absorption of light having energy greater than or equal to the band gap energy of the photocatalyst. The energy difference between the highest filled energy level (valence band) and lowest vacant
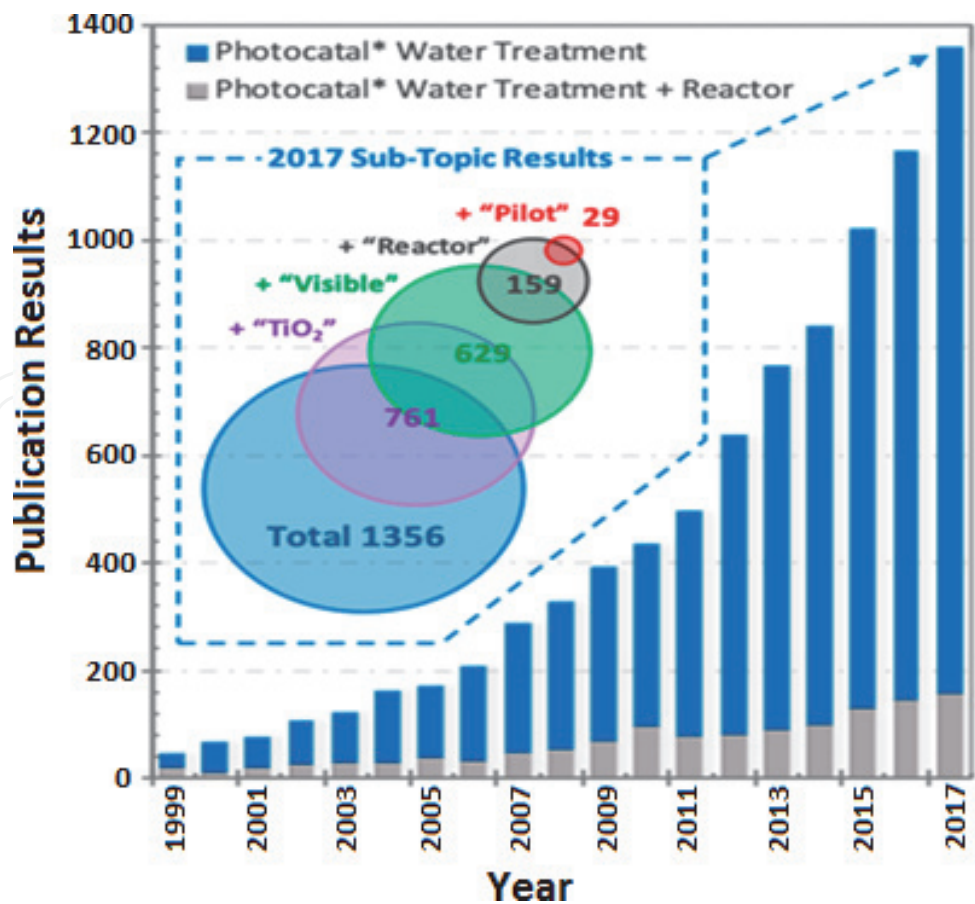
Figure 1.
Number of publications on photocatalytic treatment of wastewater. This figure is reproduced with permission from Environ. Sci. Technol. 2019, 53, 2937–2947 Copyright 2019 American Chemical Society.
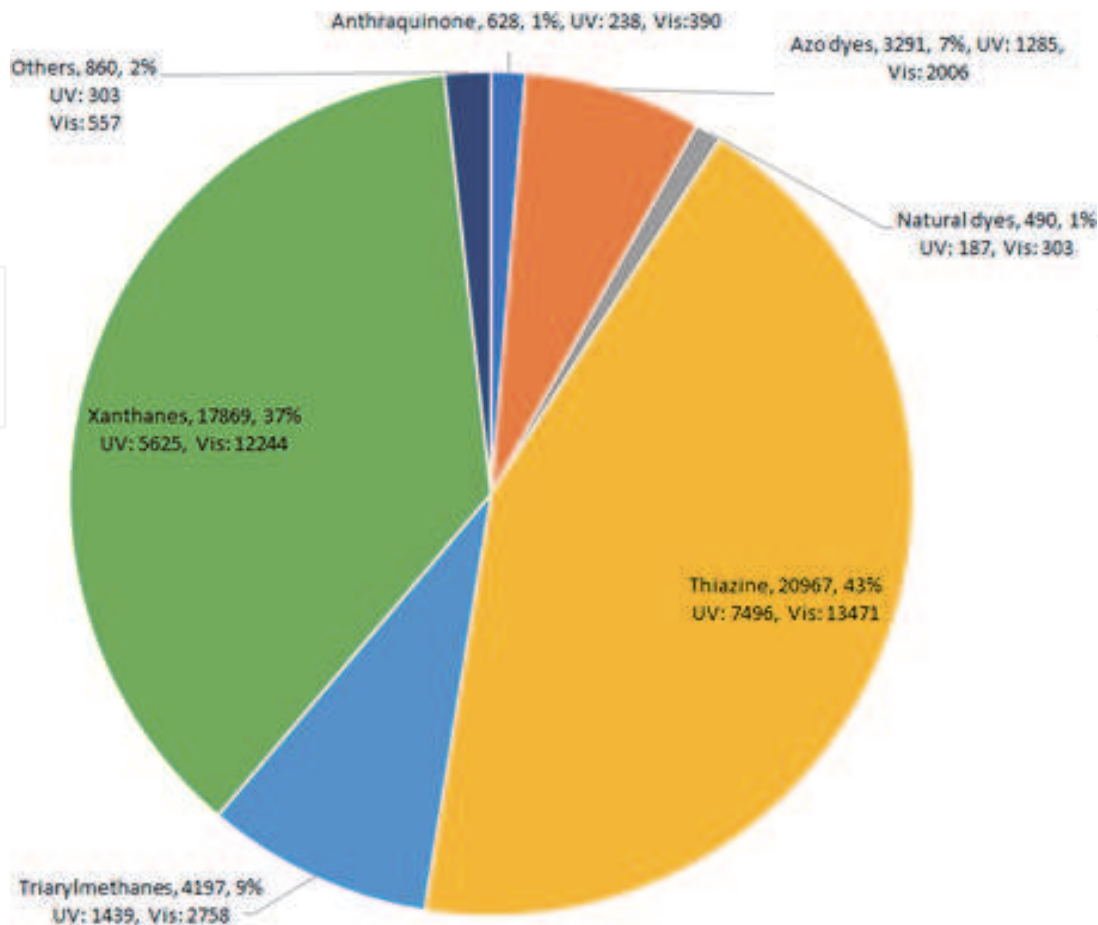

Figure 2.
Classification of available photocatalytic reports on photo catalytic degradation of various dyes.

energy level (conduction band) of photocatalytic substance is called band gap energy of the cited substance [14, 15]. The absorption of light causes the excitation of electrons from the highest filled energy level (valence band) to the lowest vacant energy level (conduction band) of the photocatalyst. This photoinduced excitation creates a positive hole (h^+) in the valence band and electrons (e^-) in conduction band of the substance. After formation of positive holes and electrons, two types of processes may proceed further.

1. The positive holes and electron recombine, and energy is released in the form of heat.

2. The positive holes and electrons take part in reactions and initiates a series of redox reactions called photocatalytic reactions.

Hence, for photocatalytic reactions, process 1 mentioned above (recombination of positive holes and electrons) must be prevented to favor the photocatalytic reactions. The goal of photocatalysis is to initiate reactions of positive holes and electrons with the reductants and oxidants to produce oxidized and reduced products, respectively [16].

Presently, photocatalysis is used in several emerging fields like photodegradation of aqueous organic pollutants, production of hydrogen by water splitting, treatment of gaseous environmental pollutants like NOx, treatment of halogenated hydrocarbon, inactivation of microorganisms, treatment of pesticides and organohalide compounds, oxidation of micropollutants and many more [17–21].

2. Titanium dioxide (TiO₂) as a catalyst

Generally, the semiconductor metal oxides are used as photocatalysts in photocatalysis. Fujishima et al., the pioneer of photocatalysis, employed titanium dioxide (TiO₂) as a catalyst for the production of hydrogen gas by splitting water for the first time [22]. Water can not be decomposed by visible light because it is transparent to it. Water can only be decomposed if it is irradiated with light having a wavelength less than 190 nm. Fujishima and co-workers electrochemically decomposed water using TiO₂ electrode. They reported that water can be electrochemically decomposed if a potential difference of 1.23 V is applied between anode and cathode. The potential difference of 1.23 V is equivalent to the energy of photons having wavelength about 1000 nm. Water can be electrochemically decomposed under any one of the following conditions.

1. The production of oxygen takes place at a potential which is more negative as compared to potential at which production of hydrogen takes place under normal conditions.

2. The production of hydrogen takes place at potential which is more positive as compared to potential at which production of oxygen takes place under normal conditions.

3. The potential at which production of oxygen takes place is made more negative and the potential at which production of hydrogen takes place is made more positive.

Fujishima and co-workers used TiO₂ electrode for electrothermal decomposition of water. They investigated the current–voltage curves under light condition and dark condition. They found that anodic current flowed under the irradiation of light

having wavelength less than 415 nm. The energy of these radiation is equivalent to 3.0 eV. This energy is equal to the band gap of TiO_2. On the basis of these observations, it was suggested that irradiation of light produced holes in the valence band of TiO_2. Similarly, the production of oxygen at -0.5 V was also confirmed by various electrochemical measurement. They constructed an electrochemical cell. The TiO_2 was used as electrode which was connected to a Pt electrode. The irradiation of surface of TiO_2 electrode caused a current to flow from Pt electrode to TiO_2 electrode. The flow of current from Pt electrode to TiO_2 electrode suggested that production of oxygen takes place TiO_2 electrode by oxidation reaction and production of hydrogen takes place at Pt electrode by reduction reaction. It was suggested irradiation caused decomposition of water in the absence of any external potential. The decomposition of water took place according to following reactions.

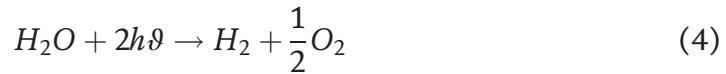1. Production of hole and electron by excitation of TiO_2

$$TiO_2 \xrightarrow{2\,h\vartheta} 2h^+ + 2e^- \tag{1}$$

1. Production of oxygen by oxidation reaction at TiO_2

$$H_2O + 2h^+ \rightarrow \frac{1}{2}O_2 + 2H^+ \tag{2}$$

1. Production of hydrogen by reduction at Pt

$$2H^+ + 2e^- \rightarrow H_2 \tag{3}$$

The net decomposition reaction is

$$H_2O + 2h\vartheta \rightarrow H_2 + \frac{1}{2}O_2 \tag{4}$$

Since the work of Fujishima et al., TiO_2 gained the attention of many researchers and presently it is the most used substance in the field of photocatalysis.

Titanium dioxide (TiO_2) exists in three crystalline phases: Brookite, Anatase, and Rutile phase. The Brookite phase of titanium dioxide is unstable and therefore it is not used in photocatalytic applications. Anatase and Rutile phases of titanium dioxide are thermodynamically stable phases. The rutile phase is mostly used in photocatalytic applications due to its easy preparation and higher catalytic performance. Studies have shown that mixed phases of titanium dioxide are used as catalysts for higher photocatalytic performances. It is believed that mixed phases titanium dioxide exhibits higher catalytic performance due to the movement of photoinduced electrons from Rutile to Anatase phase of titanium dioxide. This movement of electrons prevents the recombination of positive holes and electrons and ultimately enhances the photocatalytic performance [23–25]. However, it has also been shown that electrons move from Anatase to Rutile phase in mixed-phase photocatalysts [26]. The band gap energy of the anatase and rutile phase of titanium dioxide is 3.2 eV and 3.0 eV, respectively. Irradiation of titanium dioxide with photons havening energy equal to or greater than 3.2 eV results in the excitation of an electron from the valence band to the conduction band. This excitation results in the formation of an electron–hole pair. These photo-induced charges move to the surface of titanium dioxide and promote a series of redox reactions. The positive holes lead to the formation of vacancies in titanium dioxide as well as excite the reduced species. The photoinduced electrons produce $O_2^{\bullet}$ free radicals. These free radicals are highly reactive and unstable species, so they react further [27, 28]. This whole process can be summarized as follows.

1. Production of positive hole and electron by excitation of TiO$_2$

$$TiO_2 + Irradiation \rightarrow h^+(TiO_2) + e^-(TiO_2) \qquad (5)$$
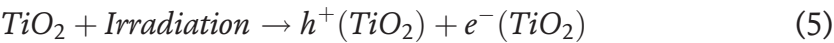
2. Recombination of positive hole and electron

$$h^+(TiO_2) + e^-(TiO_2) \rightarrow Heat \qquad (6)$$

3. Production of OH radical by oxidation of water by reaction with positive hole

$$h^+(TiO_2) + H_2O \rightarrow OH^\bullet \qquad (7)$$

4. Reduction of oxygen by reaction with electron

$$e^-(TiO_2) + O_2 \rightarrow O_2^- \qquad (8)$$

5. Production of OH radical by reaction of super oxide anion with water

$$O_2^- + H_2O \rightarrow OH^\bullet \qquad (9)$$

6. Reaction of OH radicals with reactants

$$Reactants + OH^\bullet \rightarrow Products \qquad (10)$$

The mechanism given above has been proposed based on electron spin resonance (ESR) and spin trapping studies. However, Ângelo [29] reported 82%
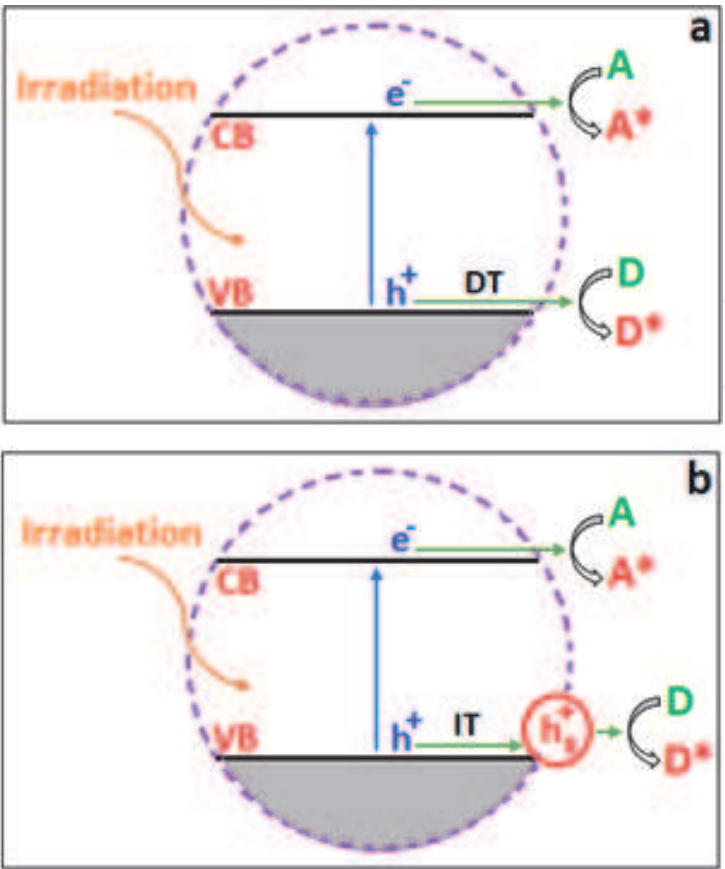

Figure 3.
Graphical representation of direct–indirect mechanism; a) direct transfer of positive holes, b) indirect transfer of positive holes.

conversion of NO for a feed containing 75% NO and 25% RH with $-20°C$ as dew point; the same work indicates that the water-adsorbed monolayer is reached for a relative humidity of 25%. If OH• were the main species in the conversion of NO, then the conversion of NO for dry feed would be much smaller. Hence, this study questions Eq. (3) in the above mechanism or otherwise the role of OH• radicals in photocatalysis. Montoya et al., [30] reported against the formation of OH• radicals by direct reaction of positive holes with water. They proposed a direct–indirect model (D-I) for titanium dioxide catalyzed reactions. The proposed mechanism is given and explained in **Figure 3**. They proposed two mechanisms for the transfer of interfacial charges.

1. In the case of stronger electronic interaction, there is a direct transfer (DT) of the photo-induced positive holes for the reactions with adsorbed species.

2. In the case of weaker interaction, there is an indirect transfer (IT) of the photo-induced positive holes. The transfer of positive holes takes place in two steps. In the first step, the positive holes are trapped by lattice oxygen of TiO_2 and generate lattice oxygen radicals. In the second step, the trapped holes are transferred to the adsorbed reactants through tunneling.

3. How to improve the catalytic performance of titanium dioxide

Although titanium dioxide has been used successfully as a photocatalyst for several reactions. However, its wide band gap (3.2 eV) limits its photocatalytic applications. Due to its wide band gap, titanium dioxide can be used as a photocatalyst under ultraviolet radiation only. The best photocatalyst is one that can be used under visible light as well as ultraviolet light because the sunlight is mainly composed of visible light. Being longer wavelength, the visible light can not excite electrons from the valence band to the conduction band of the titanium dioxide. The photocatalytic performance of titanium dioxide can be improved in two ways.

1. By prevention of recombination of photoinduced positive holes and electrons

2. By narrowing the band gap of the TiO_2

The prevention of recombination of photoinduced positive holes and electrons will permit the occurrence of redox reactions of the positive holes and electrons. These redox reactions will generate hydroxyl radicals and ultimately the photocatalytic performance will be enhanced.

The narrowing of band gap will allow the absorption of visible light by photocatalyst, so the photocatalyst will absorb a wide range of the solar spectrum. The solar spectrum consists of 47% infrared, 46% visible, and 4–5% ultraviolet light. Hence the absorption of visible light will also improve the photocatalytic performance. It has been reported that recombination of the photoinduced positive holes and electrons has a significant contribution to the photocatalytic performance of the catalysts. Most of the researchers work to develop methods and techniques to prevent the recombination of these positive holes and electrons [31–33]. The researchers have proposed that crystal structure significantly affects the photocatalytic performance of the photocatalyst as it plays a significant role in the recombination of positive holes and electrons. Hence, attempts have been made for modifications in the crystal structure to improve the photocatalytic performance of titanium dioxide.

Furthermore, the low photo conversion efficiency of the TiO$_2$ is also a challenge for the researchers. It has been reported that loss of efficiency is associated with each photo catalytic step. Due to loss of efficiency at each step, the observed photo catalytic efficiency with TiO$_2$ reported in literature is very low. This low photo catalytic efficiency of TiO$_2$ is the critical drawback associated with TiO$_2$ catalyzed treatment. Hence, the photocatalytic efficiency is expected to be low compared to other advanced oxidation processes. However, the TiO$_2$ has the ability to absorb less energetic photons. This characteristic of TiO$_2$ enable the researcher to develop TiO$_2$ based photo catalysts that can absorb light in visible region. The presence of hydrogen peroxide is not needed in visible light photocatalysis. The presenece of hydrogen peroxide is needed in other advanced oxidation processes.

4. Structural modifications of TiO$_2$

Various structural modifications in the crystal structure of titanium dioxide have been proposed for the improvement of its photocatalytic performance. All these modifications enhance the photocatalytic performance by decreasing the rate of recombination of positive holes and electrons. These modifications allow the absorption of visible light as well. Two types of structural modifications are commonly used for enhancement in the photocatalytic performance of titanium dioxide. These modifications are doping of titanium dioxide with metals or nonmetals and formation of heterojunctions with other semiconductors.

4.1 Doping

Doping is the addition of elements (impurities) into the inner structure of titanium dioxide. The doping of elements causes a red shift in the absorption of light. It also causes the prevention of recombination of photo-induced positive holes and electrons. Hence, doping improves the photocatalytic performance by absorbing of wide range of radiations and separation of charge carriers. Silver (Ag) is one of the elements used for doping of titanium dioxide. The silver (Ag) doping is used for improvement of photocatalytic performance of titanium dioxide towards photo degradation of organic pollutants [34–36]. Saeed et al., [37] have reported the improvement in photocatalytic performance of titanium dioxide for photodegradation of methylene blue and rhodamine B dyes by incorporation of silver (Ag) in the structure of titanium dioxide. They investigated the effect of silver (Ag) on the photocatalytic performance of titanium dioxide using 2, 4, 6, and 8% loading of Ag on titanium dioxide. They reported 65, 84, 97, and 78% photodegradation of methylene blue over 2, 4, 6, and 8% Ag-TiO$_2$ as a catalyst, respectively. It was found that doping of Ag enhanced the photocatalytic performance of titanium dioxide significantly. **Figure 4** shows the comparison of photocatalytic activity of TiO$_2$ and 6% Ag-TiO$_2$ for photodegradation of methylene blue and rhodamine B. The data given in **Figure 4** was obtained by performing degradation experiments with 0.1 g of Ag-TiO$_2$. A 50 mL solution of methylene blue and/or rhodamine B having concentration of 100 mg/L was used asmodel solution separately for degradation study.

It was found that higher loading of Ag decreased the photocatalytic performance of titanium dioxide. Higher loading of Ag blocks the active sites of the catalyst, therefore the photocatalytic performance decreased [38].

Similarly, Ag-TiO$_2$ with 1, 3, 5, 7, and 10% Ag have been also reported for photodegradation of methylene blue and methyl orange dyes [39]. In this study, the Ag-TiO$_2$ loaded with 5% Ag showed the highest photocatalytic performance for
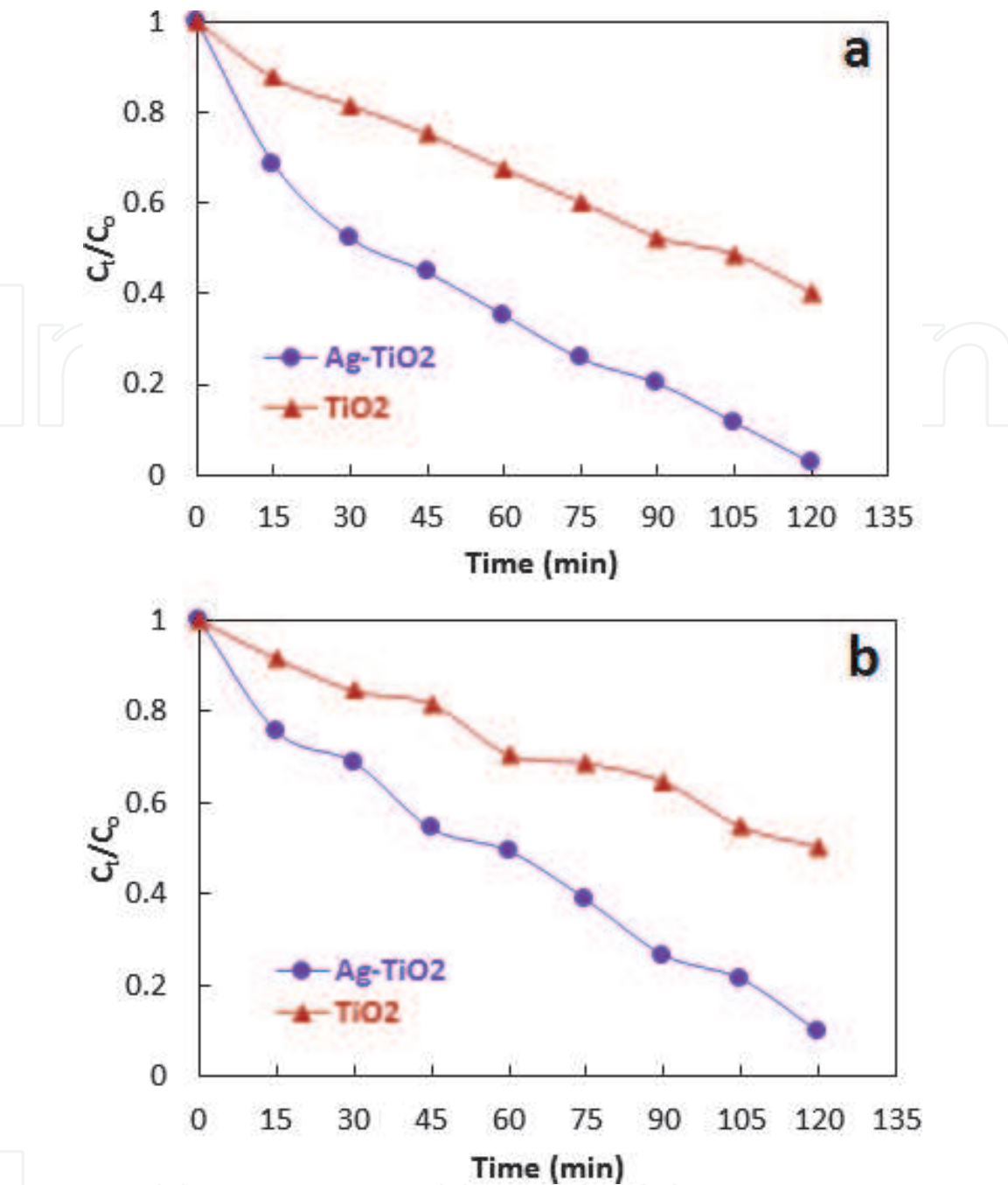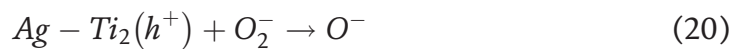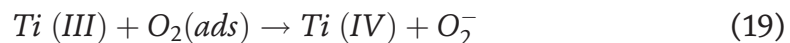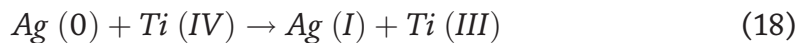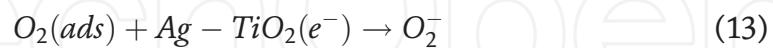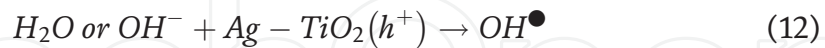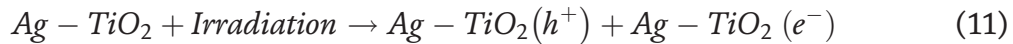
Figure 4.
Comparison of photocatalytic performance of TiO_2 and Ag-TiO_2 towards photodegradation of methylene blue dye (a) and rhodamine B dye (b) [24].

photodegradation of dyes. it was reported that doping of silver generates the surface defects by the creation of oxygen vacancies and Ti (III) sites in the structure of TiO_2. The formation of Ti (III) has been proposed by the flow of electrons from Ag to Ti (IV). The generation of oxygen vacancies leads to the formation of defect energy levels below the conduction band of TiO_2. Also, the incorporation of Ag narrows the band gap of titanium dioxide due to the formation of Ag 4 d states. These modifications favor the excitation of electrons from the valence band to the conduction band under visible light irradiations. The photogenerated positive holes and electrons flow to the surface of titanium dioxide. The positive holes initiate oxidation by reaction with H_2O or OH ions and generate reactive hydroxyl radicals (OH•). Similarly, the photogenerated electrons initiate reduction by reaction with adsorbed oxygen and give rise to super oxide anion radicals. The photo-generated positive holes are trapped by Ag as well and produce Ag (II). The Ag (II) also

initiate oxidation reactions by reaction with H$_2$O or OH ions and ultimately produce hydroxyl radicals (OH$^\bullet$). Similarly, the Ag (I) traps the photo-generated electrons and produces Ag (0) and then these trapped electrons are transferred to oxygen or Ti (IV). Hence, the recombination of positive holes and electrons is decreased and ultimately the photocatalytic performance is increased [40–44]. Chemical reactions 11 to 18 explain the whole mechanism.

$$Ag - TiO_2 + Irradiation \rightarrow Ag - TiO_2(h^+) + Ag - TiO_2(e^-) \tag{11}$$

$$H_2O \text{ or } OH^- + Ag - TiO_2(h^+) \rightarrow OH^\bullet \tag{12}$$

$$O_2(ads) + Ag - TiO_2(e^-) \rightarrow O_2^- \tag{13}$$

$$Ag\ (I) + Ag - TiO_2(h^+) \rightarrow Ag(II) \tag{14}$$

$$H_2O \text{ or } OH^- + Ag\ (II) \rightarrow OH^\bullet + Ag\ (I) \tag{15}$$

$$Ag\ (I) + Ag - TiO_2(e^-) \rightarrow Ag\ (0) \tag{16}$$

$$Ag\ (0) + O_2(ads) \rightarrow O_2^- + Ag\ (I) \tag{17}$$

$$Ag\ (0) + Ti\ (IV) \rightarrow Ag\ (I) + Ti\ (III) \tag{18}$$

$$Ti\ (III) + O_2(ads) \rightarrow Ti\ (IV) + O_2^- \tag{19}$$

$$Ag - Ti_2(h^+) + O_2^- \rightarrow O^- \tag{20}$$

$$O^- + H_2O \rightarrow OH^- + OH^\bullet \tag{21}$$

$$Pollutants + OH^\bullet \rightarrow Degradation\ products \tag{22}$$

Similarly, other elements can also be used for doping TiO$_2$. Doping of nitrogen is also one of the most studied approaches for the enhancement of photocatalytic performance of titanium dioxide. The doping of nitrogen has been used to extend the absorption of light towards the visible wavelength side. Some of the others have reported that doping of nitrogen results in narrowing of the band gap of titanium dioxide. Some researchers have argued the interaction between valance band, conduction band, and energy states of doping element cause the narrowing of band gap [13, 45, 46]. Di Valentin and co-workers [47] have reported the density functional theory (DFT) study for the evaluation of the photocatalytic performance of N-doped-TiO$_2$. They predicted that nitrogen atoms occupy either interstitial or substitutional sites in the lattice of titanium dioxide. As a result, localized energy states are generated. In the case of the interstitial position of nitrogen, discrete energy states are formed above the valence band. In the case of the substitutional position of nitrogen atoms, energy levels are formed in extension to the valence band. In the same way, the doping of other elements like carbon can also improve the catalytic performance of titanium dioxide by narrowing its band gap [48]. It has also been reported that modifications in the (101) plane of titanium dioxide take place with doping of elements. The modifications resulted from the doping of elements enhance the movement of photo-generated electrons to other places within the structure. This flow of electrons to other places increases the lifetime of photo-induced charge carriers and ultimately causes an improvement in photocatalytic performance [49].

Although the doping of elements in the lattice of titanium dioxide has been used for enhancement in the photocatalytic performance of titanium dioxide, however, these dopants may also decrease the photocatalytic performance as these dopants can promote the recombination of photogenerated positive holes and electron. Therefore, the doping of elements in high concentrations must be avoided [50].

The photo catalytic performance of TiO_2 can be enhanced by doping of iron as well. The doping ot TiO_2 with iron produces mixed oxides as well as mixture composed of mixed oxides and simple oxides. The Fe (III) and Ti (IV) have almost similar radii, therefore, Fe(III) occupies the substitutional positions. The presence of Fe (III) decrease the rate of recombination of positive holes and electrons by separating them and hence ultimately increases the catalytic performance. The Fe (III) traps the positive hole and produces Fe(IV). Then, the Fe (IV) reacts with hydroxyl ions and produce the hydroxyl radicals and O_2^- [51, 52]. The doping of TiO_2 with Fe shifts the light absorption ability towards visible light region. Under irradiation by visible light, excitation takes place (Fe(III)/Fe(IV)) to conduction band of TiO_2. By irradiation, the Fe(III) changes to Fe(IV) by absorption of visible radiation because the t2g level of d orbital of Fe(III) is above the valence band of TiO_2. The electron released from Fe(III) is shifted to conduction band of TiO_2. The shifted electron produces hydroxyl radicals by further reactions.

4.2 Heterojunction

A heterojunction is an interface that occurs between two layers or regions of dissimilar crystalline semiconductors. As stated in an earlier section that titanium dioxide is very important in photocatalysis. However, two factors limit the photocatalytic activity of titanium dioxide. These factors include the wide band gap and fast recombination of positive holes and electrons. The formation of heterojunction of titanium dioxide with other semiconductor metals oxide is also an attempt to improve the photocatalytic performance by separation of positive holes and electrons and narrowing the band gap. The synthesis of heterojunction or composite of titanium dioxide with other semiconductors has gained much attention [53]. The formation of heterojunction shifts the absorption capacity of titanium dioxide towards the visible wavelength side and thus improves the catalytic performance. Different semiconductor metal oxides can be used for the formation of heterojunction. Zinc oxide (ZnO) is one of the semiconductors that can be used for the formation of heterojunction of titanium dioxide. The zinc oxide has band gap similar to titanium dioxide and it possesses good catalytic activity. Therefore, the TiO_2-ZnO heterojunction is expected to show good photocatalytic performance under visible light irradiation [54–56]. Saeed and his coworkers [57] have reported the synthesis of ZnO-TiO_2 heterojunction as an efficient photocatalyst for the photodegradation of methyl orange. They found that photodegradation of methyl orange was 98% with ZnO-TiO_2 catalyst. The photocatalytic performance was much higher than the photocatalytic performance of ZnO and TiO_2 alone having 75 and 60% activity, respectively. **Figure 5** shows the comparison of photocatalytic performance of ZnO-TiO_2 heterojunction with pure semiconductor ZnO and TiO_2. The data given in **Figure 5** was obtained by performing degradation experiments with 50 mg of ZnO or TiO_2 or ZnO-TiO_2. A 50 mL solution of methyl orange having concentration of 100 mg/L was used asmodel solution for degradation study.

The ZnO-TiO_2 exhibited higher photocatalytic performance due to the synergistic effect between zinc oxide and titanium dioxide. This synergetic effect arises due to the formation of heterojunction. When ZnO-TiO_2 heterojunction is irradiated with light, positive holes and electrons are formed in valence band and conduction band respectively. The positive hole flows from the titanium dioxide valence band to the zinc oxide valence band. At the same time, the electrons flow from the zinc oxide conduction band to the titanium dioxide conduction band. This flow of positive holes and electrons has been explained in **Figure 6**. The flow of positive holes and electrons separates the positive holes and electrons from one another. As a result, the recombination of positive holes and electrons is suppressed. Therefore,
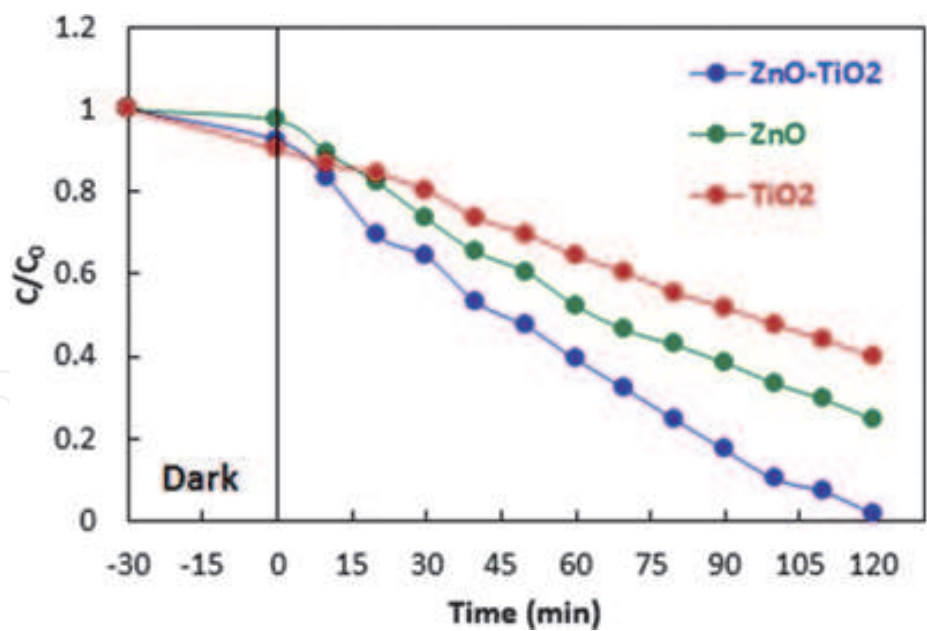
Figure 5.
Comparison of photo catalytic performance of ZnO-TiO$_2$, ZnO and TiO$_2$ towards photodegradation of methyl orange [43] (this figure has reproduced with the permission of DeGruyter).
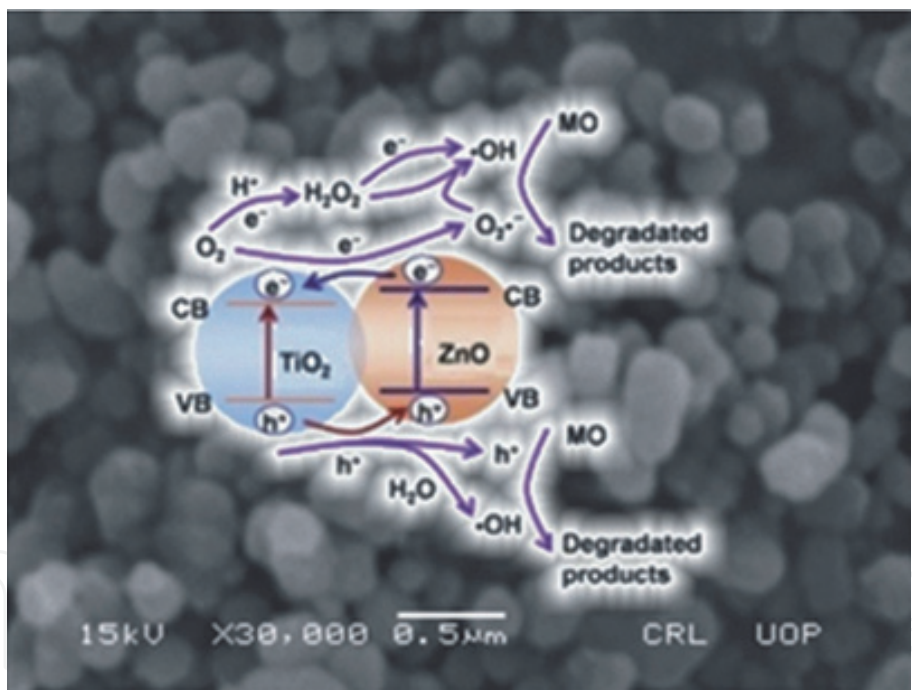

Figure 6.
Process of separation of positive holes and electrons for the improvement of photocatalytic performance towards photodegradation of methyl orange [43] (this figure has reproduced with the permission of DeGruyter).

these positive holes and electrons take proceed the redox reactions. Hence, the photocatalytic performance is increased.

Similarly, heterojunctions of titanium dioxide with other semiconductors have also been reported. For example, Abd-Rabboh and his co-workers [53] have reported the synthesis of BiVO$_4$-TiO$_2$ heterojunction as an effective photocatalyst for photodegradation of rhodamine B dye. They reported the heterojunction between BiVO$_4$ and TiO$_2$ for the production of hydrogen gas and photo degradation of rhodamine B dye. it was found that formation of heterojunction shifted that absorption of radiation by TiO$_2$ towards visible light region. The prepared heterojunction was tested as catalysts for degradation of rhodamine B dye. It was

No	Catalyst	Substrate	Comments	Reference
1	TiO_2-SiO_2	Acid Orange 7 (AO7)	TiO_2-SiO_2 was 12.3 and 2.3 times efficient than TiO_2 and P-25	[61]
2	TiO_2-zeolite	C.I. Basic Violet 10	Photodegradation followed 1st order kinetics	[62]
3	TiO_2-zeolite	Methyl Orange (MO)	TiO_2-zeolite exhibited higher performance irrespective of concentration of MO	[63]
4	TiO_2 Degussa P-25	Malachite Green (MG)	99.9% degradation achieved with 0.5 g/L catalyst, Catalytic performance was higher at pH higher than ZPC pH	[64]
5	TiO_2-graphitic carbon (TiO_2-GC)	Rhodamine B	TiO_2-GC-950 showed rate of 0.012 per min compared to rate of 0.006 per min with TiO_2	[65]
6	TiO_2-graphitic carbon (TiO_2-GC)	Phenol	TiO_2-GC-950 showed rate of 0.012 per min compared to rate of 0.008 per min with TiO_2	[65]
7	TiO_2 Degussa P-25	Triphenylmethane dye	Degussa P-25 was much active than than other TiO_2	[66]
8	TiO_2 Degussa	C.I. Reactive Red	Formation of electrons and holes by irradiation were confirmed by persulfate ions and ethaol	[67]
9	TiO_2 nanoparticles	Reactive Red	Optimum pH 3, increase in dye concentration decreased color removal	[68]
10	TiO_2-glass photoreactor	Methyl Red	TiO_2-glass photoreactor showed lower catalytic performance than TiO_2, because immobilization reduced active surface area	[69]
11	TiO_2-Carbon	Phenol	Both TiO_2-Carbon catalysts with pellet and powder carbon showed good performance	[70]
12	TiO_2 Degussa	Phenol	TiO_2 combined with hydrogen peroxide and ultra violet light showed good catalytic performance	[71]
13	TiO_2 prepared by sol–gel method	Phenol	The operating conditions significantly affected the catalytic activity	[72]
14	Commercial TiO_2	Bisphenol A (BPA)	Complete degradation achieved after 20 h under UV irradiation	[73]
15	TiO_2-MWCNTs	2,4-dinitrophenol	0.05% MWCNTs:TiO_2 was best combination	[74]
16	TiO_2-Activated carbon	2,4-dichlorophenol (DCP)	Improved catalytic performance was due to synergistic effect	[75]
17	Cerium-doped TiO_2	Phenol	The optimum doping was found as 0.4 wt %	[76]
18	Iron-doped TiO_2	Methylene blue	The optimum doping was found as 0.1 mole %	[77]
19	Vanadium-doped TiO_2	2,4-dichlorophenol and Methylene Blue	The optimum doping was found as 1 mole %	[78]
20	Bismuth-doped $TiO2$	Methylene blue	The optimum doping was found as 0.05 mole %	[79]

Table 2.
A summary of photocatalytic degradation of pollutant in the presence of TiO_2 based photocatalysts.

found that BiVO$_4$-TiO$_2$ heterojunction showed a photo catalytic performance of ten times greater than bare TiO$_2$. The rate constant for photodegradation of rhodamine B were 0.021 and 0.0023 per minute with BiVO$_4$-TiO2 and TiO$_2$ as catalyst respectively. Mousavi and Ghasemi [58] have reported TiO$_2$-CoTiO$_3$ heterojunction as photocatalyst for photodegradation of different dyes. They reported 99% photodegradation of methyl orange, methylene blue, and rhodamine b dye over TiO$_2$-CoTiO$_3$ heterojunction as photocatalyst under visible light irradiation. Another research group [59] has used TiO$_2$-Ti$_3$C$_2$ heterojunction as a catalyst for photodegradation of methyl orange with 99% performance under sunlight irradiation. CuO-TiO$_2$ heterojunction has also been reported for photodegradation of phenol with excellent photocatalytic performance [60]. Hence, it is concluded that the formation of heterojunction for titanium dioxide with other semiconductor metal oxide enhanced the photocatalytic performance of titanium dioxide.

Although a lot of literature is available on photocatalytic degradation of dyes and other organic pollutants in the presence of TiO$_2$ based photocatalysts, a summary is given in **Table 2**.

5. Conclusions

Water pollution is one the fundamental problems that have got the serious concerns of the researchers. Water poluution arises due to a number of reasons including domestic, industrial, agricultural, scinec and technology. The textile industry is the main industry that releases the dyes contaminated wastewater to the environment. A varities of protocols have been attempeted for the removal of dyes from aqueous body. Photocatalysis plays a significant role in various applications. Semiconductor metal oxides are used as photocatalysts in photocatalysis. Titanium dioxide is one of the metal oxides that has been used widely in photocatalytic applications. The titanium dioxide can be used as a photocatalyst under irradiation of ultraviolet light. The photocatalytic applications of titanium dioxide are limited by (i) wide band gap (ii) fast recombination of positive holes and electrons and (iii) activation under ultraviolet light only. Various modifications in the structure of titanium dioxide have been suggested to overcome the cited limitations. The doping of other elements in the structure of titanium dioxide and the formation of heterojunctions between titanium dioxide and other semiconductor metal oxides have been reported as effective attempts to enhance the photocatalytic performance of titanium dioxide.

Conflict of interest

The authors declare no conflict of interest.

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