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Bulletin of Chemical Reaction Engineering & Catalysis, 17 (2) 2022, 430-450

Review Article

Photocatalytic Efficiency of Titanium Dioxide for Dyes and Heavy Metals Removal from Wastewater

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Received: 26th March 2022; Revised: 19th May 2022; Accepted: 20th May 2022
Available online: 25th May 2022; Published regularly: June 2022

Abstract

The hazardous toxicity of dye materials, even in low concentrations, harms ecological systems. It releases a large number of contaminants into the water, resulting as waste water. Dyes prevent the process of photosynthesis by obstructing light passage, lowers the oxygen levels dissolved in the water. Also, a good number of the dyes and heavy metals are carcinogenic and mutagenic to human beings. Heterogeneous photocatalysis is a promising technology for removing organic, inorganic, and microbial pollutants from water and wastewater. It is preferable to other conventional wastewater treatment approaches due to its benefit, such as low cost, environmental friendliness, ability to proceed at ambient temperature and pressure conditions, and to completely degrade pollutants into environmentally safe products with suitable measures. The titanium oxide (TiO_2) is one of the most promising material that has gained enormous importance in the field of energy and environmental applications. The unique physicochemical properties of TiO_2 make it one of the best candidates among existing photocatalysts. This review provides an overview of strategies employed to augment its catalytic performance as well as the impact of different operational parameters on the removal proficiency of various organic and inorganic pollutants in water and wastewater treatment.

Keywords: TiO_2; Heterogeneous photocatalysis; Organic pollutants; Toxic heavy metal ion; Wastewater treatment

How to Cite: S. Sagadevan, I. Fatimah, T.C. Egbosiub, S.F. Alshahateet, J.A. Lett, G.K. Weldegebrieal, M.V. Le, M.R. Johan (2022). Photocatalytic Efficiency of Titanium Dioxide for Dyes and Heavy Metals Removal from Wastewater. *Bulletin of Chemical Reaction Engineering & Catalysis*, 17(2), 430-450 (doi: 10.9767/bcrec.17.2.13948.430-450)

Permalink/DOI: https://doi.org/10.9767/bcrec.17.2.13948.430-450

1. Introduction

Water pollution had been adjudged a global menace for the accessibility of clean water, especially in the developing countries [1]. The principal agents causing water pollution are organic and inorganic pollutants, such as dyes and heavy metals from cosmetics, mining, textiles, fertilizer, paints, electrical, electroplating, metallurgical and photographic industrial effluents [2]. These pollutants are often largely dis-

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charged into the environment without proper treatment and cause a lot of diseases to human beings and public health. For instance, dyes used for colour impartation to achieve product attractiveness have been reported to decrease light penetration, thereby affecting the photosynthetic process [3-6]. Equally, metals, such as zinc (Zn), copper (Cu), lead (Pb), cadmium (Cd), Chromium (Cr), iron (Fe), mercury (Hg), arsenic (As) and nickel (Ni), are regarded as heavy metals when they are present in water more than a density of 5 g/cm^3 [2,7]. These pollutants are very toxic, mutagenic, and carcinogenic which culminates in the malfunctioning of the reproductive system, liver, kidney, and nervous systems [7-9]. Since the pollutants are non-biodegradable and are accumulated in organisms through food chain transfer and direct uptake, there is a need to treat the wastewater to meet guidelines for drinking water quality by world health organizations [10].

Various conventional treatment methods are applied to remove toxic pollutants from wastewater including chemical [11], biological [12], membrane filtration [13], and adsorption [14]. Despite the use of these treatment methods for water quality improvement, some of them have prevalent disadvantages, for instance, chemical techniques involve large consumption of chemicals, pH monitoring, sludge generation and formation of secondary pollutants due to the excess chemicals used [4]. Specifically, the membrane filtration method is not cost-effective, inefficient in solute restriction and involves low throughput due to fouling challenges [9]. Also, the biological processes are difficult to control, while the adsorption technique produces secondary pollutants [4]. However, photocatalysis is a clean, environmentally friendly and sustainable process using semiconductor material for the creation of reactive chemical species that decompose toxic pollutants into non-toxic by-products. In doing that, common single photocatalysts used include titanium dioxide (TiO_2), tungsten trioxide (WO_3), zinc oxide (ZnO), tin(IV) oxide (SnO_2), cerium(IV) oxide (CeO_2), and iron(III) oxide (Fe_2O_3) [4,11,16]. Among them, TiO_2 has exhibited effective photocatalytic performance [1].

Titanium dioxide is commonly used in the photocatalytic water purification process to decompose various organic pollutants such as dyes, heavy metals, pesticides and phenols [17,18]. To obtain TiO_2 photocatalysts with high photocatalytic activity, many modifications of pristine material by metals, nonmetal species, or coupling TiO_2 with other semiconductors were performed [19-21]. One of the most promising and widely tested methods for preparing highly active photocatalysts is TiO_2 due to the enhancement of the photocatalytic activity under visible-light irradiation and the suppression of the recombination of the electron-hole pairs [22,23]. With the rapid advancement of science and technology, there has been a great deal of focus on the use of TiO_2 photocatalyst [24]. Numerous other successful materials have demonstrated improved photocatalytic activity. It is interesting to note that the use of TiO_2 has reached a sustainable level over the last half-century. Researchers have made extensive use of it due to its high photocatalytic activity, nontoxicity, ease of availability, and stability in the working environment [25]. Its unique properties make it chemically and biologically resistant and stable, while also being highly active against photoinduced chemical reactions and organisms [26]. TiO_2 can withstand high temperatures as well as work at room temperature. The physicochemical properties of TiO_2 can be altered to a greater extent as its size get reduced to the nanometer scale [27]. TiO_2 materials were prepared in the form of nanoparticles, nanowires, nanofibers, and nanotubes. As a result, it has emerged as a potential research component in terms of energy and the environment. However, TiO_2 can be excited by UV irradiation, which initiate the photocatalytic reactions such as flaking corrosion of paints and fabric degradation in the sun. Nowadays, it is also used for wastewater treatment. It is so specific that it can be effective against extremely low levels of pollution. It can be used for water splitting to generate H_2 gas.

Therefore, this review begins with the introduction of water pollution and its treatment methods including their specific qualities and limitations. When compared to conventional remediation methods, it was discovered that photocatalysis is one of the most distinctive and effective technology for water treatment, aiding in energy savings while efficiently remediating environmental concerns. Notably, the main focus of this review is the depiction of a more appealing photocatalytic property of TiO_2 towards the elimination of diverse pollutants in aqueous media. In addition, the fundamental principles of photocatalysis, its mechanism, working parameters in photocatalytic processes, and limitations that hinder photocatalytic performance of TiO_2 are discussed.

2. Water Pollution

Water is a necessary component of the ecosystem for both living and nonliving things. The availability of clean water is critical for living creatures which constantly used for drinking, cooking, cleaning, horticulture, and so on. Nature has its mechanism for recycling water to provide an adequate quantity of freshwater, with the impact on life sustainability and the standard of living beings. Current human activities such as large deforestation, decreased agricultural lands, extensive use of chemical pesticides, industrial chemical discharge, and so on have disrupted the equilibrium between usage and natural purification processes, resulting in a scarcity of clean and potable water. The majority of natural drinking water resources are contaminated with various poisonous materials and pathogenic microorganisms [28]. Water pollutants can be found in a variety of hazardous wastes, including pharmaceutical waste, pesticides, herbicides, textiles, gums, and phenolic compounds [29].

Water pollution is one of the most serious threats and challenges confronting human today. Every day, human activities pollute rivers, lakes, groundwater aquifers, and oceans with contaminant substances and wastes. This contamination alters the quality of the environment's water, resulting in large amounts of water that are unsuitable for a variety of uses, including human consumption. Common water pollutants include textile dye; herbicides and pesticides; alkanes; haloalkanes; aliphatic compounds; alcohols; carboxylic acids; aromatic compounds; detergents and surfactants; agro waste like insecticides, pesticides and herbicides [30] inorganic compounds like heavy metals, such as mercury, cadmium, silver, nickel, lead; toxic gases; and pathogens like bacteria fungi and viruses [31,32]. Organic and inorganic contaminants can be found in groundwater, wells and surface waters; these residues can harm the environment and human health. Water covers 34% of our planet. However, due to the high concentration of salt, approximately 98% of this water is seawater and thus unfit for drinking. Only about 2% of the world's water is fresh, with the remaining 1.6% trapped in polar ice caps and glaciers. An additional 0.36% is found underground in aquifers and wells. As a result, lakes, and rivers only hold about 0.036% of the world's total water supply [30]. Because of human or industrial activities, existing freshwater resources are gradually becoming polluted and unavailable. One of the most serious environmental issues confronting humanity today is the increasing contamination of freshwater systems with thousands of industrial and natural chemical compounds. The major sources of water pollution are depicted in Figure 1.

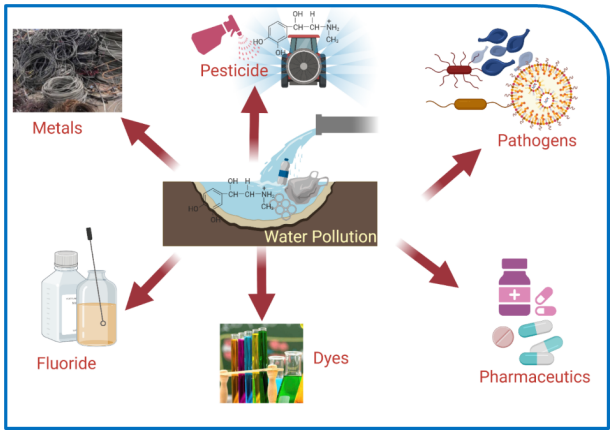

Figure 1. Different potential sources of water pollutants.

The safe and economical removal of pollutants from water has become a global concern. In the current scenario, it is crucial to reduce this spectrum of pollutants from the water in order to maintain a high-quality eco-friendly nature, which has led to the destruction of various forms of pollution in the atmosphere due to pollution occurring in the form of untreated hazardous landfills or organic substances that are discharged into water bodies and potentially impair ecological safety and the quality of life [33].

2.1 Environmental Impact of Water Pollution

The spread of industrialization has its in environmental pollution across the globe these days. By 2025, it is expected that two-thirds of the world's population will live in water-stressed areas. The main causes of water scarcity are the increasing global population's demand for water and overuse of water, as well as water pollution and climate change. Contamination in the environment has influenced various plants and creatures in the biological community, as well as people all over the world. Humans require awareness and a critical need for the development of a novel hygienically friendly purification technology. Water pollution is thought to be a significant factor in environmental contamination. Modern effluents pollute the water with distinct synthetic substances, particularly engineered colors with some of them also causing cancer naturally or due to their harmful decomposed products in water either aerobically or anaerobically. As a result, there is an urgent need for a method to

remediate polluted water. Water technology remediation necessitates a huge number of assets, procedures, maintenance, with the large sums of money, and many lands. Thus, various traditional methods of water treatment include physical and chemical techniques such as adsorption, chlorination, coagulation, ion flotation, membrane process, sedimentation, and solvent extraction. These water remediation methods have limitations, raising concerns about their widespread application. Furthermore, the final results of these systems should be handled further for complete refinement and sanitization. To degrade harmless products into carbon dioxide and water, advanced oxidation processes such as biodegradation, radiation, ozonation, photocatalysis, and others are used. Many of the contaminants are so toxic that even at low concentrations, they can cause health problems in humans. Water pollution also reduces the number of freshwater resources available to both people and ecosystems. So, it is necessary to have as many treatment approaches as possible that are ecofriendly and economically efficient. In many developing countries, freshwater scarcity is already a reality.

2.2 Dye Wastewater

Synthetic dyes are an important component of industrial effluents as they are discharged in large quantities by many processing industries. Due to the potentially carcinogenic properties of these chemicals, the environmental impact of these dyes is a major concern. Apart from that, these dyes are mostly not biodegradable, but rather accumulate in the body of the organism and can decolorize anaerobically, leading to the formation of potential carcinogens [34]. The presence of these dyes in wastewater can prevent both the penetration of sunlight and the dissolution of oxygen, both of which are necessary for aquatic life. In addition, accumulation of dyes in natural resources, such as water and soil, leads to changes in their proper-

Table 1. TiO_2 and TiO_2-based photocatalysts application in the removal of various dyes.

Photocatalyst	Target dye	Light source	Concentration (mg/L)	Removal efficiency (%)	Time (min)	Ref.
ZnO/TiO_2	Rhodamine B	200 W Xenon Lamp	10	94	45	[35]
CeO_2/TiO_2-NCC	Methyl orange		50	50	70	[36]
TiO_2	Direct dye	UV-A light	50	64	240	[37]
Ag-TiO_2	Rhodamine B	UV light	50	98.4	60	[38]
Carbonized TiO_2-coated melamine	Rhodamine B	Sunlight	12	98	60	[39]
TiO_2	Methylene blue	36 W Philips UV-C light	2.5	95	100	[40]
TiO2/ZnO/rGO	Rhodamine B/ Methyl orange	UV-C light	20	99.2/99.4	180	[41]
TiO_2/ZnO	Methylene blue	15 W UV Lamp	80	100	120	[42]
Ni–TiO_2	Congo red	UV light	10	92.31	180	[43]
NCS/CMC/TiO_2	Crystal violet	Visible light	200	95	180	[44]
TiO_2	Rhodamine B/Acid red 57	UV light	6/30	93.8/90.7	190	[45]
Bentonite/TiO_2	Direct red 80/Methylene blue	UV light	10	77/100	120	[46]
GO/TiO_2	Methylene blue	500 W Xenon lamp	5	99	240	[47]
TiO_2	Methylene blue	UV light	20	85.5	120	[48]
Fe-TiO_2/AC	Malachite Green	UV light	100	97	45	[49]
TiO_2@Bi_2O_3	Methylene blue	Sunlight	50	94	30	[50]
TiO_2 NPs	Methyl orange	Sunlight	10	97.8	300	[51]
TiO_2/GO/Ag	Methyl orange	Solar light	15	97.66	180	[52]

ties and critical challenges, such as die-off of food microbes and contamination of water resources [12]. As a result, there is a significant need to treat these colored effluents before they are discharged into various water bodies. Photocatalysis may be used for the decomposition of such colored pollutants in water. Here, the dye containing solution is exposed to radiation in the presence of a small amount of photocatalyst, such as TiO_2.

For the photocatalytic degradation of dyes in wastewater using TiO_2 catalyst, there are two possible mechanisms for explaining the photodegradation stated in Equations (1) and (2).

$$\text{Dye} + h\nu \rightarrow \text{Dye}^* \text{ (intermediate)} \quad (1)$$

$$\text{Dye}^* + TiO_2 \rightarrow \text{Dye}^+ + TiO_2^- \quad (2)$$

Accordingly, Equation (1) is an indirect mechanism whereby the excitation of the dye molecules was attributed to the visible light energy that enhances its triplet excited state with further conversion to a semi-oxidized radical through electrons injection to the titanium dioxide conduction band [35]. On the other hand, Equation (2) indicates the direct mechanism of the photodegradation of dyes, whereby the dyes molecules interact with the produced hydroxyl radicals, the electrons and the holes created as a result of the excitation at the conduction band, leading to the dyes reduction and oxidation [36]. Particularly, the indirect photodegradation mechanism of dyes dominates the direct mechanism with an enhanced degradation efficiency achieved at a faster rate [8].

Overall, the difficulty in the removal of a dye molecule at a time makes it paramount for a good catalyst that can effectively remove the dyes at a low cost. The treatment techniques such as coagulation/flocculation, biological methods, membrane processes, ion exchange and adsorption are used to remove dyes. However, these methods have not been consistent and reliable with observable structural degradation and the presence of color indicating incomplete removal. Releasing the incompletely treated water to the environment threatens the water resources and public health [17]. TiO_2 nanostructures have been identified as good photocatalytic materials for the treatment of wastewater due to their high surface area and outstanding catalytic capacity. Also, the application of TiO_2 with immobilized support has been characteristically reported as an efficient degrading material [37]. Based on the literature reports, the contributions of TiO_2 and TiO_2 incorporated with various materials towards the degradation of dyes contaminated wastewater are briefly presented in Table 1.

2.3 Wastewater with Heavy Metals Content

Heavy metals have higher density and atomic weight compared to water and are widely used in various industrial effluents due to their lower strength and reactivity [2]. Heavy

Table 2. TiO_2 and TiO_2 -based catalysts application in heavy metals removal.

Photocatalyst	Target heavy metal	Light source	Concentration (mg/L)	Removal efficiency (%)	Time (min)	Ref.
$Bi/Bi_2O_3/TiO_2$	Cu((II)	Visible light	10	96.5	300	[55]
CeO_2/TiO_2-NCC	Cr(VI)	Visible light	10	50	60	[36]
TiO_2-rGH	Cr(VI)	UV	10	100	30	[56]
Bi_2O_3-TiO_2	Pb(II)	Visible light	20	55	240	[57]
10Ag@C-TCZ	Cr(VI)	Visible light	5	95.5	120	[35]
Chitosan/g-C_3N_4/TiO_2	Cr(VI)	800 W xenon lamp	800	90	240	[58]
TiO_2@PAN-3	Cr(VI)	300 W Xe lamp	5	99	60	[59]
Pristine TiO_2	Cr(VI)	Visible light	10	100	60	[60]
Nano-TiO_2	Cu(II)	UV light	10	96.63	180	[61]
TiO_2 nanotubes	Cr(VI)	Visible light	20	94	60	[62]
$TiO_2/CoFe_2O_4$	Se(VI)	Sunlight	0.5	99	2	[63]
TiO_2-WO_3-PANI	Cr(VI)	Visible light	10	67.32	60	[64]
TiO_2/Alg/FeNPs	Cr(VI)/Cu(II)/ Pb(II)	UV light	40	98.4	72	[65]
TiO_2	As(III)	UV light	0.2	97	20	[66]

metals, such as lead, chromium, copper, zinc, selenium, arsenic, cadmium, manganese, iron, etc., are highly toxic, easily accumulate in the environment and are very difficult to remove using biological methods [53]. Heavy metals have been reported in the past to be carcinogenic and affect many organs in the body [54]. Notably, TiO_2 has been widely reported as an effective photocatalyst in removing heavy metals through the reduction of the heavy metals to lower oxidative states due to their deposition on the catalyst [2]. From this point of view, metal ions can be reduced to their ground state by electrons obtained by photoexcitation of TiO_2 at favorable reduction potentials, Equation (3).

$$M^{n+} + ne^- = M \quad (3)$$

The indirect method is an alternative technique to achieve reductive removal of metal ions by the addition of electron donors, for instance, formaldehyde and methanol.

$$M^{n+} + R\text{-}CH^{\bullet}\text{–}OH \rightarrow M^{(n-1)+} + R\text{-}CHO \quad (4)$$
$$R\text{-}CH_2OH + {}^{\bullet}OH \rightarrow R\text{-}CH^{\bullet}\text{–}OH + H_2O \quad (5)$$

In addition, hydroxyl radicals or holes can be further used to oxidize metal ions to higher oxidation states, provided they are not previously occupying the highest possible oxidation states [2].

$$M^{n+} \xrightarrow{\text{hydroxyl radicals or holes}} M^{n+1} \quad (6)$$

Over the literature, TiO_2 and its composites of various materials had been reported to be effective in the removal of heavy metals, such as copper, chromium, lead, selenium etc. at different concentrations and light sources from wastewater as presented in Table 2.

2.4 Various Treatment Methods to Purify Wastewater

To address the problem, contaminated water must be treated and reused. Various mechanical, biological, physical and chemical processes are used to treat the contaminated water. Biological treatment is ideal after filtration and the elimination of particles in suspension (initial treatment and post-treatment). Unfortunately, some products are bio-refractory (non-biodegradable), necessitating the use of much more effective non-reactive systems. Although these processes aim to purify wastewater and thereby improve water quality, some of them (such as coagulation/flocculation, chlorination, ion exchange, membrane processes and adsorption) in Table 3 merely concentrate on pollutants by transferring them to other phases. The next step is about the ways for the proper disposal of the new pollutant-rich streams. As a result, the management of toxic chemicals with strict environmental legislation is driving the development of clean and environmentally friendly processes to eliminate pollutants before they are released into the environment. In addition, for these processes to be effective, all organic and inorganic contaminants in water and wastewater must be fully mineralized and degraded.

These advanced oxidation processes outperform all existing ones, but are much more expensive. Photocatalysis is a rapidly developing technology attracting the attention of researchers due to its low cost and high efficiency in water decontamination compared to other methods. It is an excellent method for solving energy and environmental problems, which can be used for a variety of purposes such as degradation of toxic natural pollutants in sewage, harmful gases and microscopic organisms in their various media, production of hydrogen, air purification, soil sanitation and antibacterial effect. Various approaches to handling and decontaminating such effluents have been reported in the literature. The techniques, such as adsorption [67], coagulation [68], ion flotation [69] and sedimentation [70], are versatile and useful, but they all generate secondary waste that needs further processing. Advanced oxidation processes (AOPs) are a newer, more powerful and promising set of techniques that have been developed and used to treat dye-contaminated effluents [71]. The AOP technique has attracted the interest of many members in the scientific community because it is easy to use and produces significantly fewer residuals than traditional approaches.

The UV photolytic technique [72], Fenton process [73], photo-Fenton process [74], ozonation process [75], sonolysis [76], photocatalytic approach [77], biodegradation [78], and radiation-induced pollutants degradation [79] are among the many techniques used in the AOP approach. Photocatalysis-based AOPs are an innovative strategy that benefit our atmospheric conditions by fully oxidizing natural organic molecules to harmless mixtures of CO_2 and H_2O [80-83]. Apart from that, it also produces hydroxyl free radicals (OH) which act as powerful oxidizing agents that easily react with impurities to break down and remove them from the water, making the water reusable [84]. Thus, photocatalytic phenomena have

Table 3. Advantages and disadvantages of various treatment methods used for the removal of dyes and heavy metals from wastewater.

Method	Advantages	Disadvantages
Coagulation / Flocculation	Cost-efficient	Production of high sludge
Chemical precipitation	Cost-effective, process simplicity and safe operations	It involves the addition of other chemicals, the production of a high amount of sludge, toxic by-products, time-consuming and slowly aggregation and settling of metal ions precipitate.
Photocatalysis	Easy operation and high degradation efficiency.	Requires the addition of chemicals and is mostly applicable for sludges and effluents
Chlorination	Disinfection of pollutants and other microorganisms.	Formation of toxic chemicals and by-products such as dioxins and metals.
Photo-Fenton oxidation	Removed many pollutants	Produce a large amount of iron-containing sludge
Electrochemical oxidation	Efficient for metals recovering	Performance depends highly on solution pH
Ozonation	A simple and rapid operation with higher removal efficiency. Good for decolorization, does not transfer pollutants from one phase to another, and no sludge production.	Ozone has a shorter half-life. Involve chemicals. The produced oxidation products may have toxicological effects. High doses of ozone are required for effective dyes degradation. It doesn't affect salinity and produces carcinogenic bromate anions (BrO_3^-).
Biological treatment	Highly reusable, low cost, effective in the removal of suspended solids, biochemical oxygen demand and organic matters.	Highly selective, toxic, the sensitivity of microorganisms, requires large space for the bioreactors and is not suitable for all kinds of dyes.
Membrane process (reverse osmosis and nanofiltration)	A simple, rapid and effective method that does not involve the application of chemicals. Reverse osmosis effectively removes reactive dyes and nanofiltration involves low pressure.	High cost for the investment, maintenance and operations. A higher number of microbial organisms and biomass may be present in the residuals after the membrane process. Membrane fouling and high-pressure requirements for reverse osmosis.
Ion exchange	It is reusable, selective and produces less sludge.	Frequent regeneration of ion-exchange resin using chemical reagents, thus causing secondary pollution. Highly expensive and selective for some dyes.
Adsorption	This process is cheap, eco-friendly and easy to operate. Highly effective for the removal of some contaminants and have a wide pH range. No transformation or by-products are produced during the treatment. And can be applied in batch and fixed-bed reactors. Adsorbent efficiency determines its performance and a wide range of adsorbent materials can be used. Adsorption can be integrated with the other treatment techniques.	The disposal of the spent adsorbents after exhaustion requires a sustainable method. The cost of the regeneration process is high and may lead to adsorbent loss and adsorbents performance effectiveness. Adsorbents require additional modifications to improve their adsorption performances. It is dependent on numerous factors such as solution pH, contact time, adsorbent mass, adsorbate concentration, temperature and ionic strength for effective uptake performance. The coexistence of other pollutants ions may interfere with the removal of the target adsorbate.

advantages over conventional techniques, such as rapid oxidation, no formation of polycyclic compounds, complete oxidation of impurities, and high productivity. As a result, photocatalytic degradation has emerged as one of the most promising methods to treat toxic organic wastewater by using nanomaterials, such as TiO_2, ZnO, ZnS and others, as catalysts [85].

2.5 Photocatalytic Water Splitting

Photocatalytic water splitting reaction is studied for hydrogen gas production, which is one of the most intriguing methods to generate clean and renewable energy. In this reaction, photon energy interacts with TiO_2 particles to form electron-hole pairs. The hole oxidizes water to create oxygen while the electron reduces water to create hydrogen. The key factors for efficient photocatalytic activity are inhibited electron/hole recombination, enhanced light absorption, and favorable active sites for redox species. Although there are several mandatory requirements for efficient photodissociation of water, such as minimum potential difference of 1.23 V for the water dissociation energy, the TiO_2 band structure is advantageous for water splitting because of the relative position of the valence and conduction bands [86]. Since the TiO_2 conduction band energy is close to the H_2 evolution energy, the focus shifts to the valence band energy to bring it closer to the O_2 evolution energy. This is due to the high potential for O_2 evolution on the TiO_2 surface. Figure 2 depicts the photocatalytic mechanism in terms of a band energy diagram. The bandgap should be less than 3.0 eV (> 420 nm) for the photocatalyst which works on visible light. Furthermore, water's oxidation and reduction potentials require energy that should be met by the conduction and valence band positions. Therefore, band engineering is required to develop photocatalysts with these properties. These processes are strongly influenced by crystal structure and crystallinity. The lower the number of defects, the higher the crystal quality. The defects act as trapping and recombination centers for photogenerated electrons and holes, reducing photocatalytic activity. Therefore, photocatalysts need to have a high degree of crystallinity rather than a high surface area, especially for an increasing reaction, such as water splitting. In order for oxygen evolution to take place, active sites for the four-electron oxidation of water are required. Although this reaction is challenging, oxide photocatalysts do not require cocatalysts because the valence band is low enough to oxidize water to oxygen.

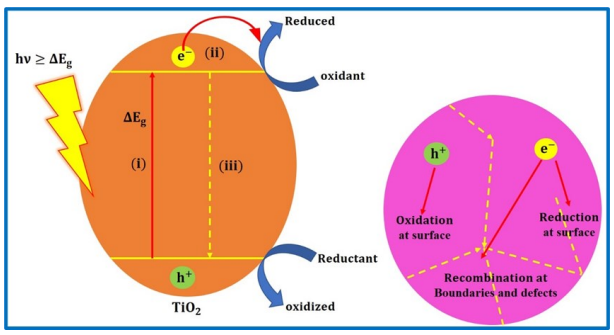

Figure 2. Schematic representation of excitons pathway in semiconductor photocatalysis (i) incident photon absorption and electron-hole separation. (ii) exciton migration, (iii) surface chemical reaction at active sites, and (iv) particle size effect on the recombination process.

A photocatalytic reaction involves both oxidation and reduction, and these opposing processes must have the same reaction rates for the photocatalyst to remain unchanged because electron transfer reactions are involved. The light activates a photocatalyst, facilitating a photocatalytic reaction. It increases the rate of the reaction by accumulating photon energy. It should not be changed physically or chemically during this time. The absorption of the incident light, bandgap excitation, separation of stimulated e^-/h^+ pairs, and redox couple reactions on the semiconductor surface are all important fundamental steps in a typical photocatalytic reaction [87]. When the incident light's energy exceeds the bandgap energy between the valence and conduction bands, the incident light absorbs. The electrons in the valence band will then have enough energy to travel to the conduction band. As a result, electron-hole separation occurs, which can either open the active sites for further redox reactions on the semiconductor surface or cause recombination [88]. The active sites are successfully initiated after the addition of chemical species in the reaction. However, the surface reaction is affected by the active sites as well as the surface area. Surface activity can be significantly increased by the use of co-catalysts. These sites can enhance the absorption of visible and infrared irradiation, as well as act as charge carrier trapping sites. A large number of lattice defects in photocatalyst material could result in a continuous trapping band in the middle with energy distributions that differ from a single defect in a crystal [89]. The photocatalyst can speed up the photoreaction in two ways: by interacting with the substrate in its original or excited state, or by interacting with the photoreaction products. Heterogeneous photocatalysis harvests incident light and drives reactions in a

variety of applications by utilizing the unique properties of semiconductor materials.

3. Photocatalysis

The photocatalysis is the science of using light and catalysts to accelerate a chemical reaction that requires light [90]. A photocatalyst is defined as a material that generates electron-hole pairs after absorbing light from a source to enable chemical transformations of reactants and regenerate their chemical composition after each rotation of e^-/h^+ pair interactions [91]. Photocatalysis is an advanced oxidation technique used for a variety of useful purposes such as the biodegradation of organic contaminants in wastewater, hydrogen production, air refinement, and antimicrobial activities. Photocatalysis is distinguished by the fact that it requires sunlight or near-UV light as a source of irradiation, making it a low-cost treatment as well as a resource technique. In recent years, heterogeneous photocatalysis is an emerging technique as this method can achieve complete degradation of toxic compounds [92]. The photocatalytic method has many potential advantages over the conventional treatment methods, which include: (i) complete mineralization of the pollutant leading to CO, H_2O and simple inorganic ions as final products, (ii) higher efficiency in terms of reaction rate, (iii) reaction temperature is not an important parameter as this method operated by light energy, (iv) no solid waste formation, (v) recycling of the processed water, (vi) reusability of the catalyst as there is no chemical change in the catalyst, and (vii) cheap method as solar energy can be utilized. In this process, carbon dioxide is converted into organic compounds, especially sugars, using the energy from the Sunlight. Fujishima and Honda reported a photocatalytic process for generating hydrogen from water using TiO_2 semiconductor oxide electrodes [93]. TiO_2 has proven to be the most suitable semiconductor for widespread environmental applications due to its exceptional optical and electronic properties. Furthermore, TiO_2 is biologically and chemically inert; it is photo corrosion resistant, and it is inexpensive. Another benefit of TiO_2 is its low cost, which is due to titanium's abundance (0.44 % of the earth's crust). However, the TiO_2 band gap (3.0–3.2 eV) causes absorption in the near UV range. Because UV makes up only 5-8 percent of the spectrum of sunlight, research has been done to develop photocatalysts that can absorb more of the visible spectrum. Several semiconductor oxides and sulfides have bandgap energies suitable to absorb light under visible and/or near UV and excite electrons and further proceed with the photocatalytic process. These include TiO_2, ZnO, ZrO_2, CdS, ZrO_2, MoS_2, Fe_2O_3, WO_3, *etc*. Among these semiconductors, the TiO_2 is considered a benchmark photocatalyst because of its high efficiency, photochemical stability, non-toxicity and low cost [25].

3.1 Fundamental Principle of Photocatalysis

The photocatalytic reaction is primarily determined by the wavelength of light (photon) energy and the catalyst. The light can be irradiated directly or indirectly as a result of the catalyst reacting with the dye. The photocatalytic mechanism associates dye degradation with the redox capabilities or potential of dyes and the energy level of the conduction band of the semiconductor or nanomaterial used. When a photon with hν energy matches or exceeds the bandgap energy (E_g) of a TiO_2, an electron in the valence band (VB) is promoted to the conduction band (CB), leaving a positive hole (h^+) in the VB. The photo-excitement can be expressed as [94].

$$TiO_2 + h\nu \rightarrow TiO_2\,(h^+)_{(vb)} + TiO_2\,(e^-)_{(CB)} \qquad (7)$$

where VB and CB represent the valance band and the conduction band, respectively. The reactive species, h^+ and e^- are the powerful oxidizing and reducing agents, respectively. Therefore, soon after the reactive species formed, the semiconductor oxide particles can act as electron donors or electron acceptors resulting in oxidative and reductive reactions. At the same time, some reactive species can recombine in bulk by releasing energy in the form of heat without any chemical reaction.

$$TiO_2(h^+)_{(VB)} + TiO_2(e^-)_{(CB)} \rightarrow TiO_2(e^-)_{(VB)} + \text{heat} \qquad (8)$$

At the surface, the excess reactive species are trapped by adsorbed species and undergo an oxidation-reduction reaction. The valence band hole is considered a strong oxidizing species, which can oxidize any organic and inorganic compounds. The redox potential for the photogenerated hole is +2.53 V regarding a normal hydrogen electrode (NHE) [95]. Also, the hole can produce secondary oxidizing species. The general principle of photocatalysis is presented in Figure 3.

For instance, the water molecule or OH^- ion oxidizes into hydroxyl radical (•OH), which is

an extremely powerful oxidant.

$$TiO_2(h^+) + H_2O_{(ads)} \rightarrow TiO_2 + \cdot OH_{(ads)} + H^+ \quad (9)$$
$$TiO_2(h^+) + HO^-_{(ads)} \rightarrow TiO_2 + \cdot OH_{(ads)} \quad (10)$$

The oxidation potential of ·OH radical is +2.85 V regarding a normal hydrogen electrode (NHE) [96]. The conduction band electron is a powerful reducing species; reduces the molecules which undergo reduction. In oxygen or air mediated solution, reduction of adsorbed O_2 leads to the formation of superoxide anion radicals ($O_2\cdot^-$), which is also considered a powerful oxidizing species. In addition to photogenerated holes, ·OH and $O_2\cdot^-$, various forms of active oxygen species, such as HO_2, H_2O_2 and O, are produced. The hydroxyl radical can be produced from either H_2O or OH^- ion and react with the photogenerated holes.

$$TiO_2\ (e^-) + O_{2(ads)} \rightarrow O_2^{-}\cdot \quad (11)$$

These superoxide ions can react with hydrogen ions (from Equation (10)), forming $HO_2\cdot$:

$$O_2^{-}\cdot + H^+ \rightarrow HO_2\cdot \quad (12)$$

H_2O_2 could be formed from $HO_2\cdot$ via the following reactions:

$$TiO_2\ (e^-) + HO_2\cdot \rightarrow TiO_2 + HO_2^- \quad (13)$$
$$HO_2^- + H^+ \rightarrow H_2O_2 \quad (14)$$

The H_2O_2 formed are further undergoing cleavage into OH· radical by the following reaction path ways (Equations (15)-(18)):

$$H_2O_2 + h\nu \rightarrow 2HO\cdot \quad (15)$$
$$H_2O_2 + O_2\cdot^- \rightarrow HO\cdot + O_2 + HO^- \quad (16)$$
$$H_2O_2 + TiO_2\ (e^-) \rightarrow HO\cdot + HO^- + TiO_2 \quad (17)$$
$$\text{Organics pollutant} + (h^+, OH\cdot, O_2\cdot^-) \rightarrow CO_2 + H_2O \quad (18)$$

Various semiconductors, such as TiO_2, ZnO, α-Fe_2O_3, and WO_3, are being investigated for their potential use as photocatalysts [97,98]. TiO_2 has proven to be the most suitable of these semiconductors for widespread environmental applications due to its exceptional optical and electronic properties. Furthermore, TiO_2 is biologically and chemically inert; it is photo corrosion resistant, and it is inexpensive. Under UV light illumination, coumarin in aqueous solution and terephthalic acid in NaOH solution was converted to highly fluorescent hydroxyl products on the TiO_2 film photocatalyst. The same research group has estimated the quantum yield of hydroxyl radical (·OH) produced during TiO_2 photocatalysis in an aqueous solution using terephthalic acid as a fluorescence probe. Similarly, the quantum yield of hole generation is estimated by iodide ion oxidation. The quantum yield values were 7×10^{-5} and 5.7×10^{-2} for ·OH radical and holes, respectively [99]. From these values, they have confirmed that the oxidative reactions on TiO_2 photocatalyst occur mainly via photogenerated holes and not through ·OH. As a result, the primary oxidants in the degradation of organic compounds are the hole and the hydroxyl radical (OH·), which results from the oxidation of adsorbed water or adsorbed OH, and the presence of oxygen can prevent the re-combination of hole-electron pairs.

3.2 Photocatalyst Activity of TiO_2

TiO_2 belongs to the family of transition metal oxides. It mainly occurs in four cryptographic forms: anatase, rutile, brookite, and titanium dioxide (B). The crystal structure of anatase is a tetragonal system. Rutile has a tetragonal crystal structure. Brookite has an orthorhombic crystal structure. TiO_2 (B) is a monoclinic mineral that is new to the titanium dioxide family. Brookite has an orthorhombic crystalline structure. TiO_2 (B) is a monoclinic mineral that is new to the titania family [100]. Anatase contains 6 atoms per primitive cell. The anatase phase is more stable than the rutile at 0 K, but the energy difference between these two phases is small (~2 to 10 kJ/mol). Rutile also contains 6 atoms per unit cell. The rutile phase is stable at most temperatures and pressures up to 60 kbar, where TiO_2 (II) becomes the thermodynamically favorable phase. The unit cell of brookite is composed of 8 formula units of TiO_2 and is formed by edge-sharing [101]. Anatase phase TiO_2 exhibits greater photocatalytic activity than the other two crystal structures, anatase, brookite, and rutile [102].

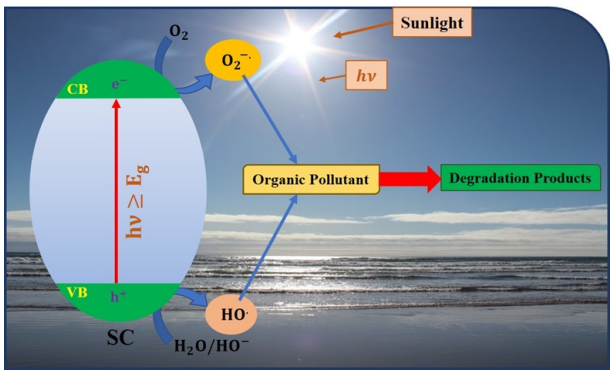

Figure 3. Schematic representation of the general principle of photocatalysis.

TiO_2 anatase was used as a powder photocatalyst in the first report of photocatalytic activity for hydrogen production. However, due to the relatively wide bandgap (e.g., 3.2 eV for anatase; 3.0 eV for rutile) and high recombination rate of electron-hole pairs (as shown in Figure 4), the low utilization efficiency of visible light and quantum efficiency of photocatalytic reactions on TiO_2 limits its practical applications. Although the rutile phase has a lower bandgap, anatase has advantages over rutile, including a higher reduction potential and a lower photogenerated carrier recombination rate.

As shown in Figure 5, the conduction band edge of anatase is higher by 0.1V (more negative) than that of rutile. Because of oxygen defects in the structure, TiO_2 is an n-type semiconductor and thus non-stoichiometric. The number of free electrons is proportional to the number of oxygen defects in the crystal structure, which results in the n-type characteristics of a semiconductor. The rutile phase of TiO_2 can harvest more light in composite junctions, and excited electrons shuttle to anatase crystals [103, 104]. To efficiently utilize solar energy, the optimal bandgap for a semiconductor should be 1.35 eV [105]. TiO_2, on the other hand, has a low solar photoconversion efficiency. This is because of its large bandgap energy (3.2 eV for the anatase phase). As a result, it can only absorb light wavelengths up to 387.5 nm, which appears to cover only 5% of solar energy.

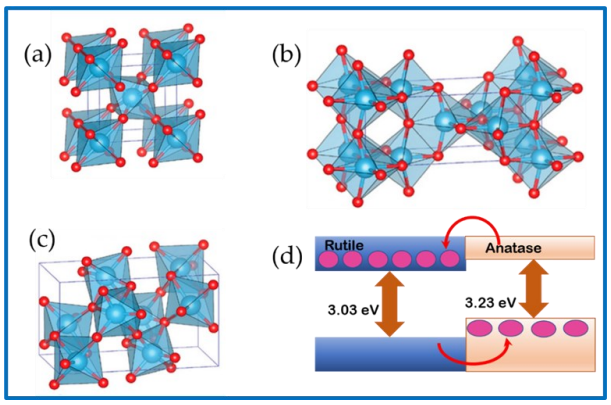

Figure 4. Crystal structure of different TiO_2 phases: (a) rutile, (b) anatase, (c) brookite, (d) the relative position of the conduction band and valence band in anatase and rutile phases.

3.3 Photocatalysts under Solar Radiation with Improved Activity

Two main strategies were used to improve the activity of the photocatalyst. On the one hand, photocatalysts with increased activity could be obtained by improving the structural properties of the photocatalysts. Particle size, crystal quality, morphology, specific surface area, surface state and other structural properties of photocatalysts are considered. The appropriate fabrication method to prepare the nanoscale photocatalysts could allow proper control of these structural properties. Another method to increase catalytic activity is to improve charge separation. Many methods for separating electron-hole pairs have been studied. To prevent recombination, O_2 and other substances were added to a water solution to trap the excited electrons that reached the semiconductor surface [106]. Due to its wide band gap, the titania photocatalyst is photoactivated only in UV light, which is a small fraction of the solar energy (3.2 eV for anatase). Therefore, efforts to increase the photoactivity of catalysts to cover the visible light spectrum are both attractive and important. Visible absorption can be improved by dye sensitization,

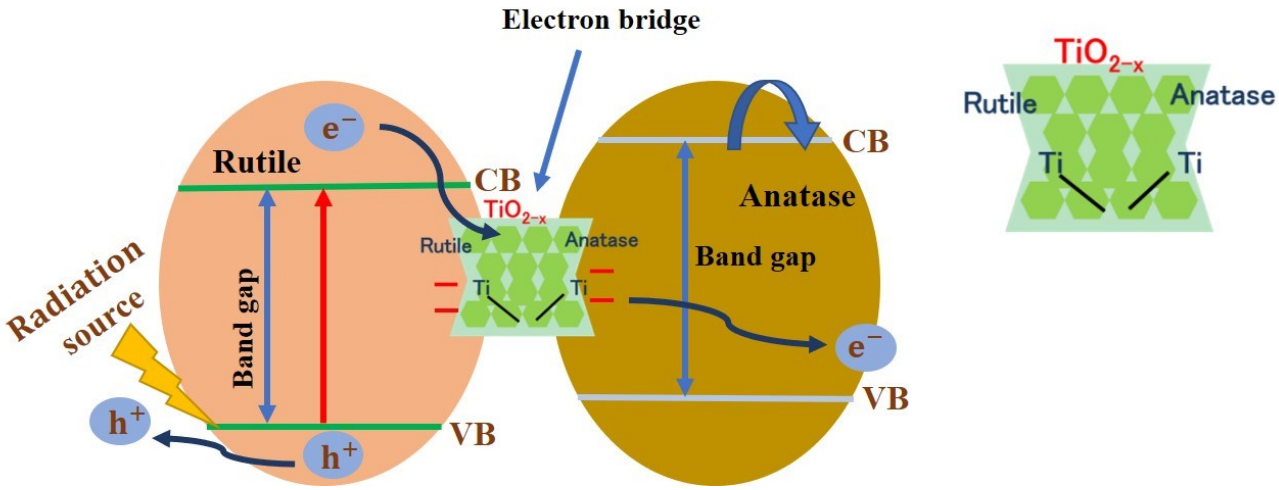

Figure 5. The photocatalytic mechanism in terms of a band energy diagram.

doping, compound semiconductors, and particle size modification.

TiO_2 anatase is a UV light active substance in general. There are several techniques for producing TiO_2 as a visible light active substance. To begin, transition metal doping in the TiO_2 lattice can broaden TiO_2's absorbance range. Second, the visible light sensitivity of TiO_2 can be greatly enhanced by the addition of dyes, dopants, and impurities. This is due to the presence of dye molecules, which can function as the device's visible-light-driven electron pump [107]. Third, incorporating organic compounds into the catalysis process can propel the photocatalytic reaction forward. In the case of photo-assisted water splitting, the H_2 and O_2 produced may recombine in a backward reaction. By modifying redox potentials, organic compounds can solve this problem. Nowadays , it had been demonstrated that by combining ethanol with the platinized TiO_2 photocatalyst during photocatalytic water splitting, oxidation of H_2 can be reduced [24,26]. They discovered that the organic compounds were oxidized first, rather than photogenerated holes producing H_2, and that this event prevents H_2 from oxidizing again. Fourth, a highly sensitive system based on visible light active heterogeneous TiO_2/WO_3 can be created. Because WO_3 has a bandgap value of 2.8 eV, it can be absorbed in a wavelength of around 440 nm, which includes fluorescent light. Thus, the TiO_2/WO_3 system demonstrated enhanced hydrophilicity via photon absorption in the visible range[108]. A fluorescent lamp with an extremely weak UV light was used. Nonetheless, high hydrophilicity was achieved. As a result, it can be concluded that hyperactive UV-sensitive TiO_2 can be used in a broader range of applications, including indoor conditions. Fifth, TiO_2 doped with nitrogen demonstrated about the significant photocatalytic activities in the visible region. Similar photocatalysts sensitive to visible light have already been reported in a variety of scientific journals. Other significant changes include TiO_2 metal-ion implantation and a reduction in TiO_2 doping. Another approach was to replace Ti sites in the Ti lattice with Cr, Fe, or Ni [109]. Furthermore, Ti^{+3} sites can be formed by creating oxygen vacancies in TiO_2 or by using the self-doping method. To create a photocatalyst with an optimal bandgap and good mechanistic properties, a thorough understanding of both hypothetical and experimental experiences is required. When conventional TiO_2 is doped with nitrogen, it can absorb more photons and thus becomes a visible light-active photocatalyst. The N doping process, on the other hand, disturbs TiO_2's redox potential. As a result, overall photocatalytic efficiency declines. As a result, whether to use nitrogen-doped TiO_2 or conventional TiO_2 is determined by the light source [110].

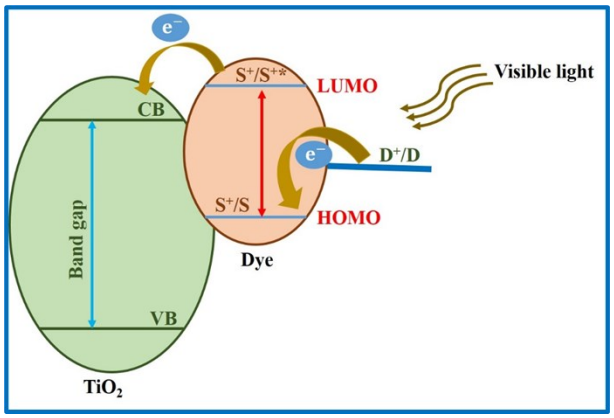

Figure 6. Schematic representation of the basic principle of dye-sensitized photocatalysis.

3.3.1 Dye sensitization

Dyes can be photocatalytically degraded by sensitizing the dye with a synthesized TiO_2 to act as the active species in the chemical reaction. The difference in valence and conduction bands of the synthesized TiO_2 affects dye degradation. When a photon (light) hits the surface of a catalyst, light-generated holes (h^+) in the valence band are easily moved to the conduction band of the nanocatalyst by the band gap shift. Dye adsorption is mainly based on the surface charge of the catalyst, catalysts play an important role in the photogenerated dynamic species [111,112]. Advanced oxidation processes use free radicals in hydroxyl and superoxide radicals to oxidize organic pollutants and lead to less toxic products such as carbon dioxide and water [113]. It is recommended for its low running costs and its simple process to improve the quality of the environment. The selection of a suitable photocatalyst is based on its stability, cost-effectiveness, and applicability in the visible light range. The materials, such as metal oxides and sulfides, have been used to break down organic pollutants in recent decades [114]. Through processes, such as sonolysis, photocatalysis, *etc.* [115]. In sensitized photocatalysis, colored compounds are adsorbed onto semiconducting surfaces; the adsorbed compound is brought into an excited state by the application of visible radiation. This molecule in an excited state injects an electron into the conduction band of the semiconductor and is oxidized to a cation radical

[116]. The cation radical generated by charge injection is less stable than the ground state of the compound and undergoes further transformation. The mechanism of sensitized photocatalysis is shown in Figure 6.

The steps involved in dye-sensitized TiO_2 photocatalysis under visible irradiation are given as follows (Equations (19)-(24)):

$$\text{Dye} + h\nu \rightarrow \text{dye}^* \quad (19)$$

$$\text{dye}^* + TiO_2 \rightarrow \text{dye}^{\bullet+} + TiO_2\,(e^-) \quad (20)$$

$$TiO_2\,(e^-) + O_2 \rightarrow TiO_2 + O_2^{\bullet-} \quad (21)$$

$$O_2^{\bullet-} + 2H^+ \rightarrow O_2 + H_2O_2 \quad (22)$$

$$H_2O_2 + TiO_2\,(e^-) \rightarrow OH^\bullet + OH^- + TiO_2 \quad (23)$$

$$\text{Organics} + (OH^\bullet \text{ or } O_2^{\bullet-}) \rightarrow \text{degraded products} \quad (24)$$

3.3.2 Pure and doped TiO_2 photocatalysis

The photocatalytic reactivity of TiO_2 can be improved by extending its light absorption into the visible region by doping it with transition metals [117,118]. This approach introduces impurity or defect states into its band gap, thereby absorbing visible light. The dopants can be noble metals, transition metals and anions. The photoactivity of doped semiconductor photocatalysts depends on the doping ion nature and concentration, the manufacturing process, and the thermal and reductive treatments [119]. Figure 7 shows the electron capture properties of a metal in contact with a semiconductor surface across its Schottky barrier.

TiO_2 can also be coupled to a narrow bandgap semiconductor with a higher conduction band than TiO_2. In the coupling of two semiconductors (e.g. CdS and TiO_2), CdS has a small band gap (2.5 eV) and can be excited in the visible part of the solar spectrum, but a TiO_2 can excite in the near UV [120]. A photoelectron generated on CdS can be injected into the (inactivated) TiO_2 conduction band while the photohole remains on CdS (Figure 8) [120].

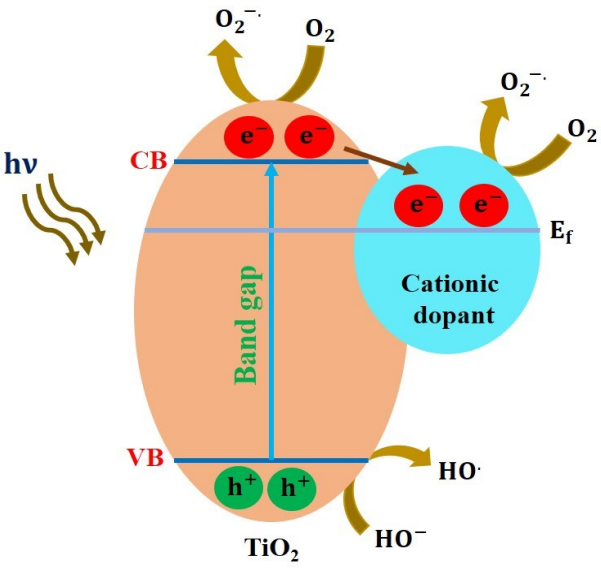

Figure 7. Schematic representation of the basic principle of metal-doped photocatalysis.

The Nobel metal-doped semiconductor photocatalysts facilitate electron-hole separation and promote interfacial electron transfer [121]. This resulted in increased quantum efficiency and so enhanced the photocatalytic activity. Also, it decreases the bandgap, which benefits the electron transfer from the valence band to the conduction band in the energy range of visible light [122,123]. Dopant level depends on the nature of dopant materials, and reaction conditions, especially the organics to be degraded. Previously, the summarized photocatalytic activity of TiO_2 particles modified with various noble metals has been presented [124-126]. These catalysts are used for the degradation of various organic molecules and also photo-splitting of water. Various transitional metal ions and rare earth metal ions were used for enhancing the TiO_2 photocatalytic activities. The improved performance in terms of activity and red-shifted photo response depends mainly on the nature of the metal ion and the preparation method. The metal ion characteristics are governed by its ability to trap the photogenerated electron. Yang *et al.* [127] reported that the preparation method influences the catalytic activity of noble metal or transition metal oxides for the degradation of formaldehyde. A more beneficiary effect was observed especially in Fe because its energy levels are near CB as well as VB edges of TiO_2. Xu *et al.* [128] compared the photocatalytic activity of various rare earth metal ions (La^{3+}, Ce^{3+}, Er^{3+}, Pr^{3+}, Gd^{3+}, Nd^{3+}, Sm^{3+}) doped on TiO_2 for the decomposition of nitrites. When compared to pure TiO_2,

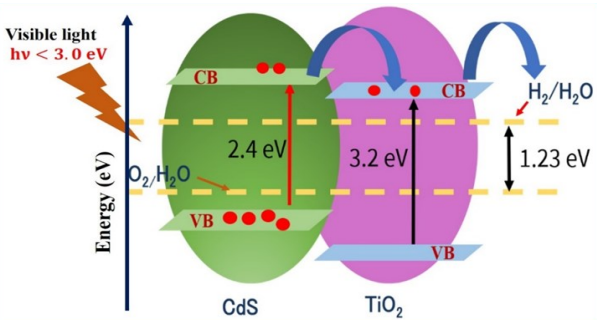

Figure 8. Schematic representation of the basic principles of coupled semiconductor oxide photocatalysis.

all samples have improved photocatalytic activity to some extent. Higher adsorption, redshifts to a longer wavelength, and an increase in the interfacial electron transfer rate contributed to the increase in photoactivity. Among these, the dopant Gd^{3+} showed the highest reaction activity because of its highest ability to transfer charge carriers to the interface. Noble metals, including Pt, Au, Pd, Rh, Ni, Cu, and Ag, have been reported to be very effective for the catalytic activity of semiconductor-mediated photocatalysis.

4. Conclusion

The enhanced water usage in households and industries had caused the persistent discharge of wastewater effluents to contaminate the environment and water resources. The contaminants of wastewater largely considered in this review are dyes and heavy metals which are toxic to the environment and human life as described. The advantages of the photocatalytic process over other conventional treatment methods, such as the effective degradation of organic pollutants by total mineralization to obtain CO, H_2O and simple inorganic ions, higher efficiency at reduced time, applicability at ambient and high temperatures, lack of sludge formation, reusability of treated water as it contains only inorganic salts, no use of chemicals and the usage of sunlight for irradiation, have been reviewed. The characteristics of TiO_2 that defines its suitability for photocatalytic removal of dyes and heavy metals with low cost and stability towards chemical reactions and corrosion have been described, while the TiO_2 limitations like reduced efficiency of incidence radiation uptake and the removal of TiO_2 particles difficulty have also been reviewed. Heterogeneous photocatalysis had been described as an emerging technique for wastewater purification, disinfection of microorganisms, water splitting to produce hydrogen fuel, and organic synthesis. Overall, the different mechanisms guiding the photocatalytic degradation of dyes and heavy metals have been investigated. The preparation techniques of modified TiO_2, such as immobilization, doping and composites of nanostructures formation, has been studied. The applications of various modified TiO_2 in the photocatalytic uptake of dyes and heavy metals have been reviewed. It had been proved that TiO_2 photocatalysis is a highly effective wastewater treatment technique, as the literature and present research interests suggest it as a highly promising research area.

Acknowledgement

This work was financially supported by the University of Malaya Research Grant (RU001-2019, RU001-2020 and RU001-2021). The authors are grateful to Mutah University for funding this work through the research group program under grant number IF019-2022.

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