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Modified Titanium Dioxide for Photocatalytic Applications

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Abstract

Titanium dioxide (TiO_2) has been widely used as a photocatalyst in many environmental and energy applications due to its efficient photoactivity, high stability, low cost, and safety to the environment and humans. However, its large band gap energy, ca. 3.2 eV limits its absorption of solar radiation to the UV light range which accounts for only about 5% of the solar spectrum. Furthermore, the photocatalytic activity of TiO_2 is also limited by the rapid recombination of the photogenerated electron-hole pairs. When used in water treatment applications, TiO_2 has a poor affinity toward organic pollutants, especially hydrophobic organic pollutants. Several strategies have been employed to reduce its band gap energy, its electron-hole recombination rates as well as enhance its absorption of organic pollutants. In this chapter, we review some of the most recent works that have employed the doping, decoration, and structural modification of TiO_2 particles for applications in photocatalysis. Additionally, we discuss the effectiveness of these dopants and/or modifiers in enhancing TiO_2 photoactivity as well as some perspective on the future of TiO_2 photocatalysis.

Keywords: titanium dioxide, photocatalysis, environmental pollution, modification

1. Introduction

The rapid growth of global population as well as industrialization has led to a concomitant increase in environmental pollution. This has very negative effects on natural elements that are vital for life on earth such as air and water. It becomes very crucial therefore to find sustainable ways to mitigate pollution in order to provide a clean and safe environment for humans. Photocatalysis has attracted worldwide interest due to its potential to use solar energy not only to solve environmental problems but also provide a renewable and sustainable energy

source. An efficient photocatalyst converts solar energy into chemical energy which can be used for environmental and energy applications such as water treatment, air purification, self-cleaning surfaces, hydrogen production by water cleavage and CO_2 conversion to hydrocarbon fuels.

Research in the development of efficient photocatalytic materials has seen significant progress in the last 2 decades with a large number of research papers published every year. Improvements in the performance of photocatalytic materials have been largely correlated with advances in nanotechnology. Of many materials that have been studied for photocatalysis, titanium dioxide (TiO_2; titania) has been extensively researched because it possesses may merits such as high photocatalytic activity, excellent physical and chemical stability, low cost, non-corrosive, nontoxicity and high availability [1–4]. The photocatalytic activity of titania depends on its phase. It exists in three crystalline phases; the anatase, rutile and brookite. The anatase phase is metastable and has a higher photocatalytic activity, while the rutile phase is more chemically stable but less active. Some titania with a mixture of both anatase and rutile phases exhibit higher activities compared to pure anatase and rutile phases [5–7]. When titania is irradiated with light of sufficient energy, electrons from the valence band are promoted to the conduction band, leaving an electron deficiency or hole, h^+, in the valence band and an excess of negative charge in the conduction band. The free electrons in the conduction band are good reducing agents while the resultant holes in the valence band are strong oxidizing agents and can both participate in redox reactions.

Titania however suffers from a number of drawbacks that limit its practical applications in photocatalysis. Firstly, the photogenerated electrons and holes coexist in the titania particle and the probability of their recombination is high. This leads to low rates of the desired chemical transformations with respect to the absorbed light energy [8, 9]. The relatively large band gap energy (~ 3.2 eV) requires ultraviolet light for photoactivation, resulting in a very low efficiency in utilizing solar light. UV light accounts for only about 5% of the solar spectrum compared to visible light (45%) [1, 10]. In addition to these, because titania is non-porous and has a polar surface, it exhibits low absorption ability for non-polar organic pollutants [10–13]. There is also the challenge to recover nano-sized titania particles from treated water in regards to both economic and safety concern [14]. The TiO_2 nanoparticles also suffer from aggregation and agglomeration which affect the photoactivity as well as light absorption [15–18]. Several strategies have been employed in the open literature to overcome these drawbacks. These strategies aim at extending the wavelength of photoactivation of TiO_2 into the visible region of the spectrum thereby increasing the utilization of solar energy; preventing the electron/hole pair recombination and thus allowing more charge carriers to successfully diffuse to the surface; increasing the absorption affinity of TiO_2 towards organic pollutants as well as preventing the aggregation and agglomeration of the nano-titania particles while easing their recovery from treated water. Several reviews have been published in recent years on the development of strategies to eliminate the limitations of titania photocatalysis [1, 19–25]. Most of these however focus on pollutant removal from wastewater, water splitting for hydrogen production, CO_2 conversion and reaction mechanisms [1, 21, 25–31]. In this chapter, we review some of the latest publications mainly covering the last 5 years, on strategies that have

been researched to overcome the limitations of TiO_2 for general photocatalytic applications and the level of success that these strategies have been able to achieve. Based on the current level of research in this field, we also present some perspectives on the future of modified TiO_2 photocatalysis.

2. Modification of TiO_2 photocatalysts

A large number of research works have been published on TiO_2 modification to enhance its photocatalytic properties. These modifications have been done in many different ways which include metal and non-metal doping, dye sensitization, surface modification, fabrication of composites with other materials and immobilization and stabilization on support structures. The properties of modified TiO_2 are always intrinsically different from the pure TiO_2 with regards to light absorption, charge separation, adsorption of organic pollutants, stabilization of the TiO_2 particles and ease of separation of TiO_2 particles.

2.1. Metal doping

Metal doping has been extensively used to advance efforts at developing modified TiO_2 photocatalysts to operate efficiently under visible light. The photoactivity of metal-doped TiO_2 photocatalysts depends to a large extent on the nature of the dopant ion and its nature, its level, the method used in the doping, the type of TiO_2 used as well as the reaction for which the catalyst is used and the reaction conditions [32]. The mechanism of the lowering of the band gap energy of TiO_2 with metal doping is shown in **Figure 1**. It is believed that doping TiO_2 with metals results in an overlap of the Ti 3d orbitals with the d levels of the metals causing a shift in the absorption spectrum to longer wavelengths which in turn favours the use of visible light to photoactivate the TiO_2.

Doping of TiO_2 nanoparticles with Li, Na, Mg, Fe and Co by high energy ball milling with the metal nitrates was found to widen the TiO_2 visible light response range. In the Na-doped sample, Ti existed as both Ti^{4+} and Ti^{3+} and the conversion between Ti^{4+} and Ti^{3+} was found to prevent the recombination of electrons and (e^-) and holes (h^+). The metal ion doping promoted crystal phase transformations that generated electrons (e^-) and holes (h^+) [33]. Mesoporous TiO_2 prepared by sol gel technique and doped with different levels of Pt (1–5 wt% nominal loading) resulted in a high surface area TiO_2 with an enhanced catalytic performance in photocatalytic water splitting for the Pt-doped samples. The 2.5 wt%Pt-TiO_2 had showed the optimum catalytic performance and a reduction in the TiO_2 band gap energy from 3.00 to 2.34 eV with an enhanced electron storage capacity, leading to a minimization of the electron-hole recombination rate [34]. Noble metal nanoparticles such as Ag [35], Pt [34], Pd [36], Rh [37] and Au [38] have also been used to modify TiO_2 for photocatalysis and have been reported to efficiently hinder electron-hole recombination due to the resulting Schottky barrier at the metal-TiO_2 interface. The noble metal nanoparticles act as a mediator in storing and transporting photogenerated electrons from the surface of TiO_2 to an acceptor. The photocatalytic activity increases as the charge carriers recombination rate is decreased.
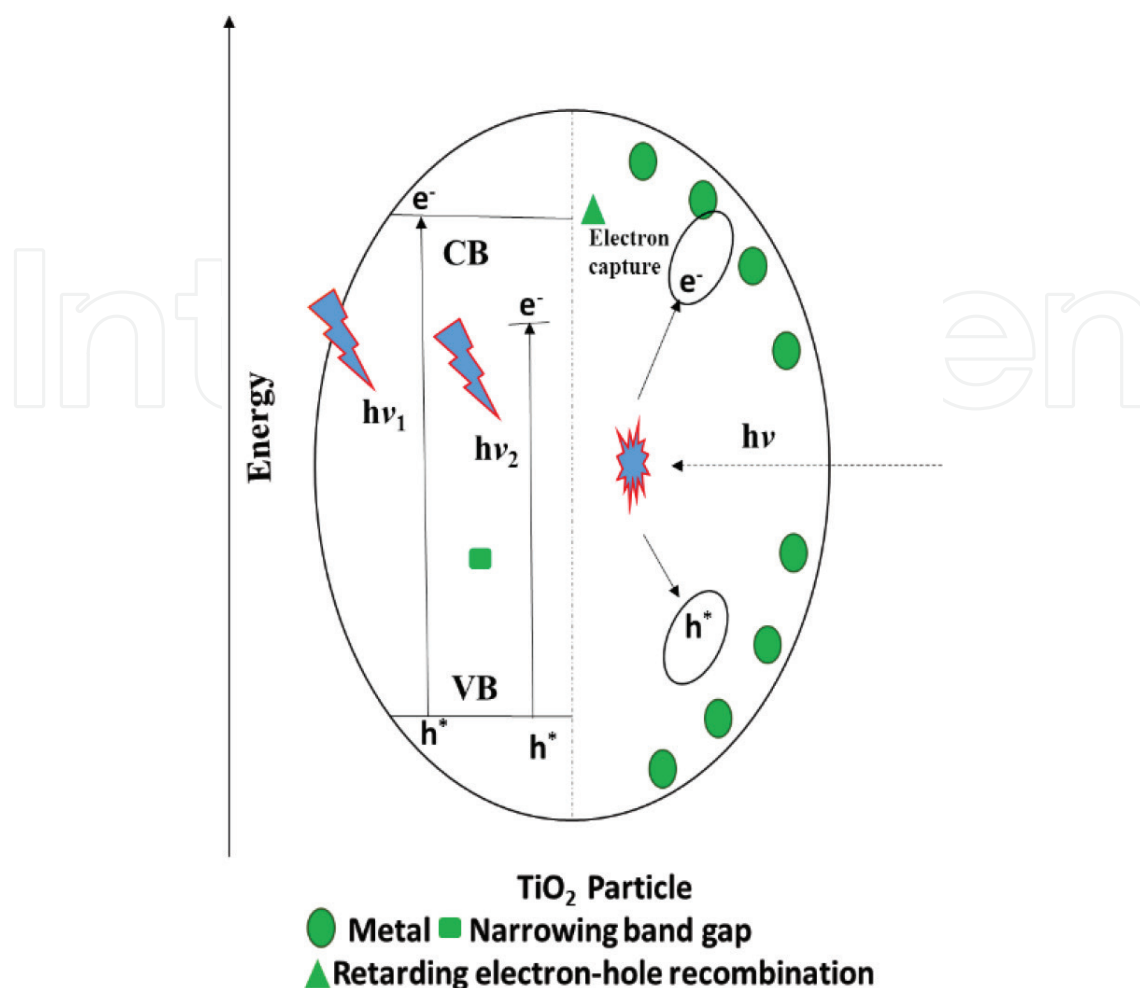
Figure 1. Band-gap lowering mechanism of metal-doped TiO_2.

In a recent review by Low et al. [21] the deposition of Au onto TiO_2 surface is reported to result in electron transfer from photo-excited Au particles (> 420 nm) to the conduction band of TiO_2, which showed a decrease in their absorption band (~550 nm) and the band was recovered by the addition of electron donors such as Fe^{2+} and alcohols. Zhang et al. [39] reported that the visible light activity of coupled Au/TiO_2 can be ascribed to the electric field enhancement near the metal nanoparticles. Moreover, numerous researchers coupled Au and Ag nanoparticles onto TiO_2 surface to use their properties of localized surface plasmonic resonance (LSPR) in photocatalysis [40]. Wang et al. [41] and Hu et al. [42] reported an improved photocatalytic performance due to the Pt nanoparticle which increased the electron transfer rate to the oxidant. It was observed that photocatalytic sacrificial hydrogen generation was influenced by several parameters such as platinum loading (wt%) on TiO_2, solution pH, and light (UV, visible and solar) intensities [43]. Moreover, complete discoloration and dye mineralization were achieved using Pt/TiO_2 as catalyst; the results were attributed to the higher Pt content of the photocatalyst prepared with the highest deposition time. For $Pt-TiO_2$ catalysts the best discoloration and dye mineralization were obtained over the catalyst prepared by photochemical deposition method and using 120 min of deposition time in the synthesis. These results may be due to the higher Pt content of the photocatalyst prepared with the highest deposition time.

Haung et al. [44] prepared Pt/TiO_2 nanoparticles from TiO_2 prepared at various hydrolysis pH values and found that the phase of TiO_2 obtained depended largely on the hydrolysis pH. The anatase/rutile intersection of a Pt/TiO_2 sample had a lower recombination rate compared to the anatase phase of Pt/TiO_2 due to the longer recombination pathway. Though, the Pt/TiO_2 anatase phase showed better degradation efficiency than the Pt/TiO_2 anatase/rutile intersection. The decrease in the anatase composition of TiO_2, and the decrease in the composition of TiO_2 resulted in the degradation rate decrease, suggesting that anatase composition in the Pt/TiO_2 system played a crucial role of increasing the photocatalytic degradation of Acid Red 1 dye.

Liu et al. [45] prepared the palladium doped TiO_2 ($Pd-TiO_2$) photocatalyst using chemical reduction method and tested it the photocatalytic degradation of organic pollutant. It was found that the TiO_2 grain size was reduced while the specific surface area increased and the absorption of ultraviolet light also enhanced after using chemical reduction method, however, all these changes had no effect on degradation of organic pollutant. But the degradation was significantly improved due to the deposition of Pd nanoparticles; the Pd/TiO_2 organic pollutant degradation was 7.3 times higher compared to TiO_2 (P25).

Repouse et al. [46] prepared a series of noble metal promoted TiO_2 (P25) by wet impregnation and found that the dispersion of the small metal crystallites on TiO_2 did not affect the optical band gap of TiO_2. The Pt-promoted catalyst exhibited the highest photocatalytic efficiency in the degradation of bisphenol A under solar irradiation. They also found the presence of humic acid to considerably improve the reaction rate of Rh/TiO_2 but had a clearly adverse effect with P25 TiO_2 photocatalyst. Fluorescence data revealed that humic acid is capable of photosensitizing the Rh/TiO_2 catalyst.

Indium-doped TiO_2 have recently been used for photocatalytic reduction of CO_2 [47]. Indium doping resulted in an increase in surface area because of suppression of TiO_2 particle growth during the TiO_2 synthesis. The light absorption ability of the $In-TiO_2$ was enhanced due to the introduction of the impurity level below the conduction band level of the TiO_2. The photocatalytic CO_2 reduction activity of the $In-TiO_2$ was about 8 time that of pure TiO_2 as a consequence of the high surface area and extended light absorption range.

The doping of TiO_2 with transition metals such as Cr [48], Co [48], Fe [48–50], Ni [48, 51], Mn [48, 52], V [53], Cu [54], Ni [51] and Zn [55], has been studied by different research groups. Numerous studies reported that doping of TiO_2 with transition metals improve the photocatalytic activity, attributable to a change in the electronic structure resulting in the absorption region being shifted from UV to visible light. The shift results from charge-transfer transition between the d electrons of the transition metals and the conduct or valence band of TiO_2 nanoparticles. Inturi et al. [48] compared the doping of TiO_2 nanoparticles with Cr, Fe, V, Mn, Mo, Ce, Co, Cu, Ni, Y and Zr and it was found that Cr, Fe and V showed improved conversions in the visible region while, the incorporation of the other transition metals (Mn, Mo, Ce, Co, Cu, Ni, Y and Zr) exhibited an inhibition effect on the photocatalytic activity. The Cr-doped TiO_2 demonstrated a superior catalytic performance and the rate constant was found to be approximately 8–19 times higher than the rest of the metal doped catalysts. It was reported that the reduction peaks in Cr-doped TiO_2 shifted to much lower temperatures, due to the increase in the reduction potential of titania and chromium. Therefore, the higher photocatalytic

efficiency of Cr/TiO_2 in the visible light can be attributed to strong interaction (formation of Cr-O-Ti bonds). Fe-doped TiO_2 nanoparticles were used in the visible light degradation of para-nitrophenol and it was found that the Fe-dopant concentration was crucially important in determining the activity of the catalyst. The maximum degradation rate of para-nitrophenol observed was 92% in 5 h when the Fe(3+) molar concentration was 0.05 mol%, without addition of any oxidizing reagents. The excellent photocatalytic activity was as a result of an increase in the threshold wavelength response as well as maximum separation of photogenerated charge carriers [49]. On the other hand, Fe-doped TiO_2 evaluated for solar photocatalytic activity for the degradation of humic acid showed a retardation effect for the doped catalysts compared to the bare TiO_2 specimens, which could be attributed to surface complexation reactions rather than the reactions taking place in aqueous medium. The faster removal rates attained by using bare TiO_2 could be regarded as substrate specific rather than being related to the inefficient visible light activated catalytic performance [50]. Ola et al. [56] reported that the properties of V doped TiO_2 were tuned towards visible light because of the substitution of the Ti^{4+} by V^{4+} or V^{5+} ions since the V^{4+} is centred at 770 nm while the absorption band of V^{5+} is lower than 570 nm. Moradi et al. [57] obtained high photocatalytic activity of Fe doped TiO_2 and studied the effects of Fe^{3+} doping content on the band gap and size of the nanoparticles. It was found that the increase in the doping content decreased the band gap energy and particle size from 3.3 eV and 13 nm for bare TiO_2 to 2.9 eV and 5 nm for Fe_{10}-TiO_2, respectively.

The rare earth metals doped TiO_2 catalyst also have good electron trapping properties which can result in a stronger absorption edge shift towards longer wavelength, obtaining narrow band gap. Bethanabotla et al. [58] carried out a comprehensive study on the rare earth doping into a TiO_2 and found that the rare earth dopants improved the aqueous-phase photodegradation of phenol at low loadings under simulated solar irradiation, with improvements varying by catalyst composition. Differences in defect chemistry on key kinetic steps were given as the explanation for the enhanced performance of the rare earth doped samples compared to pure titania. Reszczyńska et al. [59] prepared a series of Y^{3+}, Pr^{3+}, Er^{3+} and Eu^{3+} modified TiO_2 nanoparticles photocatalysts and results demonstrate that the incorporation of RE^{3+} ions into TiO_2 nanoparticles resulted in blue shift of absorption edges of TiO_2 nanoparticles and could be ascribed to movement of conduction band edge above the first excited state of RE^{3+}. Moreover, incorporated RE^{3+} ions at the first excited state interact with the electrons of the conduction band of TiO_2, resulting in a higher energy transfer from the TiO_2 to RE^{3+} ions. But observed blue shift could be also attributed to decrease in crystallite size of RE^{3+}–TiO_2 in comparison to TiO_2. The Y^{3+}, Pr^{3+}, Er^{3+} and Eu^{3+} modified TiO_2 nanoparticles exhibited higher activity under visible light irradiation compared to pure P25 TiO_2 and can be excited under visible light in the range from 420 to 450 nm. In a similar work on rare earths (Er, Yb, Ho, Tb, Gd and Pr) titania nanotubes (RE-NTs), [60] the RE^{3+} species were found to be located at the crystal boundaries rather than inside the TiO_2 unit cell and an observed excitation into the TiO_2 absorption band with resulting RE^{3+} emission confirmed energy migration between the TiO_2 matrix and RE^{3+}. The presence of the rare earth component was found to reduce recombination of the electrons and holes successfully by catching them and also by promoting their rapid development along the surface of TiO_2 nanoparticles. Lanthanide ions doping did not impact the energy gap of TiO_2 nanoparticles, however this enhanced the light absorption of catalyst. The surface range

of TiO_2 nanoparticles generally increases by La^{3+} particle doping by diminishing the crystallite size and accordingly, the doped TiO_2 nanoparticle displayed higher adsorption capacity. Based on theoretical calculations, it was proposed that during the electrochemical process, new Ho-f states and surface vacancies were formed and may reduce the photon excitation energy from the valence to the conduction band under visible light irradiation. The photocatalytic activity under visible light irradiation was attributed not to ·OH but to other forms of reactive oxygen species ($O_2\cdot^-$, HO_2, H_2O_2).

2.2. Non-metal doping

TiO_2 nanoparticles have been comprehensively doped at the O sites with non-metals such as C [61], B [62], I [63], F [64], S [65], and N [66]. Non-metal dopants are reported to be more appropriate for the extension of the photocatalytic activity of TiO_2 into visible region compared to metal dopant [67, 68]. This can be ascribed to the impurity states which are near the valence band edge, however, they do not act as charge carriers, and their role as recombination centres might be minimized [53]. As shown in **Figure 2**, the mixing of the p states of
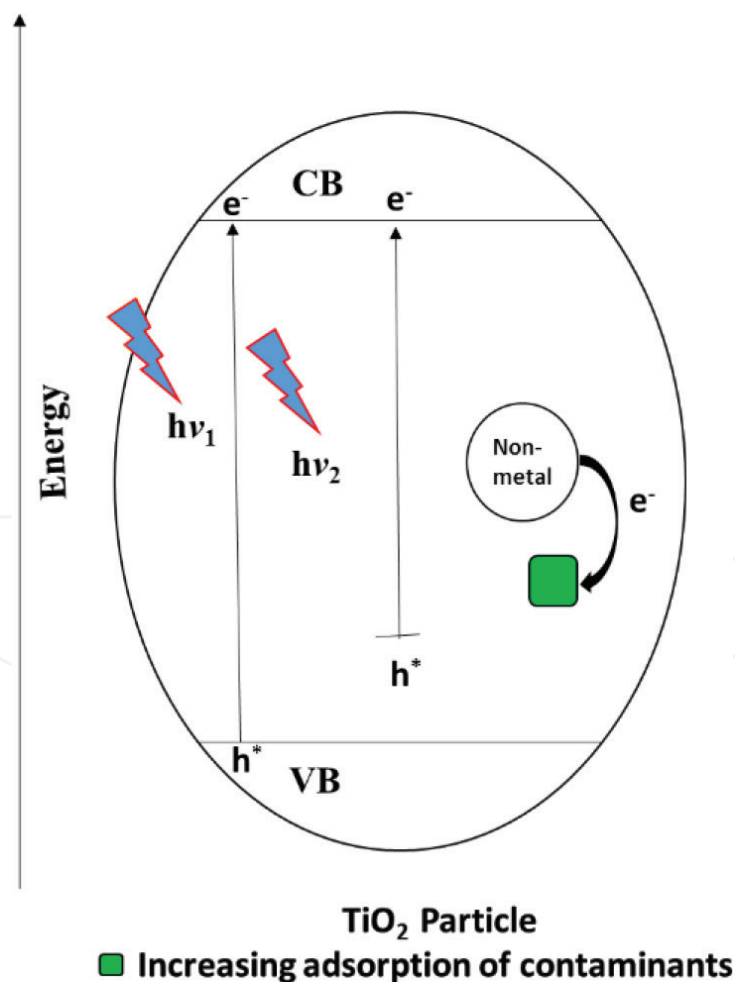

Figure 2. Band-gap energy narrowing mechanism for non-metal-doped TiO_2.

the doped non-metal with the O2p states shifts the valence band edge upward and narrows the band-gap energy of the doped TiO_2 photocatalyst. The nitrogen and carbon doped TiO_2 nanoparticles has been reported to exhibit greater photocatalytic activity under visible light irradiation compared to other non-metal dopants.

N-doped TiO_2 (N-TiO_2) appears to be the most efficient and extensively investigated photocatalyst for non-metal doping. Zeng et al. [69] reported the preparation of a highly active modified N-TiO_2 nanoparticle via a novel modular calcination method. The excellent photocatalytic performance of the photocatalyst was ascribed to excellent crystallinity, strong light harvesting and fast separation of photogenerated carriers. Moreover, the enhancement of charge separation was attributed to the formation of paramagnetic $[O-Ti^{4+}-N^{2-}-Ti^{4+}-V_O]$ cluster. The surface oxygen vacancy induced by vacuum treatment trapped electron and promoted to generate super oxygen anion radical which was a necessary active species in photocatalytic process. Phongamwong et al. [70] investigated the photocatalytic activity of CO_2 reduction under visible light over modified N-TiO_2 photocatalyst and they have found that the band gap of N-TiO_2 photocatalyst slightly decreases with increasing N content. In addition, the sub-band energies related to the impurity energy level were observed in the N-TiO_2 photocatalyst because of the interstitial N species and the sub-band gap energies were found to have decreased from 2.18 eV with 10 wt% N-TiO_2 photocatalyst. In contrast, the replacement of O by N is difficult because of the radius of N (17.1 nm) being higher compared to O (14 nm) and the electroneutrality can be maintained by oxygen vacancies, that are provided by replacement of three oxygen vacancies by two nitrogen atom [71]. N-TiO_2 photocatalyst reduces the oxygen energy vacancies from 4.2 to 0.6 eV, suggesting that N favors the formation of oxygen vacancies [72].

In contrast, O atoms (14 nm) could be substituted easily by F atoms (13.3 nm) because of their similar ionic radius [73]. Yu et al. [64] reported that the F-doped TiO_2 (F-TiO_2) is able to absorb visible light due to the high-density states that were evaluated to be below the maxima valence band, although there was no shift in the band edge of TiO_2. Samsudin et al. found a synergistic effect between fluorine and hydrogen in hydrogenated F-doped TiO_2 which enabled light absorption in UV, visible and infrared light illumination with enhanced electrons and holes separation. Surface vacancies and Ti^{3+} centres of the hydrogenated F-doped catalyst coupled with enhanced surface hydrophilicity facilitated the production of surface-bound and free hydroxyl radicals. Species present on the surface of the catalyst triggered the formation of new Ti^{3+} occupied states under the conduction band of the hydrogenated F-doped TiO_2, thus narrowing the band gap energy [73]. Enhanced photocatalytic performance of N-doped TiO_2 over pure TiO_2 has also been ascribed to efficient separation of electron-hole pairs as well as an increased creation of surface radicals such as hydroxyl The band gap can also be narrowed by doping TiO_2 with S, since replacement of S into TiO_2 can be performed easily due to larger radius of S atoms (18 nm) compared to O atoms (14 nm). S incorporation in TiO_2 has been reported to change the lattice spacing of the TiO_2 with a reduction in the band gap width from 3.2 to 1.7 eV allowing for higher photocatalytic activity [74]. N, S and C co-doped TiO_2 samples photocatalytic reduction of Cr(IV) showed that the co-doping and calcination played an important role in the microstructure and photocatalytic activity of the catalysts. The co-doped samples calcined at 500°C showed the highest activities ascribed to the synergistic effect in enhancing crystallization of anatase and (N, S and C) co-doping. The carbon doped TiO_2 (C-TiO_2) is reported to

be more active than N-TiO$_2$, therefore, C-TiO$_2$ has received special attention [75]. Noorimotlagh et al. [76] investigated the photocatalytic removal of nonylphenol (NP) compound using visible light active C-TiO$_2$ with anatase/rutile. It was found that the doping of C into TiO$_2$ lattice may enhance the visible light utilization and affect the structural properties of the as-synthesized photocatalysts. Moreover, it was reported that after C doping and changing the calcination temperature, the band gap was narrowed from 3.17 to 2.72 eV and from 2.72 to 2.66 eV, respectively. Ji et al. [61] reported the preparation of C-TiO$_2$ with a diameter of around 200 nm and the tube wall was composed of anatase TiO$_2$, amorphous carbon, crystalline carbon and carbon element doping into the lattice of TiO$_2$. The C-TiO$_2$ nanotubes exhibited much better performance in photocatalytic activity than bare TiO$_2$ under UV and visible light. The obtained results were ascribed to the C doping, which narrowed the band gap energy of TiO$_2$, extended the visible light adsorption toward longer wavelength and hindered charge recombination.

2.3. Co-doping and tri-doping

Although single metal doped and non-metal doped TiO$_2$ have exhibited excellent performance in decreasing the electrons and holes recombination, but they suffer from thermal stability and losing a number of dopants during catalyst preparation process [77]. Therefore, co-doping of two kinds of atoms into TiO$_2$ has recently attracted much interest [78]. The electronic structure of TiO$_2$ can be altered by co-doping on TiO$_2$ by formation of new doping levels inside its band gap. Abdullah et al. [77] reported that the doping levels situated within the band gap of TiO$_2$ can either accept photogenerated electrons from TiO$_2$ valence band or absorb photons with longer wavelengths. Therefore, suggesting that the TiO$_2$ absorption range can be expanded.

Zang et al. [79] evaluated the photocatalytic degradation of atrazine under UV and visible light irradiation by N,F-codoped TiO$_2$ nanowires and nanoparticles in aqueous phase. It was found that photocatalytic degradation of atrazine was higher in the presence of N,F-codoped TiO$_2$ nanowires than that of N,F-codoped TiO$_2$ nanoparticles. The higher photocatalytic performance in the presence of N,F-codoped TiO$_2$ nanowires was attributed to the higher charge carrier mobility and lower carrier recombination rate. Moreover, the speed of electron diffusion across nanoparticle intersections is several orders of magnitude smaller compared to that of nanowire because of frequent electron trapping at the intersections of nanoparticles and increasing the recombination of separated charges before they reach the TiO$_2$ nanoparticles surface. Park et al. [80] showed the best performance for novel Cu/N-doped TiO$_2$ photoelectrodes for dye-sensitized solar cells. It was found that the Cu/N-doped TiO$_2$ nanoparticles provided higher surface area, active charge transfer and decreased charge recombination. Moreover, the addition of suitable content of Cu- to N-doped TiO$_2$ electrode effectively inhibited the growth of TiO$_2$ nanoparticles and improved the optical response of the photoelectrode under visible light irradiation. Chatzitakis et al. [81] studied the photoelectrochemical properties of C, N, F codoped TiO$_2$ nanotubes. It was found that increasing surface area is not followed by increase in the photoconversion efficiency, but rather that an optimal balance between electroactive surface area and charge carrier concentration occurs.

Zhao et al. [82] investigated the photocatalytic H$_2$ evolution performance of Ir-C-N tridoped TiO$_2$ under UV-visible light irradiation. The photocatalytic activity of TiO$_2$ nanoparticles was

reported to be improved by Ir-C-N tridoped TiO_2 under UV-visible light, due the synergistic effect between Ir, C and N on the electron structure of TiO_2. It was found that Ir existed as Ir^{4+} by substituting Ti in the lattice of TiO_2 nanoparticles, whereas the C and N were also incorporated into the surface of TiO_2 nanoparticles in interstitial mode. The absorption of TiO_2 nanoparticles was expanded into the visible light region and the band gap was narrowed to ~3.0 eV, resulting in improved photocatalytic H_2 evolution under UV-visible light irradiation. Tan et al. [83] investigated the photocatalytic degradation of methylene blue by W–Bi–S-tridoped TiO_2 nanoparticles. It was found that the absorption edge of TiO_2 was expanded into visible-light region after doping with W, Bi and S and the catalytst showed the best photocatalytic activity, than that of TiO_2, S-TiO_2, W–S–TiO_2 and Bi–S–TiO_2. This might be attributed to the synergistic effect of W, Bi and S.

2.4. Nano-structured TiO_2

Amongst the various strategies that have been used to enhance TiO_2 photocatalytic activity, improvement of morphology, crystal structure and surface area have also been considered important and widely investigated approach to achieve better photocatalytic performance. The nanotitania crystallinity can simply be enhanced by optimizing the annealing temperature. However, the stability of the structure and geometries have to be considered when annealing [84]. For the nanotitania morphology and surface area, various ordered structures have been studied. TiO_2 nanotubes [85, 86], nanowires [79], nanospheres [87], etc. Tang et al. fabricated monodisperse mesoporous anatase TiO_2 nanospheres using a template material and found the resulting catalysts to show high photocatalytic degradation efficiency and selectivity towards different target dye molecules and could be readily separated from a slurry system after photocatalytic reaction [87]. Anodic TiO_2 nanotubes have been reported to allow a high control over the separation of photogenerated charge carriers in photocatalytic reactions. The nanotube array has as key advantage the fact that nanotube modifications can be embedded site specifically into the tube wall or at defined locations along the tube wall. This allows for engineering of reaction sites giving rise to enhanced photocatalytic efficiencies and selectivities [88].

2.5. Nanocarbon modified TiO_2

The design and preparation of graphene-based composites containing metal oxides and metal nanoparticles have attracted attention for photocatalytic performances. For example, Tan et al. [89] prepared a novel graphene oxide-doped-oxygen-rich TiO_2 (GO–OTiO_2) hybrid heterostructure and evaluated its activity for photoreduction of CO_2 under the irradiation of low-power energy-saving daylight bulbs. It was found that the photostability of O_2–TiO_2 was significantly improved by the addition of GO, at which the resulting hybrid composite retained a high reactivity. The photoactivity attained was about 1.6 and 14.0 folds higher than that of bare O_2–TiO_2 and the commercial Degussa P25, respectively. This high photocatalytic performance of GO–OTiO_2 was attributed to the synergistic effect of the visible-light-responsiveness of O_2–TiO_2 and an enhanced separation and transfer of photogenerated charge carriers at the intimate interface of GO–OTiO_2 heterojunctions. This study is reported to have opened up new possibilities in the development of novel, next generation heterojunction photocatalysts

for energy and environmental related applications. Lin et al. [90] also investigated photoreduction of CO_2 with H_2O vapor in the gas-phase under the irradiation of a Xe lamp using TiO_2/nitrogen (N) doped reduced graphene oxide (TiO_2/NrGO) nanocomposites. They found that the quantity and configuration of N dopant in the TiO_2/NrGO nanocomposites strongly influenced the photocatalytic efficiency, and the highest catalytic activity was observed for TiO_2/NrGO nanocomposites with the highest N doping content. Moreover, modified TiO_2/rGO demonstrated a synergistic effect, enhancing CO_2 adsorption on the catalyst surface and promoting photogenerated electron transfer that resulted in a higher CO_2 photoreduction rate of TiO_2/NrGO. Qu et al. [91] prepared the graphene quantum dots (GQDs) with high quantum yield (about 23.6% at an excitation wavelength of 320 nm) and GQDs/TiO_2 nanotubes (GQDs/TiO_2 nanoparticles) nanocomposites and the photocatalytic activity was tested towards the degradation of methyl orange. It was found that the GQDs deposited on TiO_2 nanoparticles can expand the visible light absorption of TiO_2 nanoparticles and enhance the activity on photocatalytic degradation of methyl orange under UV-vis light irradiation ($λ$ = 380–780 nm). Furthermore, the photocatalytic activity of GQDs/TiO_2 nanoparticles was approximately 2.7 times as higher than that of bare TiO_2 nanoparticles. Tian et al. [92] reported the preparation of N, S co-doped graphene quantum dots (N, S-GQDs)-reduced graphene oxide- (rGO)-TiO_2 nanotubes (TiO_2NT) nanocomposites for photodegradation of methyl orange under visible light irradiation. It was found that the S-GQDs+rGO + TiO_2 nanocomposites simultaneously showed an extended photoresponse range, improved charge separation and transportation properties. Moreover, the apparent rate constant of N, S-GQDs+rGO + TiO_2NT is 1.8 and 16.3 times higher compared to rGO + TiO_2NT and pure TiO_2NT, respectively. Suggesting that GQDs can improve the utilization of solar light for energy conversion and environmental therapy.

2.6. Immobilized TiO_2

Another drawback of TiO_2 nanoparticles mentioned above is the formation of uniform suspension in water which makes its recovery difficult, therefore hindering the application of photocatalytic in an industrial scale. As a result, many studies have attempted the modification of TiO_2 nanoparticles on support materials such as clays [93, 94] quartz [95], stainless steel [96], etc. Clays have been reported to be a significant support material for TiO_2 nanoparticles because of their layered morphology, chemical as well as mechanical stability, cation exchange capacity, non-toxic nature, low cost and availability. Therefore, TiO_2/clay nanocomposites have attracted much attention for application in both water and air purification and have been prepared by numerous researchers. Belver et al. [97] investigated the removal of atrazine under solar light using a novel W-TiO_2/clay photocatalysts. It was found that the photocatalytic activity of W-TiO_2/clay catalyst exhibited higher photocatalytic performance than that of an un-doped TiO_2/clay, which was explained by the presence of W ions in the TiO_2 nanostructure. The substitution of Ti ions with W resulted in the increase of its crystal size and the distortion of its lattice and moderately narrower band gap of photocatalysts. Mishra et al. [98] reported the preparation of TiO_2/clay nanocomposites for photocatalytic degradation of VOC and dye. They found that the photocatalytic performance of TiO_2/clay nanocomposites is highly dependent on the clay texture (as 2:1 clays show highest activity than 1:1) apart from their surface area and porosity. Moreover, the reactions involving TiO_2/Clay photocatalyst

were fast with rate constant of 0.02886 and 0.04600 min^{-1} for dye and VOC respectively than the other nanocomposites.

3. Conclusions

In this chapter, we have given an overview of the development of modified TiO$_2$ catalysts and its future prospects from a scientific point of view. We note that the field has experienced major advances in the last 5 years especially in the area of modifying TiO$_2$ with carbon nanomaterials. Based on the literature we have covered here, we believe that there is still quite a lot that can be achieved in improving the performance of TiO$_2$ catalysts for photocatalytic applications.

Conflict of interest

There are no conflicts of interest to declare.

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