Review Article

Modified titanium dioxide nanoparticles for photocatalytic splitting of waterand alternative application in environmental remediation

Abstract

Herein we reviewed Titanium dioxide (TiO_2) nanoparticles and how they are applied in the photocatalytic splitting of water to generate hydrogen but also to remove both organic and inorganic pollutants. TiO_2 has emerged as a promising photocatalyst for the efficient splitting of water into hydrogen thus acting as a sustainable and clean energy source. The efficiency of the photocatalyst can be improved by water or sacrificial agents that act as electron donors thus hydrogen production. In addition, this review explores the fundamental principles, mechanisms, and applications of TiO_2-based photocatalysis. It further, highlights the structural properties, bandgap engineering, and surface modifications that influence the catalytic activity of TiO_2. Additionally, we discuss the doping of TiO_2 with both metals and non-metals to narrow the energy band gap which lowers the recombination effects. Finally, itintroducesthe potential applications of TiO_2-based photocatalysis in the photodegradation of both organic and inorganic pollutants.

Keywords.titanium dioxide, water splitting, hydrogen, band gap, degradation

1.0 INTRODUCTION

The quest for sustainable and renewable energy sources has driven significant research into photocatalytic water splitting, a process that utilizes light energy to decompose water into hydrogen and oxygen gases[1]. To improve on the harsh climate changes that the world is experiencing and to fulfill the ever-increasing need for energy, clean, renewable energy sources have come under increased spotlight in recent years[2, 3]. The world's energy needs for a year can be met by one hour of solar energy[4]. Therefore, the most pertinent solutions to address this problem are direct solar energy capture and conversion into chemical energy through photoelectrochemical or photocatalytic processes. Traditionally, both methods depend on light gathering in semiconductor materials that have the right bandgaps to match the sun spectrum and offer high photo-conversion efficiencies. These methods have faced several drawbacks and as such are not able to replace non-renewable energy resources. The unequal electricity distribution resulting from fluctuating solar radiation and poor storage is a significant problem. The common methods of storage for the generated electricity are either electrochemical or mechanical which have serious issues associated with them.Popularly the method of storing extra power in Oceania is mechanically pumped hydroelectricity[5]. The current storage options include various batteries such as vanadium, lithium-ion, sodium-sulfur (S), etc.), supercapacitors, and hydrogen fuel cells. Hydrogen (H_2) is a cheap, non-toxic, simple in storage, and readily available energy source which is commonly applied in the long-distance transportation industry[6, 7]. The production of H_2 needs to be clean and renewable for this plan to be successful. Titanium dioxide (TiO_2) has been investigated as a photocatalytic material, and because of its exceptional stability, non-toxicity, and relative affordability, it has become a major contender.

The method known as photocatalysis has gained attention as a creative and promising approach that can transform solar energy into chemical energy[8]. Numerous uses for this method exist, including the photodegradation of toxic heavy metals and organic pollutants, hydrogen production, photoelectric detection, carbon dioxide reduction, and photodynamic therapy[9–12]. The fundamentals of semiconductor photocatalysis are illustrated in Figure 1. A positively charged hole (h^+) is created in the valence band when a photon is absorbed by the semiconductor ($hv \geq Eg$), which excites an electron from the valence band to the conduction band. To weaken or decrease the adsorbed molecules, the electron-hole pairs can move independently to the semiconductor's surface and take part in redox processes.

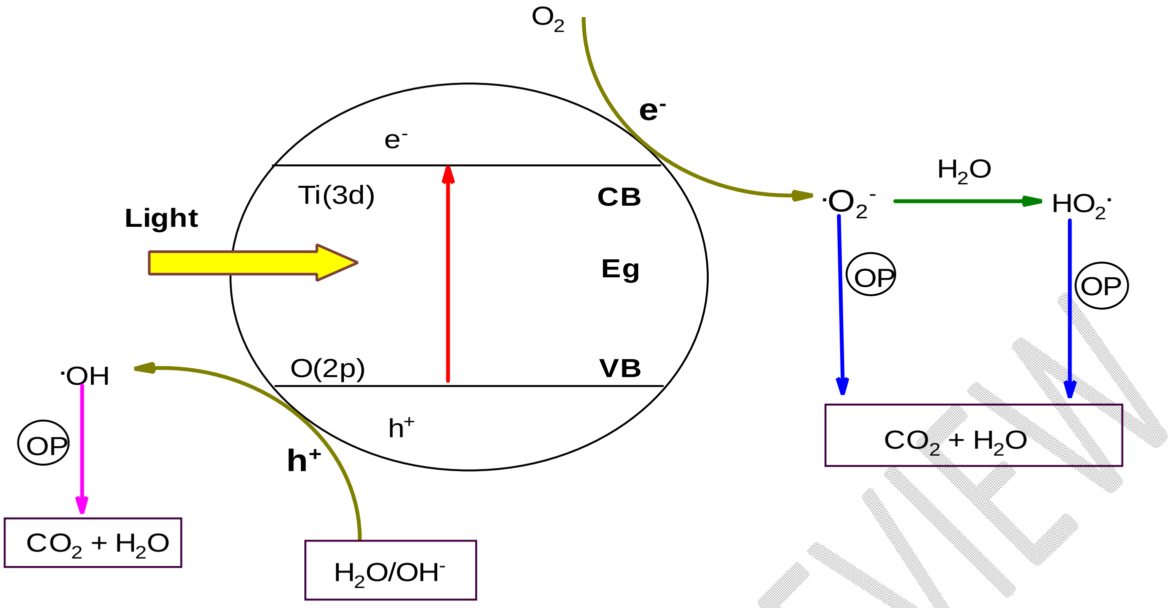

Figure 1:A diagrammatic representation of photocatalysis[13].

Since the 1970s, when water splitting garnered significant interest from academics and titanium dioxide has emerged as the foremost photocatalyst utilized. Several compelling reasons exist for this: affordability, chemical stability, abundance in the Earth's crust, and non-toxicity[14]. Nonetheless, TiO_2 possesses a broad bandgap (3.2 eV), which diminishes its capacity for visible light absorption[14]. Owing to the structural and chemical characteristics of TiO_2, it is easy to modify the bandgap thus reducing on the recombination effects, and other factors by augmenting the active sites and enhancing electrical conductivity[15]. TiO_2 manifests in several polymorphs, each exhibiting distinct behaviors. The predominant varieties include anatase, brookite, and rutile, as seen in Figure 2. Anatase and rutile TiO_2 polymorphs are predominantly utilized for water splitting;amorphous TiO_2has also been studied.

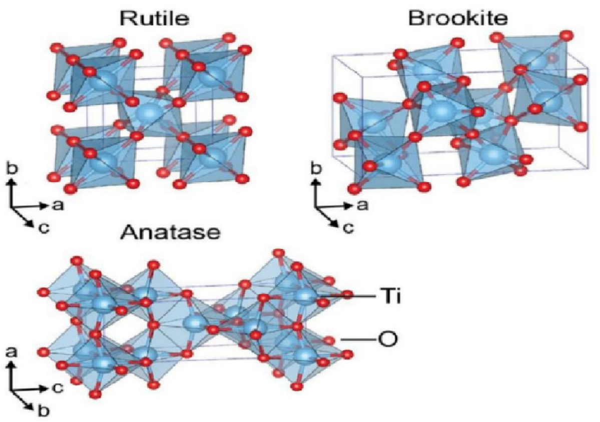

Figure 2. The crystallineforms of TiO_2 rutile, brookite, and anatase polymorphs[16].

Research has shown that varying morphologiesof a photocatalyst can lead to distinct photocatalytic characteristics [17]. Diversity may be attained using various titanium dioxide synthesis techniques [18]. The dimensions, shape, and composition of titanium dioxide may be regulated by several factors, including titanium precursor concentration, pH, temperature, treatment time, and the used chemical species.

2.0 AN OVERVIEW OF PHOTOCATALYTIC WATER SPLITTING (PWS)

Photocatalytic splitting of water results in the production of hydrogen and oxygen in the presence of a catalyst, but also resembles the natural photosynthesis process. Figure 3 presents a schematic representation of the principal steps in the photocatalytic water-splitting process.

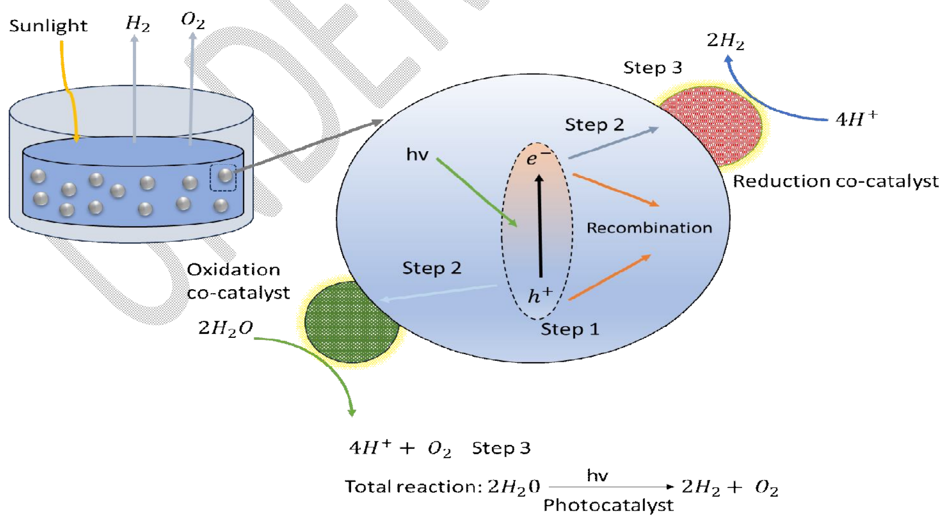

Figure 3. Photocatalytic splitting of water and the steps followed.

Initially, electron-hole pairs are produced during irradiation which causes the semiconductor to promote electrons from the valence band (VB) to the conduction band (CB) The second stage involves the separation of charges and the migration of photogenerated electron-hole pairs. Optimally, all electrons and holes should arrive at the surface without recombination to enhance the photocatalyst's efficiency. In the last step of equation (3), electrons transition from the conduction band to the catalyst surface, participating in a reduction process to produce hydrogen, while holes migrate from the valence band to the photocatalyst surface, engaging in an oxidation reaction to generate oxygen. The catalyst's efficiency can be improved by using dopants or co-catalysts, including metals or metal oxides like Pt, NiO, and RuO_2, which serve as active sites by improving electron mobility[19]:

3.0 THE BASIC MECHANISM OF HYDROGEN PRODUCTION

The process of water splitting involves several electrons, as demonstrated by the following Equation 1:

$4H^+_{(aq)} + 4e^- \rightarrow 2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)} \rightarrow O_2$………………………………………………...(1)

One hydrogen molecule (H_2) from water requires 2.458 eV of energy and 1.229 V of potential[20]. As seen in Figure 4, Stages one, two, three, four, and five of the process are light irradiation, electron absorption, (e^-/h^+) migration, and half-reactions of reduction and oxidation (stages 6 and 7)[21].

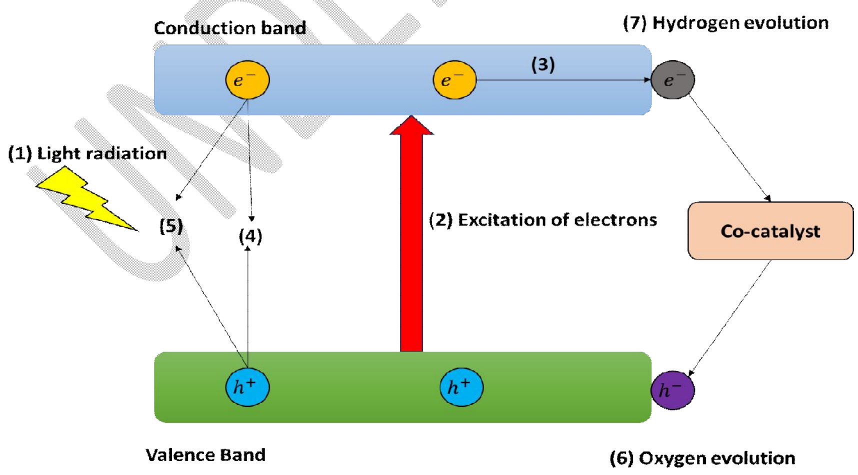

Figure 4. A representation of the steps that occur during photocatalysis on hierarchical surfaces.

The photocatalyst's shape influences light absorption in the first stage, and hierarchical order macroporous or mesoporous structures can improve light absorption (owing to the scattering effect). Wang et al. conducted research in this field and created hierarchical meso-/macroporous TiO_2 nanostructures (HOMMTs). They discovered that the HOMMTs exhibit strong photocatalytic effectiveness, presumably because of their huge surface area and ordered mesopores (11 nm) coupled to macrospores (470 nm–1350 nm)[22]. The semiconductors' electronic structures are related to their electronic excitation (stage 2). Zhu and Zäch revealed that the bandgap divides semiconductors' valence bands (VB) from their conducting bands (CB)[23]. A semiconductor bandgap larger than 1.23 eV is required for water splitting. Consequently, (e^-/h^+) pairs are formed by irradiating TiO_2 with energy larger than bandgap energy (Eg) and transferring electrons to CB, which creates positive holes in the valence band [Eq. (2)]. Two unfavorable stages pertaining to (e^-/h^+) recombination occur as a result of charge separation (stage 3), namely in the bulk (stage 4) and at the surface (stage 5).Lastly, unrestricted movement of photoexcited electrons and holes allows for semiconductor absorption. An internal energy level equilibrium is produced by the CB's lower relaxation time relative to the time needed to traverse the bandgap[25]. To initiate photoreduction [Eq. (3)] and photooxidation reactions [Eq. (4)], co-catalysts can trap only the e^- and h^+ that are transferred to the semiconductor surface. These are represented by stages (6) and (7), respectively.

Formation of (e^-/h^+) pairs Catalyst → Catalysts(e^-/h^+), (2)
Half of the reduction process is $2e^- + 2H^+ \rightarrow H_2$, (3)
Half-reaction of oxidation: $H_2O + h^+ \rightarrow O_2 + 2H^+$ (4)

The type of radiation that is transmitted through a semiconductor and its bandgap determine its performance. Table I shows the bandgaps of common photocatalysts. A semiconductor is said to be UV active if its bandgap is more than 3.15 eV and active to visible light if it stays below 3.15 eV since the wavelength of the absorbed light decreases with bandgap widening. The bandgap width must be between 1.23 to 3.26 eV in order to maximize photocatalytic activity, and the photocatalysts' bandgap limitations must contain the potential for reduction and oxidation processes.

Table 1. Energy band gap values of a number of photocatalysts.

Semiconductor	**CB**	**VB**	**E_g(eV)**	**References**
TiO_2 (anatase)	−0.5	2.7	3.2	[26]
$SrTiO_3$	−0.61	2.59	3.20	[27]
Cu_2O	−1.16	0.85	2.1	[28]
CdS	−0.9	1.5	2.4	[29]
SiC	−0.46	2.34	2.80	[30]
g-C_3N_4	−1.3	1.4	2.7	[31]
WO_3	−0.1	2.7	2.8	[32]

Phoon et al. conducted research in this field and found that the valence band should have a more positive value than the oxidation potential (+0.82 eV at NHE scale in a medium of pH 7), while the conduction band should have a more negative value than the cathodic potential (−0.41 eV at the NHE scale in a medium of pH 7)[33]. Lower CB value semiconductors lessen their ability to reduce and improve their combination with other more negative CB semiconductors. They also make it easier for electrons to go from one semiconductor to the next, which reduces H^+ to H_2 without (e−/h+) pair recombination[34].

4.0 HYDROGEN PRODUCTION WITH SOLAR ENERGY

The predominant sources of commercial hydrogen generation are oil, coal, natural gas and electrolysis. The global hydrogen generation percentage is as follows; steam reforming 48%, coal18%, electrolysis 4%, and oil 30% [35]. The initial three hydrogen generation methods are energy-intensive and reliant on non-renewable energy sources, rendering them undesirable for environmental conservation and climate change mitigation [36, 37]. Nonetheless, hydrogen creation by electrolysis necessitates just water and electrical current. To generate environmentally friendly green hydrogen, we suggest utilizing renewable energy sources like solar, hydro and windto provide the electricity required for water electrolysis. Energy from the sun is optimal because of the substantial influx of energy. Various functional approaches are employed in the electrolysis process, including thermochemical water splitting [38], photo-biological water splitting [39], and photocatalytic water splitting [40]. Moreover, photocatalytic water splitting (PWS) is regarded as the optimal choice for several reasons[40–42]:

i. PWS exhibits high solar-to-hydrogen conversion efficiency,
ii. it incurs low production costs,
iii. the separation of oxygen and hydrogen during the PWS process is straightforward, and
iv. hydrogen electrolysis is applicable in both small- and large-scale facilities

4.1 Alternative approaches that improve the photocatalytic generation of H_2

Enhancing photocatalysts' visible light activity toward water splitting is the primary goal of modification. There are several methods for modifying photocatalysts, which are outlined in sections

4.1.1 Chemical supplements (excess electron donors)

According to Guo and Ma, the addition of electron donors, to titanium dioxide can improve photocatalysis because the holes created by photogenerated light create are filled by the sacrificial reagents, by increasing the excited electrons on the catalyst surface, which facilitates the synthesis of hydrogen from protons[20]. Nada et al. conducted an experiment whereby they tested a variety of sacrificial agents for the formation of H_2 and reported their results in the following order: EDTA > methanol > ethanol > lactic acid[43]. Chen et al. observed, based on this reaction series, that the sacrificial reagent structures influence the rate of hydrogen generation, which may be accelerated by the presence of α-H next to the OH groups[44]. According to Police et al., glycerol with five α-H atoms creates more hydrogen than ethanol with two α-H atoms[45]. Inorganic ions like IO_3^-/I^-, which serve as sacrificial reagents for photocatalytic H_2 generation, have been studied by Ni et al. and Abe et al. Their studies' outcomes demonstrate an increase in H_2 production when the I^-ions (electron donor) fill the holes created in VB and make CB excited electrons available for the generation of hydrogen[46, 47].

4.1.2 Doping with ions

An essential tactic for adjusting the energy bandgap of TiO_2 for photocatalytic hydrogen generation is by doping with cationic metals at Ti sites (e.g., Co, Fe, Mn, Cr, Au, Pt, Ag, V, and Ni) and anionic non-metals (e.g., S, C and N) at O sites. Dopants have been shown to improve (e^-/h^+) migration and separation, according to Khairy and Zakaria. Because modified titania with dopants give more active site sites on the surface of TiO_2, they shift optical absorption to longer wavelengths, requiring a minimal overpotential for the creation of hydrogen[48].

4.1.2.1 Doping of TiO_2 with metal cations.

The best way to improve electron-hole separation is now to put metal onto the surface of TiO_2[49]. The formation of acceptor levels at the conduction band and donor levels at the valence band is a result of doping TiO_2 as shown in Figure.

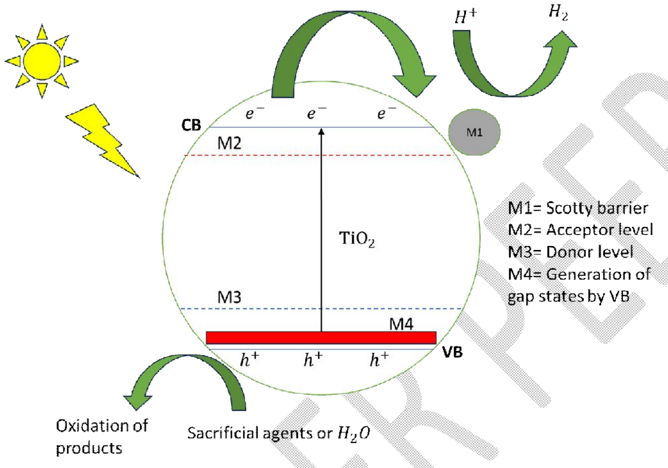

Figure 5. Mechanistic insight into the pathways for metal-doped TiO_2.

As a result, the bandgap energy is lowered and photocatalyst activity is increased. Through the Schottky barrier, photoelectrons may readily migrate from TiO_2 to the metal in the role of the metal acting as an electron sink.

Numerous transition and noble metal oxides of Au, Fe, Pd, Cu, Ag, and Pt have been studied recently. A straightforward comparison of the efficiency of hydrogen production with and without a catalyst makes evident how important a catalyst is for improving water splitting. Noble metals (such as Pt, Au, and Ag) are among the most effective metallic dopants for producing H_2 because of their large surface plasmon bands, which allow them to extend the photocatalytic activity into the visible range[34]. It is noted that the photoelectron moves from the metal to the TiO_2 CB, enablingefficient reduction at the semiconductor's surface. Doping titania with transition metals is thought to be an efficient way to boost its performance, much like with noble metals. Ni et al. reported that the varying impacts of metal ions on photocatalyst activity are related to their disparate electron/hole migration pathways[46]. Cu was shown to be an efficient co-catalyst for photocatalysis by Allen et al. among a range of metal doping possibilities for TiO_2. Cu is 100 times less expensive than noble metals because of its great abundance in the crust of the Earth[50]. Furthermore, cupric ions have been shown by Zuas and Budiman to be able to capture e− and h+ and create additional energy levels at the VB and CB of TiO_2[51].

Because transition metals' optical characteristics are nearly identical to those of noble metals, they have also recently been used as plasmonic materials for photocatalytic processes[52].50. But compared to noble metals, transition metals have higher plasmon resonance and chemical stability, which leads to a greater electron transfer into titania's conduction band. There are two types of transition metal oxides. Ti, Sc, and Nb are examples of early transition metals with vacant d orbitals. Thus, 2p oxygen orbitals have a considerable effect on their valence band. Consequently, these metals have large bandgaps and exhibit poor photocatalytic activity in contrast to late transition metals (e.g., Mn, Fe, Co, and Ni) that have tiny bandgaps and occupied d orbitals. According to Jaafarzadeh et al., Fe^{3+} is regarded as a suitable dopant among the doping transition metal ions because of its partially filled 5d orbitals[53]. In contrast, plasmon absorption characteristics of CuO and Ni_2O_3 make them attractive candidates for use as photocatalysts in the presence of visible light[54].

Photocatalytic hydrogen production is also influenced by light irradiation. Zhang et al. have established that electron transfer is very reliant on light irradiation. For example, Au–TiO_2 exhibits two opposing processes: (i) the TiO_2 to Au electronic transition under UV light irradiation, and (ii) the Au to TiO_2 electronic transition under visible light irradiation[55]. Comparing the total amount of H_2 created from various radiations, Liu et al. discovered a higher rate of hydrogen synthesis from UV-visible irradiation[56].The boost may be attributed to surface plasmon resonance and Schottky barrier creation working together synergistically.

4.1.2.2 Doping of non-metal ions to titania

Using anionic non-metals for doping can also be used to reduce semiconductor bandgaps. Regarding this, Chen et al. revealed that non-metal doping results in a hybrid 2p level between the TiO_2's valence and conduction bands[57]. Electrons in TiO_2 are shifted from the VB band to the intermediate 2p band by visual radiation as shown in Figure. Different non-metals are used in the doping of TiO_2 and the common ones are Boron (B), Fluorine (F), Carbon (C), Nitrogen (N), and Oxygen (O).

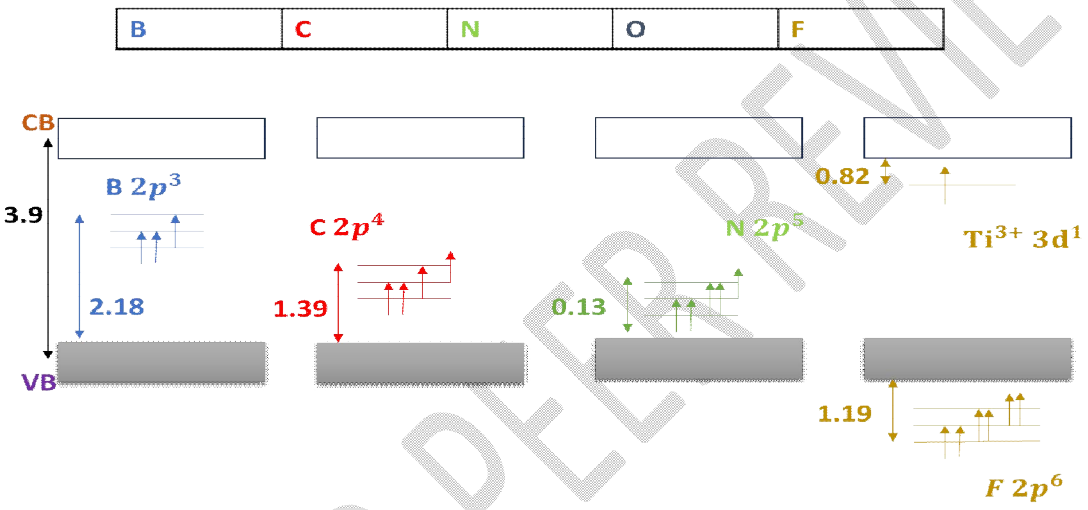

Figure 6. A schematic representation of non-metal doping and how it influences the band gap.

Non-metal doping is observed to introduce a band just above the valence band which is responsible for the absorption of light in the visible range due to the fast excitation of the electrons to the conduction band [58].

4.1.2.2.1 Modification of $TiO_2$with carbon-based materials

TiO_2's optical absorbance may be shifted into the visible spectrum by non-metal doping[59, 60]. Lately, carbon-doped TiO_2 has received a lot of attention.Etacheri et al. [61]have demonstrated that the introduction of a new state by the substitution of carbon atoms in the TiO_2 photocatalyst is what causes the observed visible light activity (C 2p) near the valence band of TiO_2 (O 2p). A large active surface area is one of the key components of C-doped TiO_2's increased photocatalytic activity. Several studies focused on TiO_2/carbon nanotube (CNT) nanocomposites[62, 63]. Because of its unique hollow design, strong adsorption capabilities, superior electrochemical stability, and high surface-to-volume ratio, carbon nanotubes (CNTs) are considered extraordinary materials. Its remarkable capacity for charge transfer reduces the recombination of electron-hole pairs in TiO_2[62, 64]. When paired with TiO_2, single-walled carbon nanotubes (SWCNTs) have shown a synergistic effect in increasing photoactivity. On the other hand, earlier studies have demonstrated that multi-walled carbon nanotubes (MWCNTs) can increase the photoactivity of TiO_2 generated by visible light by acting as a photosensitizer and promoting charge transfer in the MWCNT-TiO_2:Ni composites.

Graphene has high mechanical strength, high electron mobility, large specific surface area, and excellent heat conductivity. Because of its properties, graphene is a great option for increasing TiO_2 photoactivity[65]. Previous studies have shown that graphene enhances electron transport and prevents electron-hole pair recombination. According to their research, using a graphene-TiO_2 composite with a low amount of graphene inhibits TiO_2 agglomeration, maintaining a higher surface area and increasing the number of active sites available for pollutant degradation. Various metal and non-metal ions were added to graphene-TiO_2 composites to increase TiO_2's visible-light photocatalytic activity[66, 67].

5.0 APPLICATIONS OF TIO_2 AS A PHOTOCATALYSIS

A global challenge is the growing need for clean water resources, which is being fueled by rapid industrial expansion, population growth, and scientific and technological developments. Recently, the photocatalysis method of purifying water has received a lot of attention. Moreover, the ability of the photocatalysis process to produce hydrogen and photoreduce CO_2 into energy fuel makes it relevant to energy storage.

5.0 Degradation of pollutants

A major driver of environmental degradation, water pollution from certain industrial, pharmaceutical, and agricultural chemicals is currently receiving a lot of national and international attention. Industrial effluents have been shown to include a variety of organic and inorganic pollutants, such as pigments, heavy metals, and medicinal chemicals.

5.1 Carbon-based compounds

Many organic compounds are released into the environment as a result of the textile industry's large water consumption[68]. The following characteristics define organic pollutants: (1) environmental persistence: certain chemicals resist normal biological destruction; (2) toxicity: they have a negative impact on both human health and the environment; and (3) bioaccumulation: some molecules build up in living tissues. In addition to their bioaccumulation and persistence properties, these chemicals are also prone to wide dispersion and can accumulate far from the sources of their emissions, which include medicines, insecticides, hydrocarbons, and dyes. When it comes to the removal of organic contaminants from wastewater, photocatalysis has proven to be more effective than more conventional approaches like filtering[69]. Using TiO_2-based photocatalysts and model pollutants, several studies have demonstrated the photodegradation of dyes in visible light, including methylene blue, methyl orange, rhodamine B, brilliant green, phenol, and acid red. Wand et al.[70]Sol-gel technology was used to create carbon-sensitized and nitrogen-doped TiO_2 (C/N–TiO_2). Because the nitrogen doping caused a red shift in the absorption edge of C/N–TiO_2, and the carbon that was injected acted as a photosensitizer, they were able to accomplish highly efficient photodegradation of sulfanilamide (SNM) under visible light. Senthilnathan et al. [71]employed the herbicide lindane as the intended pollutant. In the presence of visible light, the N-TiO_2 photocatalyst destroyed lindane.

5.2 Toxic Heavy metals

There are a lot of poisonous toxic heavy metals, and how harmful they are depends on the habitat in which they are found and how concentrated they are in aquatic environments[72]. Within the field of environmental science, toxic heavy metals such as cadmium (Cd), chromium (Cr), zinc (Zn),copper (Cu), mercury (Hg), manganese (Mn), arsenic (As), nickel (Ni), and lead (Pb) are frequently associated with pollution and toxicity. When describing metal toxicity, it's critical to acknowledge that the ions are present in our everyday surroundings in several forms, which may give the metal under discussion certain characteristics (such as toxicity or solubility)[73]. Schrank et al. [74]not only determined the impact of pollutant concentration but also the influence of pH on the reaction kinetics. The scientists observed that in an acidic pH, the reduction of Cr(VI) utilizing TiO_2-P25 as a photocatalyst happened more quickly. Recently, Sreekantan et al. [75]synthesized Cu-TiO_2 nanotubes using electrochemical anodization. They determined that the Cu-TiO_2 photocatalyst attained a Pb(II) heavy metal removal efficiency of up to 97%, due to the Cu^{2+}ions that reduce charge carrier recombination. In 2016,[76]synthesized TiO_2 modified with carbon from sewage sludge (SS-carbon). Modification of TiO_2 with SS carbon led to a twofold increase in mercury adsorption capacity, while the photocatalytic removal increased to 151 g/kg, compared to 87 g/kg for SS carbon alone. Moreover, they also demonstrated that the removal of Hg(II) increased at high pH values.

6.0 CONCLUSIONS

Titanium dioxide (TiO_2) is a promising photocatalyst for water splitting: Its unique properties, including high stability, non-toxicity, and low cost, make it a suitable material for this application.Various modifications can enhance TiO_2's photocatalytic activity: Doping with metals or non-metals and altering its morphology can improve its efficiency in utilizing visible light and reducing the recombination of electron-hole pairs.Photocatalytic water splitting using TiO_2 has potential applications in renewable energy: The production of hydrogen as a clean fuel can contribute to a sustainable energy future. Degradation of both organic and inorganic pollutants is another alternative application of the photocatalyst.

7.0 FUTURE PERSPECTIVES

Further optimization of TiO_2-based photocatalysts: Continued research is needed to develop materials with higher efficiency and stability for practical applications.

Integration with solar energy systems: Combining photocatalytic water splitting with solar panels can create a more efficient and sustainable energy solution.

Addressing challenges such as recombination and electron-hole separation: Developing strategies to overcome these limitations will be crucial for improving the overall efficiency of the process.

Exploring new materials and combinations: Investigating alternative materials or combinations of TiO_2 with other semiconductors may lead to even better performance.

Scaling up for industrial applications: Research and development efforts should focus on scaling up photocatalytic water-splitting processes to meet the demands of large-scale hydrogen production.

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Availability of data and materials

Not applicable.

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