

## Review Article

# An Overview: Recent Development of Titanium Oxide Nanotubes as Photocatalyst for Dye Degradation

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Today, organic dyes are one of the largest groups of pollutants release into environment especially from textile industry. It is highly toxic and hazardous to the living organism; thus, the removal of these dyes prior to discharge into the environment is essential. Varieties of techniques have been employed to degrade organic dyes and heterogeneous photocatalysis involving titanium dioxide (TiO<sub>2</sub>) appears to be the most promising technology. In recent years, TiO<sub>2</sub> nanotubes have attracted much attention due to their high surface area and extraordinary characteristics. This paper presents a critical review of recent achievements in the modification of TiO<sub>2</sub> nanotubes for dye degradation. The photocatalytic activity on dye degradation can be further enhanced by doping with cationic or anionic dopant.

## 1. Introduction

*1.1. Overview of Organic Dye Degradation.* Nowadays, global warming poses one of the most serious threats to the global environment ever faced in human history. The environment pollutions will cause an unprecedented onslaught of deadly and costly weather disasters, such as severe storms, droughts, heat waves, and rising seas and floods all over the world [1–3]. One of the major water pollutions is the residual dyes from different sources (e.g., textile industries, paper and pulp industries, dye and dye intermediates industries, pharmaceutical industries, tannery, and craft bleaching industries, etc.) which are considered a wide variety of persistent organic pollutants introduced into the natural water resources or wastewater treatment systems [4]. Dyeing and finishing industry produces as much as 50–100 L wastewater/kg of finished textile products [5]. As shown in Figure 1, World Bank has estimated that textile industries in many countries contribute to 17 to 20% of global industrial water pollution [6]. There are about 10–15% of 700 thousand tons of 10 thousand types of dyes that have been discharged without any proper physicochemical treatment [7].

There are more than 100 000 commercially available dyes and an annual worldwide production of synthetic dyes of nearly 1 million tons [8–10]. Reactive dyes have been estimated to contribute the most to the discharge of dye wastewater, as much as 57 thousand tons (Figure 2) because of their low fixation rate. As shown in Table 1, the reactive dye has a very poor fixation rates. The fixation rate is influenced by the extent of hydrolysis of the dye [11], signifying the vulnerability of reactive dyes to hydrolysis in dye bath.

The release of the persistent organic dyes structure with toxicity property may cause negative effects on the environment and human health. These negative impacts mainly attributed to the nonbiodegradable nature of the persistent organic dyes as well as their high colour intensity and are able to reduce aquatic diversity by blocking the passage of sunlight through the water [12]. In particular, the discharge of persistent organic dye effluents into the natural water resources or wastewater treatment systems is undesirable because most of these organic dyes released and their breakdown products are very toxic, carcinogenic, or mutagenic to life forms mainly due to the carcinogens, such as benzidine, naphthalene, and other aromatic compounds in the structure of persistent

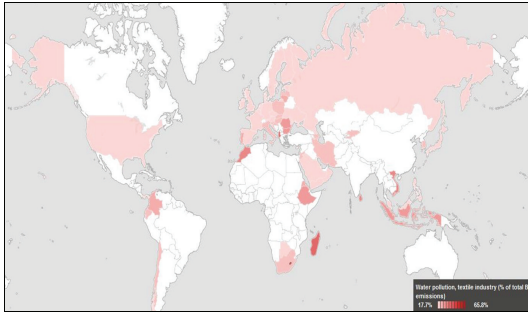


FIGURE 1: Water pollution caused by textile industrial from various countries. The darker icon signifies higher level of water pollution which is based on percentage of total biochemical oxygen demand (BOD) emissions [20].

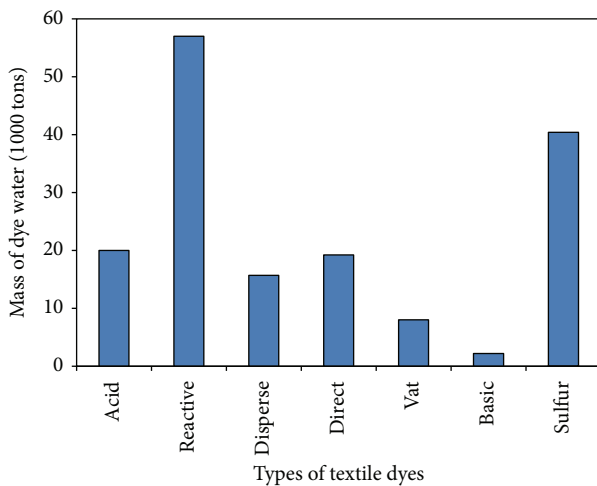


FIGURE 2: Mass loss of global dyes into the wastewater [21].

organic dyes [5, 13, 14]. These pollutants can cause irritation of the eyes, skin, respiratory tract, sore throat, asthma, and allergic contact dermatitis [15]. The persistent organic dye effluent will remain in the environment for a long period of time if incomplete or inadequate treatments during the water cleaning stage [5]. For instance, the half-life of hydrolyzed Reactive Blue 19 is about 46 years at pH 7 and 25°C [16].

Wastewater containing dyes is very difficult to treat, since the dyes are recalcitrant organic molecules, resistant to aerobic digestion, and are stable to light. Many traditional textile wastewater treatment studies have been applied at many textile mills. However, a synthetic dye in wastewater can not be efficiently decolorized by these traditional methods. This is because of the high cost and disposal problems for treating dye wastewater at large scale in the textile and paper industries [17]. As such, several wastewater treatments for colour removal can be divided into 3 categories, which include physical, chemical, and biological treatments [18, 19]. Nevertheless, most of the conventional dye removal techniques will have their respective limitations in textile industry.

TABLE 1: General fixation rates for different dye classes [22].

Dye class	Fixation rate (%)	Fibers
Acid	83 to 93	Wool, nylon
Basic	90 to 96	Acrylic
Direct	70 to 95	Cellulose
Disperse	80 to 92	Synthetic
Pigments	95 to 98	Wool
Reactive	50 to 80	Cellulose
Sulphur	60 to 70	Cellulose
Vat	80 to 95	Cellulose

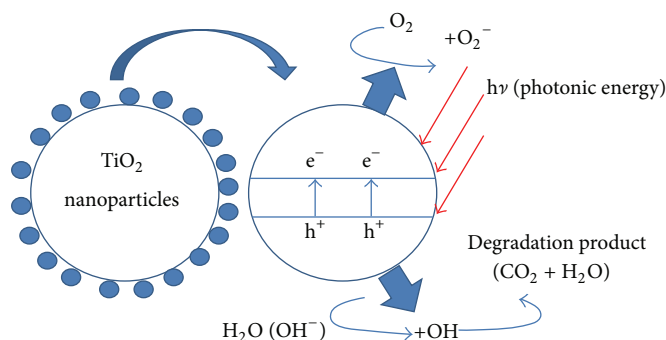
*1.2. Dye Removal Techniques.* The most popular method for the removal of pollutants from wastewater is using liquid-phase adsorption. In fact, liquid-phase adsorption provides an attractive alternative for the treatment of contaminated waters, especially if the sorbent is cheap and does not require an additional pretreatment step before its application. The adsorption is a well-known equilibrium separation process and an effective method for water decontamination applications due to the water reuse in terms of initial cost, flexibility and simplicity of design, ease of operation, and insensitivity to toxic pollutants [23]. Adsorption and ion exchange reactions play an important role in decolorization [24, 25]. This decolorization process is strongly dependent on the physiochemical factors (e.g., interaction between dye and sorbent, active surface area of sorbent, particle size, reaction time, environment temperature, and pH) [26]. The most important aspect of the adsorption technique is that no harmful substance will be generated and released throughout the reactions. Besides, the adsorption process using activated carbons has been widely used to remove persistent organic dyes from wastewaters [27, 28]. However, commercially available activated carbon is still far from being a potential candidate in dyes removal applications due to the high production cost and regeneration problems [2]. The regeneration activated carbons involve restoring the adsorptive capacity of saturated activated carbon by desorbing adsorbed dyes on its surface. In addition, the adsorption involves a phase transfer of pollutants to other secondary wastes that subsequently require additional treatment of proper disposal procedure.

In general, several types of filtration technology (physical methods) have been widely used for wastewater and textile effluents treatment, such as membrane-filtration processes (microfiltration, ultrafiltration, nanofiltration, and reverse osmosis) and adsorption techniques [23, 29–33]. However, major disadvantages of the membrane-filtration processes are that they are only applied in small wastewater flow rate, require higher production cost of membrane and cost of periodic replacement, require high working pressure to push the wastewater flow through membrane filtration, and are unable to reduce dissolved solid content. In addition, this technique requires frequent cleaning and replacement of the modules to maintain effectiveness in removing organic dyes.

Besides, biodegradation of organic dyes is often the most economical alternative as compared to physical and chemical processes. The possible microorganisms used for

TABLE 2: Oxidation potential of several powerful oxidants [34].

Oxidant	$\cdot\text{OH}$ (hydroxyl radical)	$\text{O}_3$ (ozone)	$\text{H}_2\text{O}_2$ (hydrogen peroxide)
Oxidation potential (V)	2.80	2.07	1.77

FIGURE 3: Overall mechanism of the photocatalytic degradation of organic dye compounds using  $\text{TiO}_2$ -based nanomaterial.

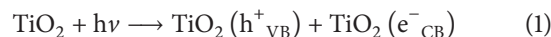
biodegradation dyes are fungi, bacteria, yeasts, and algae. They are involved in fungal decolourization, microbial degradation, and adsorption by (living or dead) microbial biomass and bioremediation systems that are commonly applied to the treatment of industrial effluents [9, 35]. However, the limitations of this technique are often restricted because of technical constraint. The high toxicity of some chemicals could decrease the numbers of active organisms used in the aerobic biological process and long hydraulic retention time [36]. In addition to that, biodegradation of organic dyes normally is incapable of obtaining satisfactory colour elimination with current conventional biodegradation processes [37]. In this manner, many other organic dyes are recalcitrant due to their complex chemical structure and synthetic organic origin [38]. In this case, azo dyes are not totally degraded or show slow degradation because of their xenobiotic nature [39].

The chemical treatment includes coagulation and flocculation for separation of dyes. The major disadvantages of these techniques are high cost of coagulating or flocculating agent and pH dependency for effective dye removal as well as disposal problem resulted from accumulation of concentrated sludge. In addition, secondary pollution problems will arise due to the excessive chemical used. Meanwhile, the main reaction involved in chemical wastewater treatment is ion exchange, which is ineffective in removing several types of persistent organic dyes. The low removal in the case of anionic dyes (disperse dyes), diffusion limitation that can affect reaction rate while the use of organic solvent for regeneration is very expensive [18] and thus, they are commercially unattractive.

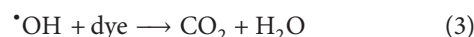
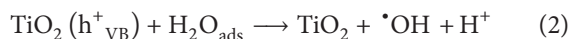
**1.3. Photocatalytic Degradation of Organic Dye by Titanium Dioxide.** In recent years, photocatalysis system has attracted great interest from science community as the most promising way to solve the environmental problems, especially getting rid of residual dyes pollutants from wastewater stream [2, 40–42]. In this manner, photocatalysis system is considered to

be ideal green environmental solution to realize our green economy future. In this case,  $\text{TiO}_2$ -based nanomaterials have been broadly studied as the most promising photocatalyst for environmental remediation such as air purification, water purification, heavy metals degradation, and hazardous waste remediation [3, 43–49]. The reasons mainly attributed to the nontoxicity, cost effective, long-term stability, widespread availability, and high stability against photocorrosion with great capacity for oxidation and high photocatalytic property. The development of the nanoarchitecture of  $\text{TiO}_2$  assemblies with precisely controllable nanoscale features has gained significant scientific interest [42–54].

According to Ibhaddon and Fitzpatrick (2013) [34], the principle behind the photocatalysis involves the photoexcitation of the metal oxides with light energy (Figure 3). In this case, only UVL ( $\lambda \leq 387 \text{ nm}$ ) greater than the band gap of the anatase  $\text{TiO}_2$  ( $E_{\text{bg}} = 3.2 \text{ eV}$ ) generates electron-hole pairs as shown in (1). The photoinduced electrons and holes diffuse to the particle surface of the  $\text{TiO}_2$ , in which they can be exploited for various redox processes analogous to those of an electrochemical cell. The positive holes react with water, an electron donors, to produce the most crucial and powerful oxidizing free radicals,  $\cdot\text{OH}$  ((2) and Table 2). Thus, any organic compound adsorbed on the surface of the photocatalysts is oxidized by  $\cdot\text{OH}$  (3). The photoexcited negative electrons react with oxygen to become superoxide radicals,  $\text{O}_2^{\cdot-}$ , and perform the similar oxidative attack on organic compounds. Consider



where  $\text{TiO}_2(h^+_{\text{VB}})$  is the positive hole in valence band (VB) and  $\text{TiO}_2(e^-_{\text{CB}})$  is the photoexcited electron in conduction band (CB) (Figure 4). Consider



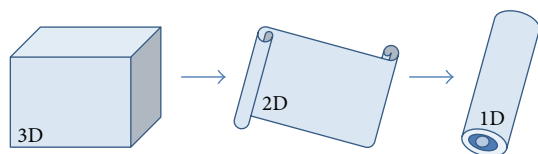
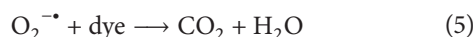
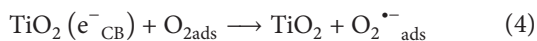


FIGURE 4: A schematic model for the formation of TiO<sub>2</sub> nanotubes [55].



In this manner, TiO<sub>2</sub> can act as an ideal semiconductor material for photocatalysis because it is nontoxic, relatively cheap, and highly photostable. It is interesting to note that TiO<sub>2</sub> exists in six different polymorphs, namely, rutile (tetragonal), anatase (tetragonal), brookite (orthorhombic), TiO<sub>2</sub> (B) (monoclinic), TiO<sub>2</sub> (II) (alpha-PbO<sub>2</sub>), and TiO<sub>2</sub>(H) (hollandite) [56, 57]. TiO<sub>2</sub> nanoparticle has been widely used as an active photoelectrode applied in variety of environment and energy system since the discovery by Fujishima and Honda [58]. In particular, the particulate TiO<sub>2</sub> in the form of suspension requires appropriate substrates as support to form compacted film [44, 59]. TiO<sub>2</sub> possessing a large bandgap energy of 3.2 and 3.02 eV for anatase and rutile, respectively. Thus, they only can be excited under UV light irradiation. When TiO<sub>2</sub> is excited by UV light irradiation, electrons from valence band will jump to the conduction band leaving behind positive holes (h<sup>+</sup>) [34]. The electrons and holes diffuse to the particle surface of the TiO<sub>2</sub> in which they can be exploited for various redox processes analogous to those of an electrochemical cell. The holes react with water, an electron donor, to produce the most crucial and powerful oxidizing free radicals capable of degrading the organic dyes.

However, the major drawback of such nanoparticle TiO<sub>2</sub> is the random pathway of photoinduced electrons during photocatalytic reactions, which will eventually lead to the recombination through trapping/detrapping of electron/hole pairs as well as longer electron transporting time in the particulate TiO<sub>2</sub>. In addition to that, the probability of recombination losses of photoinduced charge carriers will be increased significantly due to the presence of defects or trapping sites, more grain boundaries, and disordered contact areas [50, 60–63]. Meanwhile, it was found that two-dimensional TiO<sub>2</sub> thin film is able to eliminate the reusability of photocatalyst issues and ease the filtration procedure after photoreaction [47, 50]. In order to further maximize specific surface area of TiO<sub>2</sub> thin film for better photons absorption from illumination, design and development of TiO<sub>2</sub>-based nanostructure assemblies have gained significant interest and triggered enormous effort in physics, chemistry, and material science [45–47, 50, 51, 60]. In this paper, the nanotubular structure of TiO<sub>2</sub> is extensively reviewed. This is because TiO<sub>2</sub> nanotubes are becoming more popular due their high photocatalytic activity for various types of dye degradation.

## 2. Preparation of TiO<sub>2</sub> Nanotubes

TiO<sub>2</sub> nanotubes can be produced by several methods such as using a template of nanoporous alumina [64], sol-gel transcription process using organogelator templates [65], seeded growth mechanisms [66], and hydrothermal techniques [67–69]. However, none of these methods offer superior control on the nanotube dimensions than the electrochemical anodization technique [52, 70, 71]. In the following sections, several techniques to prepare TiO<sub>2</sub> nanotubes were discussed.

**2.1. Sol-Gel Transcription Synthesis.** Sol-gel transcription process is a wet-chemical technique used to synthesize oxides at relatively low temperature. The process consists of hydrolysis of precursor species and subsequently polycondensation to form solid network which is known as gel. The common precursors employed in sol-gel processing are metal alkoxides and metal chlorides. This sol-gel template processing making use of porous alumina, polymer fibers or super molecular compound as a template, and their diameters was normally larger than 50 nm [72–74]. The walls of the TiO<sub>2</sub> nanotubes, prepared by deposition in porous alumina membrane, consisted of anatase nanoparticles and contained mesopores arising from the spaces between the anatase particles [75, 76]. Hoyer's research team firstly reported the formation of the pore diameter of 70–100 nm TiO<sub>2</sub> nanotubes via sol-gel transcription process in 1996.

Sol-gel transcription process in formation of high-ordered TiO<sub>2</sub> nanotubes was reported by Kang et al. (2009) [77]. In this report, titanium isopropoxide, Ti(OC<sub>3</sub>H<sub>7</sub>)<sub>4</sub>, in ethanol was used as precursor. The TiO<sub>2</sub> nanotubes were grown on an alumina template. Then, the resultant sample was dried at room temperature for 12 hours in an ambient environment and calcined at 500°C to convert into crystalline phase. After that, the isolated TiO<sub>2</sub> nanotubes were obtained by removing the alumina template. However, the main drawback of sol-gel method is that it is difficult to form aligned and well-ordered nanotubular structure. Besides that, this method is time consuming because it is relatively difficult to remove the solvent and organic by-products and not practical from the economic point of view due to high chemical and energy consumption. Furthermore, raw materials used in this experimental works are expensive and caused many research groups to try to find an alternative way to produce TiO<sub>2</sub> nanotubes.

**2.2. Hydrothermal Synthesis.** Hydrothermal synthesis can be defined as a heterogeneous reaction in the presence of aqueous solvents or mineralizers under high pressure and temperature. This is an important technique to produce big, pure, and dislocation-free single crystals [78–80]. The crystal growth is performed in a steel pressure vessel known as autoclave where nutrient is supplied along with water. A temperature gradient needs to be maintained in the growth chamber so that the hotter end dissolves the nutrient whereas the cooler end causes seeds to take additional growth. The growth rate of the seeds will increase with increasing

TABLE 3: Comparison of the most widely used synthesis methods for preparing TiO<sub>2</sub> nanotubes.

Synthesis method	Characteristics
Sol-gel transcription process	(a) Ordered arrays (b) Advantages: the scale of nanotubes can be controlled by the applied template (c) Disadvantages: the nanotubular structure can be damaged or destroyed during the after removal of the templates; raw materials used are expensive
Hydrothermal synthesis	(a) Random alignment (b) Advantages: easy route to obtain nanotubes in relatively large amount (c) Disadvantages: difficulty in producing uniform size of nanotubular; long reaction duration; and random distribution of nanostructured tubes
Electrochemical anodization	(a) Oriented arrays with high aspect ratio (b) Advantages: self-organized anodic oxides in the form of nanotubular structures with almost perfect vertical, relatively simple alignment and can be adopted for large-scale industrial production (c) Disadvantages: fabrication apparatuses are costly; massive organic waste will be produced after the anodization process

concentration of solvent, crystallization temperature, and temperature gradient [76, 81, 82].

In a typical hydrothermal experiment, the TiO<sub>2</sub> nanoparticle powder is processed in alkaline solution such as NaOH in a Teflon-lined autoclave at a temperature up to 150°C for time range from 15 h and above [69]. TiO<sub>2</sub> nanoparticles will transform to nanotubes when the reactive Na<sup>+</sup> and OH<sup>-</sup> species react with TiO<sub>2</sub> and forms Ti–O–Na and Ti–OH bonds. At this stage, the particles will be transformed to lamellar structure and finally roll up to form tubular structure to reduce the high energy [68, 83]. Figure 4 shows the schematic model for the formation of TiO<sub>2</sub> nanotubes. However, the main drawback of hydrothermal technique is the inability to form nanostructured tubes which are well aligned and ordered. Besides that, hydrothermal treatment required long reaction duration and addition of highly concentrated NaOH having difficulty in obtaining uniform size of TiO<sub>2</sub> nanotubes.

**2.3. Electrochemical Anodization Synthesis.** Highly ordered and vertically oriented TiO<sub>2</sub> nanotubes can be fabricated by potentiostatic anodization of Ti metal under suitable electrolyte and processing conditions. TiO<sub>2</sub> nanotubes are gained after the process which initially involves the formation of barrier layer and followed by rather well-defined nanoporous structure [51, 53, 84, 85]. The Ti metal was used as substrate for TiO<sub>2</sub> nanotubes to grow. The amorphous TiO<sub>2</sub> nanotubes can be obtained at the end of the anodization process. This amorphous phase of nanotubes needs to be crystallized via high temperature annealing process [70, 86, 87].

Electrochemical anodization is an electrolytic process that creates a protective or decorative oxide layer over a metallic surface [88]. Synthesis of TiO<sub>2</sub> nanotubes using electrochemical anodization method is preferred due to the simplicity in preparation and handling and being more controllable than the other methods [58]. Generally, vertically oriented nanotubes offer large specific surface area, which have tube-like structures with circular nanotubular opening that serve as a scaffold to anchor light-harvesting assemblies [50, 51]. The diameter of the opening ranges from 20 nm to

350 nm and the length of the tube can vary from 0.2 μm to 1000 μm depending on the processing parameter. The bottom part of the nanotubes which are in the form of domes is called barrier layer with typical shape of hexagonal or pentagonal [89–91].

In anodizing cell, Ti is used as an anode and it is connected to positive terminal of power source, whereas platinum is used as cathode being connected to negative terminal of power source [84, 92]. There are few other candidates for cathode, which consist of carbon, lead, nickel, or stainless steel. The cathode has to be an inert electrode and nonreactive in the electrolyte bath [90, 93]. Generally, the geometrical feature of the nanotubes is controlled by a variety of parameters such as anodization potential, electrolyte composition, and properties such as conductivity and viscosity, as well as anodization time and temperature. From theoretical perspective, an anodic oxide layer growth involved field-assisted oxidation of anodic Ti film. The high electric field across the anodic oxide layer will induce the Ti–O bond polarization. Then, Ti–O polarization will lead to the pit formation. These random pits will then etch into nanotubular structure in the presence of fluoride ions via chemical dissolution reaction. The comparison between the unique features of sol-gel transcription process, hydrothermal synthesis, and electrochemical anodization techniques is summarized in Table 3.

### 3. Titanium Dioxide Nanotubes for Dye Degradation

In this manner, one-dimensional TiO<sub>2</sub> nanotubes are considered a promising candidate because of their inner and outer wall surface area of nanotube that greatly increases the active sites available for photon absorption [43, 48, 50, 80, 94]. One-dimensional TiO<sub>2</sub> with well-aligned nanotube arrays provides unique electronic properties, such as high electron mobility, low quantum confinement effects, and high mechanical strength [95–97]. Furthermore, vertical charge transport in well-aligned TiO<sub>2</sub> nanotube structure greatly contributes to better photocatalytic efficiency due to the

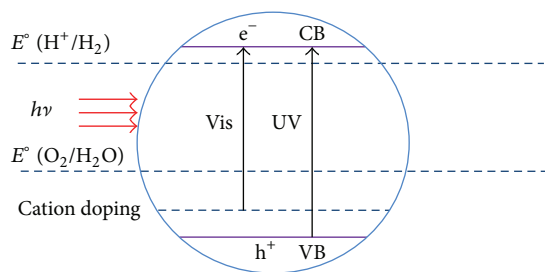


FIGURE 5: Band structure of a cationic loaded on wide band gap of semiconductor photocatalyst with visible light response [105].

grains of  $\text{TiO}_2$  that are stretched in the tube growth direction and low recombination losses at grain boundaries as compared to randomly oriented particulate  $\text{TiO}_2$  [47, 50, 63, 97]. Quan et al. (2005) [98] have reported that  $\text{TiO}_2$  nanotubes give a higher kinetics constant than  $\text{TiO}_2$  nanoparticles for photoelectrochemical degradation of pentachlorophenol. In terms of dye degradation in  $\text{TiO}_2$  nanotubes, it is also performed far much better as compared to that of  $\text{TiO}_2$  nanoparticles. Xu et al. (2011) [99] show that  $\text{TiO}_2$  nanotubes efficiency was two times much better than nano- $\text{TiO}_2$  in degrading Acid Orange 7 dye.

**3.1. Cationic Doping on Titanium Dioxide Nanotubes.**  $\text{TiO}_2$  nanotube is considered the noble photocatalyst in organic dye degradation because of its many intrinsic properties [88, 100], but it has its own limitations which are critical to photocatalytic techniques such as recombination of photogenerated electron-hole pairs, fast backward reaction, and inefficient visible light utilization. These drawbacks are very much related to the wide band gap of  $\text{TiO}_2$  nanotubes. In fact,  $\text{TiO}_2$  nanotube can only effectively function under the UV region ( $\lambda < 400$  nm) and it only contains about 4-5% of UV rays from our solar energy. Thus, the efficient use of visible light from our solar energy is essential for effectively degrading organic dye. These drawbacks can not be overcome by only optimizing the dimensions of  $\text{TiO}_2$  nanotube itself. Therefore, considerable efforts that have been exerted to solve these drawbacks by modifying  $\text{TiO}_2$  nanotubes with the addition of electron donors (hole scavengers), carbonates salts, metal ion doping [101], anion doping [102], and dye sensitization [62] have been investigated. Among these, doping of  $\text{TiO}_2$  using metal ions (Fe, Cr, V, Nb, Si, Al, Li, Na, K, Cu, Mn, Co, and Gd) and nonmetal (C, N, S, and P) has reported to show a promising result under visible light irradiation though the mechanism under which this process occurs still remains controversial. The following are some of the attempts made to modify the electronic structures of  $\text{TiO}_2$  nanotubes to improve their effectiveness under visible light.

In 2004, Komornicki et al. [103] proposed that binary oxide photocatalysts are promising candidates with enhanced properties for photocatalytic system. Such photocatalysts may benefit from the combination of the best properties of their pure components and modification of the electronic structure of the system could be expected. Later, in 2006,

Higashimoto et al. [104] suggested that binary oxide photocatalyst can promote better charge carriers separation by accumulating electrons and holes in two different semiconductor layers with suppression of charge carriers recombination. The useful features of the individual components in the mixed oxide systems can be complementary with each other, while alleviating the disadvantages at the same time. Generally, numerous studies have proved that visible light absorption of  $\text{TiO}_2$  photocatalyst could be improved and recombination of charge carriers could be suppressed by coupling with another cationic species [43, 105–107]. The replacement of cationic ions within the crystal lattice may create impurity energy levels that facilitate better absorption in the visible light region, as depicted in Figure 5. Furthermore, different redox energy levels for their corresponding conduction and valence bands provide another attractive approach to achieve much more efficient charge carrier separation to minimize the recombination losses. When  $\text{TiO}_2$  photocatalyst is loaded with sufficient content of cationic species in lattice, the electrons would be injected from the semiconductor with a more negative CB level to the positive one, while holes would be transferred from the semiconductor with a more positive VB level to the negative one. Thus, separation of charge carriers could be achieved; as a consequence, the lifetime of the charge carriers and the efficiency of the interfacial charge transfer to water are increasing significantly [49, 100, 108].

Based on the literature, majority of the cationic species-loaded  $\text{TiO}_2$  photocatalysts studied were prepared using the coprecipitation, incipient wet impregnation method and sol-gel method. Details of the cationic species-loaded  $\text{TiO}_2$  photocatalysts by several researchers and their findings are summarized in Table 4. Transitional metal and rare earth metal ions have been tried as dopants to improve the photocatalytic efficiency of  $\text{TiO}_2$  in the visible light region. However, performances of those binary oxide photocatalysts were strongly dependent on the content of cationic dopants. The impurity levels created by cationic dopants in the binary oxide photocatalyst are usually discrete, which would appear disadvantageous for the migration of the charge carriers if the content of cationic dopants exceeds the optimum value [43, 47, 109]. Furthermore, there are a few drawbacks of cationic species doping such as different morphological and crystalline properties of the photocatalyst due to different methods of doping and the shift of the absorption edge in the metal ion doped system may have a complex origin, due to either homogeneous substitution of  $\text{Ti}^{4+}$  or segregated  $\text{M}_x\text{O}_y$  clusters.

Although cationic species doping can improve the visible spectrum response, the photogenerated electron-hole pair lifetime decreases causing the overall efficiencies to be at similar level [126]. This reason might be attributed to the doped sites that often behave as recombination centers for photogenerated charged carriers due to the substitution of  $\text{Ti}^{4+}$  with metallic ions. Also, transition metal species-loaded  $\text{TiO}_2$  samples often suffer from thermal instability. These cause the photocatalytic activity of cationic species-loaded  $\text{TiO}_2$  to often decrease because of the thermal instability or an increase in carrier recombination centers [127, 128]. Thus,

TABLE 4: Summary of the works reported on the different cationic-loaded TiO<sub>2</sub> photocatalyst.

Cationic	Author (year)	Findings	Reference
Cu	Li et al. (2008)	Cu ions on TiO <sub>2</sub> nanotubes effectively acted as electron trappers prohibiting the recombination of photoexcited electrons and holes in Cu-loaded TiO <sub>2</sub> nanotubes, hence improving the photocatalytic degradation of Rhodamine B under UV light irradiation within 50 min. The catalytic performance is also better than the undoped TiO <sub>2</sub> nanotubes.	[110]
Pd	Mohapatra et al. (2008)	Self-organized TiO <sub>2</sub> nanotubes with Pd nanoparticles were found to be an excellent photocatalyst that can decompose nonbiodegradable azo dyes (methyl red and methyl orange) due to the fact that lifetime of the charge carriers has been increased significantly	[111]
Ru	Khan et al. (2009)	Doping of Ru by the ion exchange method to the hydrothermally synthesized TiO <sub>2</sub> nanotube was found to be an effective photocatalyst active under visible light for degradation of methylene blue dye	[112]
Fe	Deng et al. (2009)	The methyl orange was completely degraded using 0.5% Fe-doped TiO <sub>2</sub> nanotubes under UV light irradiation within 3 h	[113]
Nd	Xu et al. (2009)	Nd-doped TiO <sub>2</sub> nanotubes showed a high photocatalytic activity by degrading 99.6% of methyl orange within 20 min under UV irradiation	[114]
W	Xiao et al. (2009)	5 wt% of W-loaded TiO <sub>2</sub> nanotubes enhanced photocatalytic activity of RhB degradation compared to the pure TiO <sub>2</sub> nanotubes due to the better charge separation efficiency and the extension of the wavelength range of photoexcitation	[115]
Co	Hsieh et al. (2009)	Codoped TiO <sub>2</sub> nanotubes showed a promising candidate in a photocatalysis degradation of basic Violet 10 Dye under visible light irradiation	[116]
W	Paramasivam et al. (2010)	The improvement of the photocatalytic degradation of Rhodamine B was observed for the addition of low WO <sub>3</sub> content (0.2 at.% W) to the Ti nanotubes	[59]
W	Sajjad et al., (2010)	4% WO <sub>x</sub> -TiO <sub>2</sub> nanotubes composite demonstrated the best reactivity under visible light in degradation of acid Orange 7 Dye	[117]
La	Wu et al. (2010)	La-doped TiO <sub>2</sub> nanotubes have been tested by using methyl orange dye under UV light irradiation.	[118]
Cu	Ma et al. (2010)	Cu-doped TiO <sub>2</sub> nanotube has been employed to degrade methyl orange. However, only 21% of methyl orange was removed using Cu-doped TiO <sub>2</sub> nanotube arrays after 240 min of UV illumination	[119]
W	Das et al. (2011)	The high efficiency of photodegradation of Rhodamine B is observed for the 0.2 at.% W content	[120]
Pt	Su and Deng (2011)	The Pt-doped TiO <sub>2</sub> nanotubes possess high photocatalytic activity for degrading methyl orange under UV and visible light irradiation	[121]
Fe	Pang and Abdullah (2012)	The Fe-doped TiO <sub>2</sub> nanotubes were evaluated based on oxidation of Rhodamine B under ultrasonic irradiation	[122]
Fe	Wu et al. (2012)	The incorporation of Fe into TiO <sub>2</sub> nanotubes has increase the efficiency of methylene blue degradation under visible light region	[123]
Cu	Sreekantan et al. (2014)	Cu loaded on TiO <sub>2</sub> nanotube arrays demonstrates the highest photocatalytic activity with 84% degradation of methyl orange under visible light	[124]

TABLE 4: Continued.

Cationic	Author (year)	Findings	Reference
Bi	Natarajan et al. (2013)	Bismuth-doped TiO <sub>2</sub> nanotubes were successfully synthesized and capable of degrading Rhodamine B completely under direct sunlight	[125]

making intuitive prediction is impossible, and conducting a focused research is challenging. It is important to fine-tune the content of the cationic substitution into TiO<sub>2</sub> photocatalysts to develop an efficient visible light driven photocatalyst.

**3.2. Anionic Doping on Titanium Dioxide Nanotubes.** Anion doping is another type of elemental doping to modify the band gap of TiO<sub>2</sub> nanotubes. It has been proven that anion-doped TiO<sub>2</sub>, such as nitrogen-, carbon-, phosphorus-, or sulphur-doped TiO<sub>2</sub>, exhibits visible photoresponse and reduced the band gap of native TiO<sub>2</sub>. According to Tang and Li (2008), this is because the atomic orbitals of nonmetal elements (e.g., N<sub>2p</sub>, S<sub>3p</sub>, and C<sub>2p</sub>) have higher potential energy than O<sub>2p</sub> [129]. This will form a new VB instead of a pure O<sub>2p</sub> atomic orbital which reduce the band gap energy without affecting the conduction band level. This doping required the creation of surface oxygen vacancies where the anions will incorporate into the anatase as well as rutile by substitution in oxygen lattice sites [130].

The nonmetal ion doped catalysts are better for extending the photocatalytic activity of TiO<sub>2</sub> into visible region compared to metal cationic species loading methods because their impurity states are near the VB edge and their roles as recombination centers may be minimized. Table 5 shows the characteristics of anion-doped TiO<sub>2</sub>. However, the photocatalytic activity of conventional TiO<sub>2</sub> doped with nonmetal elements is still limited or at early stage. It is expected that a combination of doping elements could result in a marked increase in the photocatalytic activity of TiO<sub>2</sub> under both UV and visible light. Most of the researchers have doped the TiO<sub>2</sub> with nitrogen in order to enhance the photocatalytic activity and expand the photoactivity response toward the visible light region. In addition, codoped species may be more appropriate for extending the photocatalytic activity of TiO<sub>2</sub> into the visible light region. For example, nonmetal codoping of TiO<sub>2</sub> such as F-B-codoping, C-N-codoping, and S-N-codoping was studied to further enhance the visible light activity.

The purpose of the modification of TiO<sub>2</sub> is believed to improve the performance of TiO<sub>2</sub> nanotubes by introducing new energy level into the forbidden gap, therefore causing the effect of band gap narrowing and provide site that slow down the recombination process. This improved the performance of the TiO<sub>2</sub> nanotubes in photocatalytic degradation of organic dyes [131]. The following sections are some of the attempts made to modify the electronic structure of TiO<sub>2</sub> nanotube to improve its effectiveness under visible light. The electronic structure of TiO<sub>2</sub> by the substitution of metal

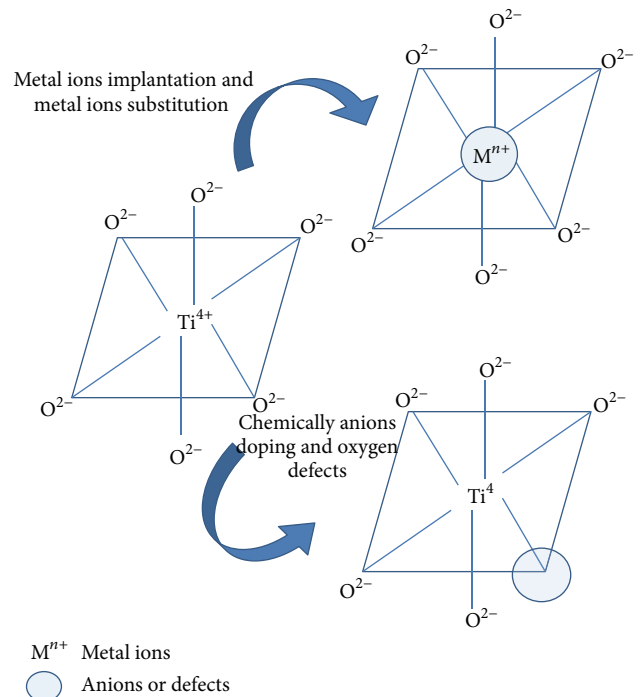


FIGURE 6: Electronic structure of TiO<sub>2</sub> by the substitution of metal ions or anions to harvest visible light response [101].

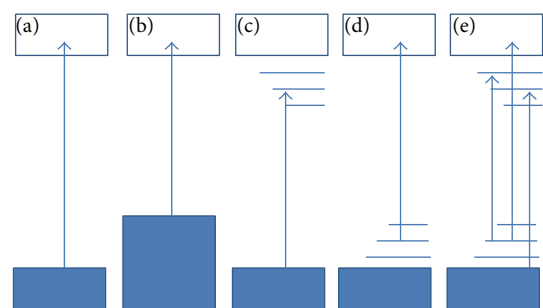


FIGURE 7: Various schemes illustrating the possible band gap electronic structure and excitation processes of visible-light-responsive TiO<sub>2</sub> materials: (a) pure TiO<sub>2</sub>; (b) band gap narrowing model for nonmetal-doped TiO<sub>2</sub>; (c) oxygen-deficient TiO<sub>2</sub>; (d) localized mid-gap level model for nonmetal-doped TiO<sub>2</sub>; (e) oxygen vacancy and nonmetal-doped mid-gap levels are considered together [41].

ions or anions to harvest visible light response is shown in Figure 6. The various schemes illustrating the possible band gap electronic structure and excitation processes of visible-light-responsive TiO<sub>2</sub> materials are shown in Figure 7.



TABLE 5: Summary of the works reported on the different anionic-doped TiO<sub>2</sub> photocatalysts.

Anionic	Authors	Findings	Reference
N	Dong et al. (2009)	N-doped TiO <sub>2</sub> nanotubes exhibit enhanced photocatalytic degradation of methyl orange under visible light irradiation by narrowing the band gap energy	[132]
N and C	Liu et al. (2009)	The C–N doping shifts the absorption edge of TiO <sub>2</sub> nanotubes to the visible light regions and promotes the charge carrier transfer from the TiO <sub>2</sub> surface to the electrolyte. The C–N doped TiO <sub>2</sub> higher photocatalytic activity in the degradation of methyl orange than the undoped TiO <sub>2</sub> nanotubes	[133]
N	Lai et al. (2010)	The N-doped titanium dioxide nanotubes exhibited higher photocatalytic activity in degrading methyl orange under UV and simulated sunlight irradiation	[134]
N	Peng et al. (2010)	N-doped titanate nanotubes completely degraded methyl orange within 240 minutes under 15 W fluorescent lamps	[135]
N and Zr	Liu et al. (2010)	N/Zr-codoped TiO <sub>2</sub> nanotubes significantly improved the photocatalytic efficiency of TiO <sub>2</sub> nanotube arrays under both UV and visible light irradiation	[136]
N	Z. He and H. Y. He (2011)	The N-doped TiO <sub>2</sub> nanotubes with 25.7 at.% nitrogen content were capable of degrading methyl orange under visible and sunlight irradiation	[137]
N and C	Wang et al. (2011)	The photocatalytic activity of the codoped TiO <sub>2</sub> nanotubes with C and N shows a superior photocatalytic activity in degradation of Rhodamine B under visible light irradiation	[102]
N	Wang et al. (2012)	N-doped TiO <sub>2</sub> nanotubes associated with iron oxide photocatalyst successfully decomposed methyl orange in air under visible light irradiation	[138]
N	Lv et al. (2012)	N-doped TiO <sub>2</sub> nanotubes showed further enhancement in photodegradation activity of methylene blue in the visible region	[139]
N and F	Lee et al. (2012)	F–N-codoped TiO <sub>2</sub> nanotubes effectively photodegraded the aniline blue dye within 200 min under visible light irradiation	[140]
F and S	Liao et al. (2012)	The binary F- and S-doped TiO <sub>2</sub> nanotubes were capable of degrading methyl orange using xenon lamp to simulate natural sunlight	[141]
N	Dang et al. (2012)	N-doped TiO <sub>2</sub> nanotube array films effectively degraded 81% of methyl orange in 150 min under visible light irradiation	[142]
N and S	Wang et al. (2013)	Thiourea-doped TiO <sub>2</sub> nanotubes composed of N and S successfully decomposed 81.5% of methyl orange under visible light illumination within 90 min	[143]
N	Yuan et al. (2013)	The N-doped TiO <sub>2</sub> exhibited higher photocatalytic degradation of methyl orange as compared to undoped TiO <sub>2</sub> under UV and visible light irradiation	[144]

#### 4. Conclusion and Future Works

Nanosize TiO<sub>2</sub> especially TiO<sub>2</sub> nanotubes seems to be the most promising photocatalyst for organic dye degradation. It is very obvious that many researchers have been trying to synthesize not only higher active surface area of nanotubes but also sunlight-driven photocatalyst for effective dye degradation. The industrial application of TiO<sub>2</sub> nanotubes is anticipated for the future due to its high photocatalytic

activity, photostability, and nontoxicity. Nevertheless, further modifications are essential to improve its photocatalytic activity under the direct sunlight irradiation. Thus, various potential cationic and anionic elements have been employed to increase TiO<sub>2</sub> nanotubes efficiency for organic dye degradation under sunlight irradiation. It is believed that TiO<sub>2</sub> nanotubes still permit extensive and in-depth study on the electronic and lattice structure in order to truly understand the effect of different doping method and elements on TiO<sub>2</sub>

nanotubes. This is crucial because it is obvious that same elements with different doping methods demonstrated a different photocatalytic activity on dye degradation.

### Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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