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Review Article

An Overview on the Photocatalytic Activity of Nano-Doped-TiO_2 in the Degradation of Organic Pollutants

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This paper aims to review and summarize the recent works on the photocatalytic degradation of various organic pollutants in the presence of nano-doped-TiO_2 photocatalysts. In this regard, three main aspects are examined: (a) the presence of various dopants (metal dopants, nonmetal dopants, halogen dopants, metalloid dopants, and codopants) in the formation of nano-doped-TiO_2 photocatalysts, (b) the effect of the presence of dopants on the photocatalytic degradation of organic pollutants, and (c) the effects of various operating parameters on the photocatalytic degradation of organic pollutants in the presence of nano-doped-TiO_2 photocatalysts. Reports resulted suggest that the formation of a high percentage of the anatase phase, small crystallite size, and high specific surface area of the nano-doped-TiO_2 photocatalysts depends on the presence of various dopants in the photocatalysts. The majority of the dopants have the potential to improve the photocatalytic efficiency of nano-doped-TiO_2 in the degradation of organic pollutants. The photocatalytic degradation of organic compounds depends on the calcination temperature of the prepared doped TiO_2, initial reactant concentration, dosage of doped TiO_2, and dopant doping concentration.

1. Introduction

Water reuse has emerged as a critical issue in preserving global water resources in recent times. In many developing countries, industries contribute around 22% of the total world water usage and around 70% of untreated industrial wastes are simply discarded into wastewater without prior filtering or processing. The world faces enormous challenges ahead as drinkable water runs short due to natural disasters, population increase, and water pollution. To address these problems, advanced oxidation processes (AOPs) play an important role in the wastewater treatment. In AOPs, highly reactive radicals are generated that can treat the toxic and nondegradable pollutants in the wastewater efficiently without involving complex technologies [1].

The nano-TiO_2 photocatalyst is a well-known photocatalyst among the metal oxides recognized for its high efficiency, low cost, physical and chemical stability, widespread availability, and noncorrosive property [2]. When nano-TiO_2 is irradiated with ultraviolet (UV) light, electron is promoted from the valence band to the conduction band, resulting in the generation of energized "holes" in the former. Free electrons react with the oxygen to form superoxide radical anions ($O_2^{\bullet -}$), while energized holes react with water (H_2O) or hydroxyl ion (OH^-) to form hydroxyl radicals ($^{\bullet}OH$). However, these reactive species are lost when the excited electrons and energized holes recombine without invoking a photocatalytic effect. Such electron-hole recombination diminishes the efficiency of photocatalysis.

To achieve high photocatalytic degradation efficiency, nano-TiO_2 should be mesoporous and should exhibit high crystallinity and high specific area [3]. Nano-TiO_2 is normally synthesized using various titania precursors such as titanium tetra-iso-propoxide (TTIP) [4], tetrabutyl titanate (TBOT) [5], titanium tetrachloride ($TiCl_4$) [6] besides other titanium compounds. Different starting materials can influence the morphology of the nano-TiO_2 produced. For example, Verma et al. [7] reported that various types of alkoxy group in titanium alkoxide ($Ti(OPr)_4$ and $Ti(OPr^i)_4$) showed different properties of the mixed CeO_2-TiO_2 films. Zhang et al. [8] also stated that different types of starting

materials of nano-TiO_2(titanium alkoxides and inorganic titanium, which are titanium sulfate and titanium chloride) could affect the properties of TiO_2/adsorbent nanostructured composites (TNC). Zhang et al. [8] found that chloride (Cl^-) ions could promote the aggregation of titanium oxide species on the surface of activated carbon and the formation of the rutile TiO_2 phase. On the other hand, the presence of sulfate (SO_4^{2-}) ions could enhance the photocatalytic activity of nano-TiO_2 [8]. At present, the effects of starting materials on the formation of nano-TiO_2 have not been fully explored despite efforts that have been made to this end. Even though a complete understanding has yet to be achieved, it is generally accepted that titanium dioxide precursors affect the morphology of nano-TiO_2 in aspects such as specific surface area, crystallinity phase, and crystallite size that play an important role in the photocatalytic degradation of organic pollutants [9].

It is clear from the literature that small crystallite size, high percentage of the anatase phase, and high specific surface area of nano-doped-TiO_2 increase the photocatalytic degradation efficiency. For example, Venkatachalam et al. [10] found that the addition of magnesium nitrate during the formation of nano-doped-TiO_2 by the sol-gel method promoted the exclusive formation of the anatase phase. The consequent enhanced adsorption of 4-chlorophenol over nano-doped-TiO_2 and the decrease in particle size of nano-doped-TiO_2 increased photocatalytic degradation of 4-chlorophenol [10].

Doping techniques have been applied in photocatalysis to overcome the limitations of nano-TiO_2, such as a wide band gap, ineffectiveness of photocatalysis under sunlight, and thermal instability [8, 11]. Basically, nano-TiO_2 can only utilize 6% of the total solar irradiation in photocatalysis due to the large band gap of anatase nano-TiO_2 (3.2 eV), but doping techniques shift the activity of nano-doped-TiO_2 from the UV region to the visible light region [12]. This paper appraises different doping techniques [13] that widen the photocatalytic range from the ultraviolet to the visible light region, thus allowing for the photocatalytic degradation of organic pollutants under solar irradiation [14–17].

There are also negative effects of doping techniques in the photocatalytic performance of nano-doped-TiO_2. Firstly, the dopant can act as a charge recombination center that acts against the separation of excited electron and hole. Secondly, doping techniques can inhibit the production of oxygen radicals in the photocatalysis reaction [18]. However, these problems can be countered by controlling the dosages of the dopants. Besides shifting the wavelength sensitivity of nano-doped-TiO_2 into the visible light range, doping techniques can also improve the physical properties of TiO_2. Cai et al. [19, 20] reported that suitable amounts of dopants helped to control the crystallite size of nano-doped-TiO_2 while producing a high specific surface area of nano-doped-TiO_2. A judicious rate of doping also prevented the transformation of the anatase phase to the rutile phase.

In this paper, studies on the modification of nano-TiO_2 photocatalysts with various types of dopants are reviewed. The photocatalytic activity of TiO_2 incorporating various dopants doping processes on the photocatalytic degradation of organic pollutants are assessed. The effects of various operating parameters on the photocatalytic degradation of organic pollutants in the presence of nano-doped-TiO_2 photocatalysts are also appraised.

2. Short Background Regarding Photocatalytic Degradation Process

According to Pirkanniemi and Sillanpää [21], the overall heterogeneous photocatalysis can be summarized into the following five steps: (1) reactant diffusion to catalyst surface, (2) adsorption of reactant onto the surface, (3) chemical reaction on the catalyst surface, (4) desorption of final products off the catalyst surface, and (5) diffusion of final products from the catalyst surface. Heterogeneous photocatalysis is a favorable combination of charge transport features, electronic structures, excited-state life spans, and light absorption effects. The basis of photocatalysis is the photo-excitation of a semiconductor that is solid as a result of the absorption of electromagnetic radiation, often, but not exclusively, in the near UV spectrum. When the energy (photon) supplied is equal to or greater than the band gap energy, ΔE_g of the photocatalyst, the excited electron in the valence band is transferred to the empty conduction band. (The band gap energy is the difference in energy between the valence band and conduction band of the photocatalyst. It is in the order of a few electron volts.) This leads to the generation of a positive hole (h_{vb}^+) in the valence band and an electron (e_{cb}^-) in the conduction band. As a result, electron-hole pairs are generated in the photocatalytic reaction

$$TiO_2 + h_\nu \longrightarrow e_{cb}^- + h_{vb}^+ \tag{1}$$

where h_ν is energy required to transfer the excited electron from the valence band to the empty conduction band.

In this reaction, the positive hole and electron are powerful oxidizing and reducing agents, respectively. Generally, the positive hole reacts with either surface-bound water (H_2O) or pollutant to produce hydroxyl radical ($^\bullet OH$) and surface adsorbed hydroxyl radical ($^\bullet OH_{ad}$).

$$\begin{aligned} h_{vb}^+ + H_2O &\longrightarrow {}^\bullet OH + H^+ \\ h_{vb}^+ + OH^- &\longrightarrow {}^\bullet OH_{ad} \end{aligned} \tag{2}$$

On the other hand, the electron in the conduction band is picked up by an electron acceptor such as oxygen to produce superoxide radical anion ($O_2^{\bullet -}$).

$$e_{cb}^- + O_2 \longrightarrow O_2^{\bullet -} \tag{3}$$

Basically, the oxidative and reductive reactions do not occur concurrently. Hence, when an accretion of electron occurs in the conduction band, the electron is then recombined with the positive hole in the absence of the photocatalyst. As the photocatalytic reaction proceeds in preference to the positive hole-electron recombining, efficient electron

consumption is hence essential to promote the photocatalytic oxidation. The equation of the recombination of positive hole and electron is shown below:

$$e_{cb}^{-} + h_{vb}^{+} \longrightarrow TiO_2 \quad (4)$$

Thus, the organic pollutant is oxidized to form salts, carbon dioxide, and water in the complete photocatalytic oxidation process.

$$^{\bullet}OH + \text{pollutant} + O_2 \longrightarrow \text{products (salts}, CO_2, H_2O) \quad (5)$$

3. Effects of Dopants in the Formation of Nano-Doped-TiO_2

Titanium dioxide is a well-known photocatalyst that is not only sensitive to light and corrosion resistant, but also inexpensive as an industrial material [22]. However, there are disadvantages linked to the use of TiO_2 as a photocatalyst. These include the difficulty in producing high-grade TiO_2 with tightly controlled physical properties and the fact that, in its basic form, it functions only under UV irradiation [23]. Many factors govern the physical-chemical properties of TiO_2 during its production such as the speed of growth, the diffusion coefficient, and the ionic radii [24]. The method of preparation and posttreatment conditions also play prominent roles in synthesizing a high efficiency TiO_2 product [25]. To overcome some of the difficulties encountered, different dopants (metal and non metal) are being investigated with the aim of enhancing the morphology of TiO_2 in the photocatalysis [26].

Dopants modify the electronic structure of nano-TiO_2 to broaden its effective range of light sensitivity for photocatalysis from the ultra-violet (UV) region to the visible light region [27]. Doping techniques have been shown to be effective and efficient despite their being susceptible to thermal instability and their requirement for expensive ion-implantation facilities [28]. Dopants are valued for their ability to confer excellent physicochemical properties such as high crystallinity (high percentage of anatase phase), high specific surface area, and small crystallite size [20, 29]. There are three types of crystalline phases of nano-TiO_2, *namely,* the rutile, anatase, and brookite phases. The anatase and rutile phases are the common crystallographic phases found in the formation of nano-TiO_2, with the former particularly favored for its high photocatalytic activity [30] and exceptional thermodynamic stability in nanoscale dimensions [9]. The crystalline structure of nano-TiO_2 is represented as a TiO_6 octahedral. The formation of the anatase and rutile phases or phase transformation from anatase to rutile is strongly dependent on the thermal dehydration process during which time; Ti–O–Ti bonds are formed by the interaction between –OH groups and the protonated surfaces.

Specific surface area of TiO_2 is one of the factors that determine the morphology of TiO_2 in photocatalysis. A large specific surface area of TiO_2 enhances the photocatalytic degradation rate of organic pollutants as availability of active sites in TiO_2 is increased [31, 32]. Crystallite size is another important characteristic that determines the quality of TiO_2. The performance of nano-TiO_2 can be enhanced in the photocatalysis by producing nano-doped-TiO_2 with high crystallite size up to a certain limit [33]. Thereafter, the photocatalytic performance of nano-doped-TiO_2 decreases when the crystallite size falls beyond this limit because of the trapping of charge carriers during the diffusion process. With the presence of dopants in the formation of nano-doped-TiO_2, the phase transformation from anatase to rutile inhibits when the thermal energy is low enough to overcome the nucleation barrier during the thermal dehydration process, and this occurs more readily with the smaller crystallite size of nano-doped-TiO_2 [34]. In short, dopants suppress the crystallite size of nano-TiO_2 by inserting itself into the lattice structure of the nano-doped-TiO_2 octahedral to modify its physicochemical properties. In general, a smaller crystallite size of nano-doped-TiO_2 is favored compared to larger crystallite size of nano-doped-TiO_2 since the smaller size reduces the recombination of the photogenerated charge carriers [35]. Some researchers reported that smaller crystallite size of nano-doped-TiO_2 induced a larger band gap due to the increased redox ability [31]. The resultant photocatalytic activity benefits from the quantum size effect of nano-doped-TiO_2 that enhances its photocatalytic activity [32].

In another studies, some researchers found that the presence of dopants did not affect the morphology of nano-doped-TiO_2 [36, 37]. For example, Nahar et al. [36] noted that Fe dopant, even at high concentrations, did not change the crystalline phase of nano-doped-TiO_2. Li et al. [37] stated that cerium ions had no obvious effect on the particle size, morphology, and crystalline phase of nano-doped-TiO_2.

Although nano-doped-TiO_2 with large specific surface area, high percentage of anatase phase, and small crystallite size all contribute towards high photocatalytic activity, a complete understanding of the interlinkages between these variables has yet to be achieved and their detailed underlying mechanisms remain a challenge to researchers.

3.1. Effect of Metal Doping. Metal dopants have been used to improve the morphology and photocatalytic activity of nano-doped-TiO_2. In previous studies, various metal dopants, including cobalt (Co) [38, 39], barium (Ba) [40], manganese (Mn) [41], nickel (Ni) [42], copper (Cu) [43], zinc (Zn) [44], and iron (Fe) [45, 46], have been analyzed for their abilities to enhance the photocatalytic performance of nano-doped-TiO_2. They improve nano-doped-TiO_2 performance under visible light irradiation by shifting the absorption spectra to a lower energy region [47]. In addition, various approaches have been attempted to sustain photocatalytic activity by limiting the recombination of the photogenerated electron-hole pairs in photocatalysis.

Hsieh et al. [38] produced codoped titania nanotubes with a specific surface area of 379 m^2/g, outer diameter of 10–15 nm, and inner diameter of 5–10 nm. Suriye et al. [39] found that codoped TiO_2 exhibited high anatase phase based on X-ray diffraction (XRD) patterns. Smaller particle size of Ba-doped TiO_2 were synthesized by Atashfaraz et al. [40] who reacted titanium dioxide and barium hydroxide

at high temperature in the flow reactor. Zhang et al. [41] produced Mn-doped TiO_2 using the sol gel method. Based on their observations, the band gap of the photocatalyst was narrowed due to the formation of an impurity level near the bottom of the conduction bands. Xu et al. [44] showed that Zn which was located on the titania nanotube surface had little effect on the titania nanotube morphology. Fe-doped titania prepared by Janes et al. [45] using the sol gel method prevented the phase transformation of anatase to rutile at low dopant levels. The interaction was applicable to a maximum Fe dopant loading of 5.64 wt%. Deng et al. [46] also investigated the morphology of Fe-doped titania nanotubes synthesized by the sol gel and hydrothermal methods. They found that the addition of Fe slowed the crystallization process and prevented the growth of crystallite TiO_2.

Besides metal dopants, transition metals dopants such as palladium (Pd), chromium (Cr), and silver (Ag) have been investigated by Wu et al. [48] to enhance the photocatalytic performance of nano-doped-TiO_2. Among the transition metals dopants tested, Pd ion had the strongest interaction with nano-TiO_2 and improved its morphology most effectively. Some researchers are of the opinion that doping techniques promote the production of smaller crystallite nano-doped-TiO_2 with the resultant larger surface area helping to prevent the problem of particle agglomeration [49].

Among the metal dopants, Fe^{3+} ions reportedly benefit from uniform distribution into the lattice structure of TiO_2 because of the similarity of their ionic radii [50]. Fe^{3+} ions are also thought to control the crystallite size of TiO_2 and prevent the phase transformation of the anatase phase to the rutile phase. Deformation of the TiO_2 crystal lattice occurs when Fe^{3+} ions (0.690 A) merge with Ti^{4+} ions (0.745 A), restricting the growth of Fe-TiO_2 crystallite size in the process.

Fe^{3+} ions have also been reported to act as shallow charge traps in the lattice of TiO_2, and this accounts for its high photocatalytic activity [51]. This is explained by the conduction band edge of TiO_2 being above the energy level for Fe^{3+}/Fe^{2+}, whereas the valence band edge of TiO_2 is below the energy level for Fe^{3+}/Fe^{4+} [49]. Hence, Fe^{3+} can react easily with the photogenerated electron (from conduction band of TiO_2) and the hole (from valence band of TiO_2) to form Fe^{2+} and Fe^{4+} ions. In this manner, Fe^{3+} ions can enhance the lifetime of the electrons and holes by acting as both electron and hole traps (Fe^{2+} and Fe^{4+} ions). Nevertheless, Fe^{2+} and Fe^{4+} ions are not stable compared with Fe^{3+} ions due to the half-filled $3d^5$ orbital.

The choice of different starting Fe materials affects the morphology of TiO_2 that is produced. For instance, $FeCl_3$ is widely used as a dopant because its Cl^- ions are weakly bonded to the TiO_2 surface as compared with Fe^{3+} ions. This facilitates the incorporation of Fe^{3+} ions, in preference over Cl^- ions, onto the TiO_2 surface. Consequently, Fe-doped TiO_2 with Brunauer-Emmett-Teller (BET) surface area of 100 m^2/g, crystallite size of <9 nm, and the presence of anatase phase can be obtained by adding less than 1 wt% Fe [49, 50, 52–54].

Some of the researchers found that judicious doping with Fe improves TiO_2 morphology, but specific surface area suffers beyond the optimum doping level [50, 52]. This is because Fe acts as a recombination center for both free electrons and energized holes [53, 54], thus limiting the interaction between Fe and TiO_2 [49]. In addition, Fe induces the formation of amorphous titanium(IV)-iron(III)-oxide that leads to the inhibition of the anatase phase of TiO_2 [55]. The optimum Fe loading (0.007–1.200 wt%) gives a combination of crystallite size (9.0–23.7 nm) and specific surface area (55.5–175.0 m^2/g) of TiO_2 [49, 50, 53–56].

The foregoing notwithstanding, there are other researchers who are of the view that the Fe is not requisite for the improvement of TiO_2 characteristics. Li et al. [51] produced Fe-doped TiO_2 with particle size of 10–15 nm via the hydrothermal method. They also reported that increasing the amount of Fe could narrow the band gap of TiO_2 by shifting its activity from UV region to the visible light region. Based on an observation from X-ray photoelectron spectroscopy (XPS), Fe was thought not to be located on the TiO_2 surface, but was positioned within the matrix interior. Thus, the isolated Fe^{3+} had a lower chance of transferring the trapped charge carriers to the interface and this could account for a decrease in photocatalytic activity, for example, in the degradation of methylene blue.

Sakthivel et al. [57] investigated the performance of TiO_2 after supplementing with platinum (Pt) dopant. Pt acted as an electron trap in the formation of TiO_2, decreasing its surface area. While the generated free electrons gravitated towards Pt that served as a temporary electron trap preventing electron-energized hole recombination, increased Pt also competed with TiO_2 as an electron trap to decrease effective surface area in the latter. A further increase in Pt dopant might lead to the following possible consequences: (1) shortening of the charge carrier space distance [57], (2) recombination of free electron and energized hole [58], (3) agglomeration of Pt and TiO_2 [58], and (4) decrease in the probability of oxygen being photo-adsorbed on TiO_2 [57]. The crystallite size of 9.15–31.00 nm and a specific surface area of 19.1–118.7 m^2/g of TiO_2 was produced by loading Pt at the rate of 0.1–1.5 wt% [56, 58–61].

Chromium (Cr), cerium (Ce), and vanadium (V) have also been used as dopants for TiO_2. The addition of vanadium (V) increases the surface area and porosity of TiO_2 [62]. The advantages of Ce as dopants include (1) decrease of the rate of crystallite growth, (2) promotion of mesoporous materials formation, (3) promotion of the stability of the active phase, (4) prevention of thermal loss in the catalyst area [63], and (5) prevention of the phase transformation of the anatase to the rutile phase [63].

Metal-doped TiO_2 products reveal the presence of the anatase phase and a crystallite size of TiO_2 ranging from 2.59 to 12.00 nm. The specific surface area of TiO_2 is in the region of 100–500 m^2/g [49, 50, 52–60, 62–66]. Table 1 which summarizes the dopants used in TiO_2 formation shows that different dopants are responsible for different structural properties of the TiO_2. Further studies are needed to understand the mechanism of metal doping in the

Table 1: Properties of metal-doped TiO_2 photocatalysts under various conditions.

Type of metal dopant	(Metal dopant/TiO_2) molar ratio	Preparation of doped TiO_2	Starting material of TiO_2	Starting material of metal dopants	Crystallite size (nm)	Phase	BET surface area (m^2/g)	Reference
Fe	0.090	Hydrothermal	TTB	$FeCl_3$,$FeCl_2$	11.40	Anatase	101.40	[50]
	0.100	Hydrothermal	$(Ti(OC_4H_{9-n})_4$	$Fe(NO_3)_3 \bullet 9H_2O$	14.50	Anatase	102.00	[53]
	1.200	Hydrothermal	$TiCl_3$	$FeCl_3 \bullet 6H_2O$	23.70	Anatase	55.50	[55]
	0.007	Sol gel	TTIP	$Fe(NO_3)_3$	—	Anatase	175.00	[54]
	0.700	Sol gel/microemulsion	TTIP	$Fe(NO_3)_3$	12.70	Anatase	83.00	[52]
	0.980	Sol gel	$Ti(OPr^i)_4$	$Fe(NO_3)_3 \bullet 9H_2O$	9.00	Anatase	126.10	[49]
Pt	0.800	Impregnation	TiO_2 Degussa P25	$PtCl_2$	22.28	Anatase	29.17	[57]
	1.000	Impregnation/Photodeposition	TiO_2 Degussa P25	H_2PtCl_6	20.00	Anatase	107.00	[64]
	1.500	Impregnation	TTIP	H_2PtCl_6	31.00	Anatase	19.10	[61]
	0.500	Photochemical deposition	TBOT	$H_2PtCl_6 \bullet 6H_2O$	9.15	Anatase	116.10	[60]
	1.500	Photochemical reduction	TNBT	$H_2PtCl_6 \bullet 6H_2O$	—	Anatase	118.70	[58]
Ce	0.100	Sol gel	$TiCl_4$	$H_2PtCl_6 \bullet 6H_2O$	14.00	Anatase	68.00	[59]
	0.010	Hydrothermal	$Ti(SO_4)_2$	$Ce(NO_3)_4$	—	Anatase	454.00	[63]
	4.000	Reflux	$Ti(OBu)_4$	$Ce(NO_3)_4$	8.30	Anatase	—	[65]
V	1.000	Sol gel	$Ti(OBu)_4$	$VO(OPr)_3$	12.00	Anatase	107.00	[62]

formation of TiO_2 and the influence of metal dopants in its morphology.

3.2. Effect of Nonmetal Doping. Various approaches have been made in the bid to hinder recombination of the photogenerated electron-hole pairs in nano-TiO_2. Nonmetal anion doping has been exhaustively investigated because the electronic states of nonmetals are above the valence band edge of TiO_2 compared with pure TiO_2. Accordingly, different nonmetal dopants including carbon (C), nitrogen (N), and sulfur (S) have been tested for their ability to improve the morphology and photocatalytic performance of TiO_2 [73, 74]. The presence of nonmetal anions increases the percentage of the anatase phase in TiO_2, restrains the growth of crystallite size of TiO_2, and increases the specific surface area of TiO_2 [75]. Besides, doping with nonmetal anions broadens the band gap of TiO_2 in its electronic structure and affects the red-shift in the absorption spectra of nano-doped-TiO_2. In this way, various photocatalytic, photochemical, and the photoelectrochemical properties of TiO_2 are enhanced by shifting the wavelength sensitivity of TiO_2 from ultra violet region into the visible light region [73]. A summary of properties of various nonmetal dopants of TiO_2 under various conditions is given in Table 2.

Phosphorus (P) is used as a nonmetal dopant to enhance the thermal stability of TiO_2 through the formation of titanyl phosphate [68]. In addition, P also improves the surface properties of TiO_2 and reduces the oxygen vacancies, thus improving the performance of TiO_2 in other applications such as photocatalysis and gas sensing [67]. High specific surface area of 154 m^2/g and crystallite size of 8.6 nm of nano-doped-TiO_2 have been successfully produced at a P/Ti molar ratio of 0.14 [68]. Phosphorus doped TiO_2 displays a larger specific surface area and smaller crystallite size as compared with pure titania [67].

Nitrogen (N) has been reported to generate better dispersion, uniform particle size distribution, and uniform surface area when used to dope TiO_2 in the hydrothermal process [76]. Senthilnathan and Phillip [70] obtained 22 nm of crystalline size of N-doped TiO_2. Nitrogen atoms substitute for the oxygen atoms in TiO_2 lattice to form O-Ti-N. This substitution phenomenon is consistent with the findings of Peng et al. [69] who established 21% as the highest acceptable nitrogen dopant concentration in N-TiO_2.

Doping sulfur atoms into the TiO_2 lattice improves the photocatalytic efficiency under visible light irradiation [72]. When fine crystalline S-doped TiO_2 was synthesized in the study of Ho et al. [72] through a simple hydrothermal method, the optical absorption of S-doped TiO_2 in the visible light region increased in tandem with the increase in the S content. This may be related to the finding by Tian et al. [71] that the anatase/rutile phase composition ratio was strongly influenced by the amount of S. The phase composition ratio increased with the increase in S amount, with TiO_2 doped with 1.5% S displaying the best crystallite size (around 30 nm).

3.3. Effect of Metalloid and Halogen Doping. Halogen doping techniques have been made in the bid to hinder the transformation of anatase to rutile phase in nano-doped-TiO_2 photocatalysts. The developments of halogen-doped TiO_2 photocatalysts have attracted high attentions due to their ability in substituting into TiO_2 matrix. Meanwhile, halogen doping could improve the surface properties as well as

Table 2: Properties of non metal-doped TiO_2 photocatalysts under various conditions.

Type of non-metal dopant	(Non metal dopant/TiO_2) molar ratio	Doped TiO_2 preparation method	Starting material of TiO_2	Starting material of non metal dopants	Particle size (nm)	Phase	BET surface area (m^2/g)	Reference
P	0.020	Hydrothermal	TNBT	H_3PO_2	14.50	Anatase	104.00	[67]
	0.140	Sol gel	TiO_2 Degussa P25	H_3PO_4	8.60	Anatase/rutile	154.00	[68]
N	0.265	Hydrothermal	TiO_2 Degussa P25	TEA	15.40	Anatase/rutile	—	[69]
	1.600	Hydrothermal	TTIP	$CH_3CH_2NH_2$	25.40	Anatase	—	[70]
S	1.500	Hydrothermal	$TiCl_4$,	$CS(NH_2)_2$	30.00	Anatase	—	[71]
	2.800	Hydrothermal	TiS_2	TiS_2	2.80	Anatase	—	[72]

the optical properties of TiO_2 photocatalysts [77]. Accordingly, different halogen dopants including iodine (I), bromine (Br), and fluorine (F) have been investigated in order to improve the morphology and the photocatalytic performance of TiO_2. A list of physical-chemical properties of metalloid-and halogen-doped TiO_2 and their advantages are given in Table 3.

Fluorine (F) has been doped into TiO_2 to increase the percentage of the anatase phase [78]. The substitution of F atoms and oxygen (O) atoms in TiO_2 lattice forms ≡Ti–F bond which has strong electron-withdrawing ability that prevents the recombination of photogenerated electron-hole pairs. However, some researchers have raised concern that beyond an optimal doping rate (F concentration > 0.5%), fluorine no longer acts as a mediator of interfacial charge transfer but serves as a recombination center [79]. The pH character of fluorine precursors plays an important role in determining the crystalline phase of photocatalyst formed. Basic fluorine precursors favor the formation of pure anatase phase TiO_2, whereas acidic fluorine precursors favor the formation of rutile/anatase or pure rutile phase TiO_2. On the other hand, fluorine was reported that it has no effect on the changes of band gap width [80]. Xu et al. [81] reported that the fluorine-doped TiO_2 prepared by hydrolysis process can improve the crystallinity as well as inhibit the grain growth of photocatalyst. Instead of this, fluorine doping can enhance the formation of hydroxyl groups on the titania surface, and thus, increase the phenol photodegradation rate.

Iodine is used to enhance the surface properties as well as the optical properties of TiO_2. Iodine is an effective dopant in shifting the absorption spectra of TiO_2 from UV light region to visible light region and facilitating the charge separation. The presence of iodine can also narrow the band gap of I-TiO_2, and hence improve the absorption ability of photocatalyst in the visible light region [88]. The red-shift of the band edge of iodine-doped TiO_2 is related to the formation of Helmholtz potential on the surface of TiO_2 with the presence of iodine. The presence of iodine facilitates the reduction of TiO_2 band gap energy from 3.2 eV to 3.0 eV and thus extends the photo-response region of I-TiO_2 to the visible light region [90]. This phenomenon was due to the shirting of the electron configuration of elements where I 5p states mix with Ti 3d while O 2p moves to high energy region [91]. Wang et al. [89] successfully prepared single anatase phase of iodine-doped TiO_2 using hydrothermal method and they also showed that the iodine dopants hindered the growth of crystal particles by enhancing the energy barrier mutual diffusion between grains. From their results, the existence of iodine mainly improved the photosensitivity of the photocatalyst, broadened the visible light range, and decreased the band gap energy of TiO_2. Iodine dopants were proven to increase the formation of surface hydroxyl groups and thus improve the photocatalytic activity of TiO_2 [90]. However, beyond an optimal doping rate, iodine dopants serve as recombination centers for the charge carriers and hence inhibit the photocatalytic activities of the doped TiO_2 [88].

Boron (B) is known as a metalloid compound, which can be termed either a metal or a nonmetal. Some researchers contend that boron inhibits the growth of TiO_2 crystalline and thus increases the surface area of B-doped TiO_2 as well as inducing the crystalline process [63]. The formation of anatase phase is also promoted by adding boron dopants in the formation of nano-doped-TiO_2. For example, Xu et al. [66] found that B increased the surface area of nano-doped-TiO_2 by controlling the growth of TiO_2. Lu et al. [92] synthesized B-TiO_2 with the mixture of anatase and brookite phase by sol gel method. The foregoing notwithstanding, there are other researchers who are of the view that boron inhibits the transformation of amorphous phase to anatase phase. For instance, Zaleska et al. [82] found that no anatase phase was formed in the formation of boron-doped TiO_2 using sol gel method. Grabowska et al. [83] found out that boron-doped TiO_2 had lower surface area as compared to undoped TiO_2. One of the important features in boron doping is the red shift in the absorption band of TiO_2. The formation of Ti-O-B species enables the B-TiO_2 active in phenol photodegradation under visible light irradiation [82]. The incorporation of boron atoms into TiO_2 matrix by occupying O sites to form O-Ti-B induced the visible light photocatalytic activity of B-TiO_2 [92]. However, beyond an optimal doping rate, diboron trioxide phase (B_2O_3) was formed in the doped TiO_2, which led to lower the photocatalytic activity [82].

Table 3: Properties of metalloid or halogen-doped TiO_2 photocatalysts under various conditions.

Type of dopant	(Metal dopant/TiO_2) molar ratio	Preparation of doped TiO_2	Starting material of TiO_2	Starting material of dopants	Crystallite size (nm)	Phase	BET surface area (m^2/g)	Reference
Metalloid								
B	0.001	Hydrothermal	$Ti(OBu)_4$	$NaBH_4$	2.59	Anatase	268.31	[63]
	9.000	Sol gel	$Ti(OBu)_4$	$VO(OPr)_3$	6.00	Anatase	127.00	[66]
	0.040	Sol gel	TTIP	H_3BO_3	—	Anatase	219.00	[82]
	0.148	Sol gel	TiO_2	$(C_2H_5O)_3B$	7.00	Anatase	192.00	[83]
Si	0.111	Destabilization	HFTA	HFSA	6.50	—	155.00	[84]
	0.030	Hydrothermal	$Ti(OC_4H_9)_4$	$(C_2H_5)_4SiO_4$	8.20	Anatase	191.70	[85]
	0.150	Templating	TBOT	TEOS	10.00	Anatase	120.00	[86]
Halogen								
F	0.050	Hydrothermal	$Ti(OC_3H_7)_4$	NH_4F	—	Anatase	48.00	[75]
	0.500	Hydrothermal	TBOT	NH_4HF_2-H_2O	11.20	Anatase	122.00	[77]
	0.770	Hydrothermal	TIP	NaF	10.00	Anatase	148.00	[78]
	0.039	Sol gel	$Ti(C_2H_5O)_4$	CF_3COOH	13.20	Anatase	—	[80]
	0.190	Spray pyrolysis	H_2TiF_6	H_2TiF_6	—	Anatase	27.10	[87]
	0.001	Sol gel	$Ti(OBu)_4$	NH_4F	3.78	Anatase	169.48	[81]
I	0.033	Hydrothermal	TTIP	HIO_3	5.50	Anatase/brookite	137.60	[88]
	0.117	Hydrothermal	TNBT	KI	4.46	Anatase	184.87	[89]
	0.025	Sol gel	$Ti(OBu)_4$	HIO_3	5.50	Anatase	259.10	[90]

Silicon is another common metalloid used to dope TiO_2. Silicon dopants were proven to increase the thermal stability of anatase as well as suppress the anatase-to-rutile phase transformation [86]. Estruga et al. [84] studied the effect of silicon dopant on the formation of TiO_2 nanopowders. It was reported that the incorporation of silicon did not affect the crystalline phase or TiO_2 optical properties as compared to undoped TiO_2. However, silicon doping did increase the surface area of doped-TiO_2 with respect to undoped powders. In other study on the effects of the silicon dopants [85], Si-TiO_2 of smaller crystal size, larger pore volume and surface area, and single anatase phase was successfully synthesized using hydrothermal method. Meanwhile, the presence of Ti-O-Si bonds preserved high surface hydroxyl group concentrations, which influenced the subsequent photocatalytic activity of TiO_2. The nature behaviors of silicon metalloid can easily produce the hybridization bands in both valence and conduction bands which are beneficial in increasing the photogenerated charge carriers. Furthermore, the silicon doping can also reduce the band gap energy of TiO_2 and broaden the absorption spectra of TiO_2 [93].

3.4. Effect of Codoping. In order to further improve the morphology of TiO_2, the co-doping technique with double metal dopants, double nonmetal dopants, and double metal-nonmetal dopants has gained wide attention. Co-doped TiO_2 shifts the absorption edge of TiO_2 successfully from ultraviolet region to visible light region. The co-doping technique also improves the physical properties of the TiO_2 such as specific surface area and crystallite size while it sustains the phase transformation of anatase to rutile phase [94]. Improved performance of TiO_2 under visible light is achieved up to an optimal doping level, after which performance deteriorates when the dopants become recombination centers for photogenerated electron-hole pairs [95].

A variety of rare metal dopants, including niobium (Nb), tungsten (W) and samarium (Sm) have been used in the co-doping technique by several researchers [96–98]. As with the other classes of dopants, Nb prevents the recombination of free electron and energized hole and extends the wavelength of absorbance of TiO_2 to increase its functionality. [97]. Ti atoms have been replaced with W atoms to form W–O–Ti bonds, which can induce the formation of the anatase phase as well as act as electron traps to suppress the recombination of energized holes and free electrons. Similar to other dopants, an excess of W levels decreases the performance of TiO_2. W is deposited on the surface of $TiO_2$to blue-shift the absorption edge, thus increasing the band gap energy of TiO_2 under visible light [98]. Sm is also used to dope into TiO_2, which again restrains the phase transformation of the anatase phase to solid form and also stabilizes it in the final product. It also prevents the growth of the crystallite size of TiO_2 [96].

In the co-doping technique, the functions of metal dopants are generally to facilitate the charge separation of free electrons and energized holes and to decrease their recombination [97–99]. On the other hand, the functions of nonmetal dopants are generally to shift the absorption region of TiO_2 from the UV light region to the visible light region, besides narrowing the band gap of TiO_2[100–102]. For example, Cu is applied in the co-doping technique to slow the growth of crystallite size of the TiO_2 by forming a complex with oxygen on the surface of TiO_2. At the same

Table 4: Properties of codoped-TiO_2 catalysts under various conditions.

Type of dopants used(x,y)	Optimum molar ratio of the dopants ($M_x : M_y$)	Codoped TiO_2 preparation method	Starting material of TiO_2	Starting material of co-dopants	Particle size (nm)	Phase	BET surface area (m^2/g)	Reference
F, N	1.00	Sol gel	TTIP	NH_4F, NH_4Cl	—	Anatase	102.00	[74]
Sm, N	1.50	Coprecipitation	$Ti(SO_4)_2$	$Sm(NO_3)_3$, NH_3	8.80	Anatase/Rutile	170.00	[96]
Fe, Nb	0.12	Sol gel	TTIP	$Fe(NO_3)_3 \bullet 9H_2O$, $C_4NH_4NbO_9 \bullet 10H_2O$	10.00	Anatase	120.20	[97]
W, N	1.60	Hydrolysis	$TiCl_4$	$(NH_4)_2WO_4$	11.00	Anatase	80.00	[98]
B, Fe	3.00	Sol gel	$Ti(OBu)_4$	H_3BO_3, $Fe(acac)_3$	12.00	Anatase	60.00	[99]
N, S	1.00	Hydrolysis	$Ti(SO_4)_2$	$NH_3 \bullet H_2O$, $Ti(SO_4)_2$	38.20	Anatase	56.10	[100]
S, I	1.00	Sol gel	TIP	Thiourea, HIO_3	8.80	Anatase	85.00	[101]
N, S	33.33	Hydrothermal	$Ti(SO_4)_2$	CH_4N_2S, $Ti(SO_4)_2$	16.20	Anatase	—	[102]
Cu, S	2.00	Sol gel	TIP	$CuCl_2 \bullet 2H_2O$, Thiourea	8.00	Anatase	—	[103]
F, N	1.00	Sol gel	$TiCl_4$	NH_4F	11.90	Anatase	160.70	[104]
Pt, Cu	12.50	Impregnation	Titanium Tetraisobutyloxide	H_2PtCl_6, $Cu(NO_3)_2$	8.90	Anatase	105.90	[105]
Fe, C	0.57	Sol gel/Solvothermal	Tetrabutyl titanate	$Fe(NO_3)_3 \bullet 9H_2O$	10.80	Anatase	158.00	[106]
Pt, N	0.02	Sol gel	TTIP	H_2PtCl_6, NH_2CONH_2	5.00	Anatase	72.50	[107]
Cr, W	2.00	Pyrolysis	$Ti_2(C_2O_4)_3 \bullet 10H_2O$	$(NH_4)_2Cr_2O_7$, Dimethylammonium tungstate	30.00	Anatase	60.00	[108]

time, Cu also prohibits the phase transformation from the anatase phase to the rutile phase [103]. carbon (C) and iodine (I) are similarly used as dopants to improve the performance and properties of TiO_2 [101].

The co-doping technique generates synergistic effects which enhance the properties of the final TiO_2 product [74, 96–109]. For example, when W and N are co-doped to TiO_2, the excited electrons are easily transferred from valence band into the new conduction band due to the narrowing of the band gap difference, while the recombination of free electrons and holes are not permitted [98]. Livraghi et al. [74] researched the effects of the co-doping technique using F and N on the formation of TiO_2. F could activate the active site of N by producing extra electrons to the low energy orbital of $N_b^{\bullet}$. Doping with F and N created a synergism in which F improved the incorporation of N dopant into TiO_2.

Hamadanian et al. [103] showed that the use of Cu and S could form co-doped TiO_2 with TiO_2 displaying high performance under visible light irradiation. In this instance, Cu shifted the absorption range of TiO_2 from the UV region to the visible light region, while S lowered the band gap energy of TiO_2 by mixing its electron orbital with the O 2p orbital.

Overall, the co-doping technique is an effective method to improve the performance of TiO_2. A list of physical-chemical properties of co-doped TiO_2 and its advantages is given in Table 4. Three main benefits of co-doping are (1) high percentage of the anatase phase can be obtained, (2) phase transformation of the anatase phase to the rutile phase is inhibited, and (3) small crystallite size and high specific surface area of TiO_2 are obtained [74, 96–109].

4. Effect of the Presence of Dopants on the Photocatalytic Degradation of Organic Pollutants

Various attempts at metal doping, nonmetal doping, and co-doping have been made to limit the recombination of the photogenerated electron-hole pairs in photocatalysis. Generally, doped TiO_2 performs better in the degradation of organic pollutants as compared with pure TiO_2 due to the modifications of the physical and chemical properties of TiO_2. In terms of physical properties, the doped TiO_2 has smaller crystallite size, larger specific surface area, and higher proportion of the anatase phase. The smaller crystallite size of doped TiO_2 reduces the likelihood of energized holes and free electron recombining, while the photocatalytic activity of TiO_2 is furthered enhanced by the charge carrier space distance being increased. Ma et al. [96] stated that dopants played an important role in the photocatalysis to create a charge space carrier region on the surface of TiO_2 that prevents the recombination of electron-hole pairs. The photodegradation process takes place on the surface of the photocatalyst, and a larger specific surface area makes available more active sites on the catalyst surface that increases the photodegradation potential of the photocatalyst [49, 66, 69, 70, 98, 106].

Table 5: Comparison on the photocatalytic degradation rate of different organic pollutants between pure TiO_2 and doped TiO_2.

Dopant(s)	Light source	Organic pollutant	Initial pollutant concentration (mg/L)	Irradiation time (h)	Degradation efficiency (%)		Reference
					Doped TiO_2	Pure TiO_2	
Fe	Visible light	Malachite green	5.00	1.00	78	63	[49]
	Visible light	Yellow XRG dye	100.00	8.00	37	18	[50]
	Visible light	Methyl orange	20.00	6.00	70	50	[53]
	UV light	Dichloromethane	96.00 ± 3.00	2.00	88	82	[54]
Pt	UV light	Methyl orange	20.00	1.50	98	90	[58]
		Acid green 16	1.20	1.00	100	98	[57]
Ce	UV light	Rhodamine B	0.50	2.00	80	98	[62]
B	Visible light	4-chlorophenol	50.00	4.00	78	20	[63]
	UV light	Methylene blue	19.00	4.00	98	78	[66]
Cu	Visible light	Methylene orange	10.00	0.75	100	70	[103]
F	UV light	Methylene blue	8.00	1.00	92	30	[79]
N	Visible light	Methylene orange	20.00	1.00	14	1	[76]
S	Visible light	4 chlorophenol	0.32	6.00	88	5	[70]
	UV light	Methylene orange	20.00	1.67	98	70	[69]
S, I	Visible light	Methylene blue	8.00	4.00	90	20	[101]
W, N	UV light	Phenol	60.00	4.00	93	83	[98]
Sm, N	Visible light	Salicylic acid	50.00	5.00	65	3	[96]
Fe, C	Visible light	Acid orange 7	50.00	5.00	90	8	[106]

Dopants narrow the band gap of the photocatalysts and enhance their photocatalytic abilities by shifting their photocatalytic activity from the ultra violet region to the visible light region. For example, Hamadanian et al. [103] reported that Cu and S could alter the optical absorption wavelength of TiO_2 from UV light to visible light and hence lower the band gap of TiO_2 through the combination of electron orbital between S and O, respectively.

The photocatalytic activity of TiO_2 can be improved when chemical properties of doped TiO_2 are altered. Free electron and energized holes are the most important species in photocatalysis as hydroxyl radical can be produced from the energized holes during the reaction between water and the energized holes [79, 103]. The addition of dopants elevates TiO_2 efficiency by reducing the recombination of energized holes and free electrons. This accelerates the formation of hydroxyl radicals to speed up the photodegradation process [57, 106]. When Fe is used as a dopant, for example, the stable form of Fe^{3+} can be oxidized or reduced to form Fe^{2+} and Fe^{4+}. Hence, Fe with its d orbital can act as intermediate for both energized holes and free electrons transfer. This speeds up the degradation of organic pollutants by preventing the recombination of energized holes and free electrons. Fe also lowers the conduction band energy and increases the valence band energy of TiO_2. The end result is the enhancement of photodegradation efficiency under visible light [49, 50, 53, 54].

In short, dopants can act as active sites for pollutant adsorption to facilitate the photodegradation reaction [96]. However, excessive amounts of dopants can retard the photocatalysis process. They reduce the opportunity of oxygen photoadsorbed on the surface of TiO_2 to react with free electrons to form O_2^- or the corresponding hole to form $^\bullet OH$. Excess amounts of dopants deposited on surface of TiO_2 also increase the recombination rate of free electrons and energized holes, thus inhibiting the photodegradation process [57].

A summary of various dopants of TiO_2 applied in photocatalysis for the removal of organic pollutants is given in Table 5, which also compares the degradation efficiency between doped TiO_2 and pure TiO_2. Overall, dopants improve the performance of pure TiO_2 in the degradation of organic pollutants under visible light irradiation. They narrow the band gap of TiO_2 by shifting the optical absorption wavelength of TiO_2 from UV light to visible light.

5. Operational Factors Affecting the Photocatalytic Degradation

Based on the critical analysis of the existing researchers on the photocatalytic degradation of the organic pollutants, the important operating parameters affecting the efficiency of the photocatalytic degradation process are selected and discussed as follows: calcination temperature of nano-doped-TiO_2, initial concentration of photocatalyst, initial concentration of the reactant, and initial concentration of dopant dosing.

5.1. Effect of Calcination Temperature of Nano-Doped-TiO_2. Calcination process is commonly applied in the formation of TiO_2 photocatalyst as it can enhance the photocatalytic activity of photocatalyst. Deng et al. [46] studied the effect of calcination temperature on the photocatalytic performance of Fe-TiO_2. As shown in their results, the calcined Fe-TiO_2

Table 6: Effect of calcination temperature of nano-doped-TiO_2 on the photocatalytic degradation process.

Type of dopant	Doped TiO_2 preparation method	Doped TiO_2 loading (g/L)	Range of calcination temperature (°C)	Optimum calcination temperature (°C)	Organic pollutant	Initial pollutant concentration (mg/L)	Light source	Degradation efficiency, %	Reference
Fe	Sol gel	5.0	200–400	400	Methyl orange	20	UV-vis	99.7	[46]
Pt	Photochemical reduction	2.0	110–500	110	Methyl orange	20	UV	87.8	[58]
I, F	Sol gel-impregnation	1.0	500–700	500	Methylene blue	10	Sunlight	98	[94]
Sm, N	Coprecipitation	1.0	300–600	400	Salicylic acid	50	Visible light	67	[102]
Fe	Sol gel	1.0	0–900	500	Reactive blue 4	70	Ultrasonic	82	[110]
N, S	Hydrolysis	0.02	400–800	500	Formaldehyde	350	Sunlight	65	[100]
Cu, S	Sol gel	1.0	500–850	500	Methyl orange	10	Visible	100	[103]
Pt, Cu	Impregnation	1.0	300–700	300	Nitrate	10	UV	90	[105]
Pr	Sol gel	1.0	100–800	600	Phenol	50	UV	96	[111]
KOX	Sol gel	1.0	.0–1000	800	Methylene blue	20	Fluorescence blacklight	100	[112]

showed higher photocatalytic activity compared to that Fe-TiO_2 formed in the absence of calcination process. It was attributed to the formation of anatase phase from titanate.

However, beyond the optimum calcination temperature, the photocatalytic activity of photocatalyst is observed to decrease due to the agglomeration and sintering damage of Fe-TiO_2 at high temperature [94]. Huang et al. [58] studied the effect of calcination temperature on the photocatalytic activity of Pt-doped TiO_2. Based on their results, the calcined Pt-TiO_2 was confirmed to have higher efficiency and activity in the photocatalytic degradation of pollutant up to certain optimum calcination temperature. Beyond the optimum calcination temperature, the photocatalytic activity was observed to decrease due to the agglomeration of particles which reduce the specific surface area of the photocatalyst.

Calcination process can influence the surface area, morphology, and crystallinity of the prepared photocatalyst. Ma et al. [96] synthesized and calcined the co-doped Sm/N-TiO_2 at different temperatures. The prepared photocatalysts were tested on the photodegradation of salicylic acid under visible light irradiation. They found out that calcination process improved the crystallinity, particle size, and surface area of photocatalyst as compared to undoped photocatalysts.

The calcination temperature affects greatly the optical absorption of the photocatalysts. High calcination temperature can promote the replacement of nitrogen by oxygen in the air. Consequently, the absorption of photocatalyst in the visible light region decreases, and hence, decreasing the photocatalytic activity of TiO_2. Many researchers have confirmed that the calcination process is important in the formation of doped TiO_2 and that the properties of photocatalyst such as surface area and crystallinity of doped TiO_2 are strongly dependent on the calcination temperature [100, 103, 110]. With further increase in the calcination temperature, the surface area of TiO_2 started to decrease as well as the transformation of anatase to rutile phase, and thus, the photocatalytic activity of TiO_2 decreased. Li et al. [105] studied the effect of calcination temperature on benzene photodegradation using Pt/Cu-TiO_2. They also agreed that high calcination temperature produced low specific surface area, large particle size, and low crystallinity phase of the agglomerated doped-TiO_2. Subsequently, the less active site eventually lowers the photocatalytic activity of TiO_2.

Suwanchawalit and Wongnawa [112] studied the photodegradation of methylene blue using potassium oxalate-doped TiO_2. Based on their result, noncalcined samples have high specific surface area but low percentage of anatase phase in the TiO_2. These resulted that non-calcined samples showed higher adsorptive capacity but lower photocatalytic activity as compared to calcined samples. As the calcination temperature increases, the adsorptive property of photocatalyst decreases with increasing the photocatalytic activity. In addition, the optimum calcination temperature provides the moderate adsorptive capacity and excellent photocatalytic activity of the photocatalysts. On the other hand, further increase of calcination temperature decreases the photocatalytic performance of photocatalyst. Kemp and McIntyre [113] studied the photodegradation of poly(vinyl chloride) using V-TiO_2 and reported that lower calcination temperature samples showed better photodegradation rate compared to that sample produced at high calcination temperature (1000°C).

Table 6 summarizes the effect of calcination temperatures of nano-doped-TiO_2 on the photocatalytic degradation of various organic pollutants. The table reveals that different optimum calcination temperatures have been reported by different researchers. Such differences in the preparation and posttreatment conditions contribute different morphology of nano-doped-TiO_2.

Table 7: Effect of initial organic pollutant concentration on the photocatalytic activity of nano-doped-TiO_2.

Type of dopant	Doped TiO_2 preparation method	Doped TiO_2 loading (g/L)	Organic pollutant	Range of pollutant concentration (mg/L)	Optimum pollutant concentration (mg/L)	Light source	Irradiation time (h)	Degradation efficiency (%)	Reference
Ag	Sol gel	1	Crystal violet	10–80	10	UV	1.75	100	[115]
Ba	Sol gel	0.2	4-chlorophenol	50–300	250	UV	—	100	[10]
C	Sol gel	1	Methylene blue	5–50	5	Solar light	2/3	100	[116]
Ce	Coprecipitation	4	Phenol	1000–5000	1000	UV	2	100	[117]
Fe	Sol gel	1.5	Reactive blue 4	70–120	70	Ultrasonic	1	92	[110]
N	Sol gel	0.4	Phenol	10–200	20	UV	—	—	[118]
P	Sol gel	0.2	Rhodamine B	5–50	12	Solar light	—	85	[119]
Pr	Sol gel	1	Phenol	12.5–200	25	UV	1	100	[111]
W	Liquid phase deposition	—	Dodecyl-benzenesulfonate	250–100	250	Visible	1.5	98	[120]
Zr	Sol gel	0.2	4-chlorophenol	50–300	250	UV	—	100	[121]

5.2. Effect of Initial Reactant Concentration. The influence of initial reactant concentration on the photocatalytic degradation is a great aspect of the study. The relationship between initial reactant concentration and photocatalytic activity of TiO_2 is associated with the adsorption of reactant on the surface of photocatalyst and the screening effect due to overloading of reactant [110]. In general, it is found that the photocatalytic activity of the photocatalysts decreases with increasing the initial reactant concentration. This may be due to the limitation of the numbers of active sites of photocatalyst available on the photocatalyst surface. On the other hand, Andronic et al. [114] reported that the photodegradation efficiency decreased when initial reactant concentration increased. This is due to the decrease of the path length of the photon when entering the reactant solution, with direct consequence on the formation of electron-hole pairs.

In other study on the effect of initial reactant concentration [117], the adsorption of phenol intermediates could lead to the irreversible deposition on the surface of Ce-TiO_2 photocatalyst and thus reduce the photodegradation efficiency. Meanwhile, the excessive of reactant concentration could lead to the screening effect that prohibited the penetration of light irradiation [121]. Beyond the optimum concentration of reactant, more reactant molecules will adsorb on the photocatalyst surface, prohibiting the absorption of photon to form charge carriers. Otherwise, it will also prevent the excessive adsorption of reactant on the active sites of the photocatalyst, inhibit the generation of hydroxyl radical and hence decrease the photocatalytic activity of the photocatalyst [110].

Table 7 summarizes the effect of initial reactant concentration on the photocatalytic degradation of various organic pollutants.

5.3. Effect of Photocatalyst Dosage. The effect of photocatalyst dosage on the photocatalytic degradation process has been widely studied. The reason generally advanced for this is that the optimum photocatalyst dosage maximizes the photocatalytic performance and minimizes the cost and energy.

In most of the studies, the increase in the photocatalyst dosage increases the number of photons absorbed on the photocatalyst surface, which in turn increases the generation of electron/hole pairs and increases the number of hydroxyl radicals. The increase in the photocatalyst dosage also increases the number of organic pollutant adsorbed on the surface of photocatalyst and facilitates the photocatalytic activity [111, 122].

However, when the photocatalyst dosage increases above the optimum level, the photocatalytic activity decreases, which is due to the shadowing effect and the penetration depth of light irradiation by the high turbidity suspension [116]. Huang et al. [58] added that as the excess catalyst prevent the penetration of light in the photocatalytic degradation process, the light scattering and the screening effect decreased among the photocatalyst particles and the efficiency of the photocatalytic degradation reduced accordingly. Furthermore, the increase of the photocatalyst dosage beyond the optimum level may result in the deactivation of the catalyst particle and the collision between the active molecules and ground state molecules of titania [10] and hence degradation rate decrease.

Wang et al. [123] studied the effect of photocatalyst amount on the photocatalytic activity of the catalyst. Based on the result obtained, the photocatalytic degradation was significantly affected by the photocatalyst dosage and that the optimal photocatalyst dosage was 1000 mg/L. When in excess, existence of dopant on the particle surface of TiO_2 lessens the active sites on the surface of TiO_2, aids the agglomeration TiO_2, and thus hinders the photocatalytic activity.

There are several considerations affecting the optimum photocatalyst dosage on the photocatalytic degradation process. These include the type of dopants, light intensity, and initial reactant concentration. Thus, further study is still required to provide a complete understanding of the

Table 8: Effect of photocatalyst dosage on the photocatalytic activity of nano-doped-TiO_2 in the photocatalytic degradation of various organic pollutants.

Type of dopant	Doped TiO_2 preparation method	Range of photo-catalyst dosage (g/L)	Optimum photocatalyst loading (g/L)	Organic pollutant	Initial pollutant concentration (mg/L)	Light source	Irradiation time (h)	Degradation efficiency (%)	Reference
Sn	Sol gel/dip coating	5–15	12.5	Orange-G	50	UV	1	99.1	[122]
Zr	Sol gel	100–500	2.0	4-chlorophenol	250	UV	—	—	[121]
Ba	Sol gel	100–500	2.0	4-chlorophenol	250	UV	—	—	[10]
Fe	Hydrothermal	0.25–1.25	1.0	Azo fuchsine	10	Ultrasonic	1	60	[123]
	Sol gel	0.5–2.0	1.5	Reactive Blue 4	70	Ultrasonic	1	90	[110]
Ag	Photo reduction	326–2608	3.0	Direct Red 23	326	UV	2.5	55	[124]
C	Sol gel	0.5–4.0	1.0	Methylene blue	10	Solar lgiht	1.67	100	[116]
P	Sol gel	0.2–1.2	0.4	Rhodamine B	12	Sunlight	4	93	[119]
Pr	Sol gel	0.0–1.2	1.0	Phenol	50	UV	2	96.5	[111]
	Sol gel	0.5–6.0	3.0	Methyl orange	20	UV	0.5	90.5	[58]

relationship between photocatalyst dosage and other parameters. Table 8 shows the effect of photocatalyst dosage on the photocatalytic degradation of various organic pollutants.

5.4. Effect of Dopant Concentration. Dopant concentration on the photocatalytic activity of photocatalysts has been investigated. The photocatalytic activity was found to be directly proportional to the dopant concentration. However, it was noticed that above a certain level of concentration, the photocatalytic performance decreases.

In Deng et al.'s research [46], the increasing rate of the photocatalytic degradation slowed down when the dopant concentration of Fe was higher than 0.5%. This indicated that Fe^{3+} ions acted as photogenerated electron trap, so the recombination of hole-electron pairs was inhibited. Meanwhile, the transfer of electron from Fe^{2+} to Ti^{4+} surface due to the proximity of the energy levels was also one of the factors in enhancing photocatalytic activity. This is in agreement with recent reports [50, 53, 55]. Zhu et al. [50] also reported an enhancement degradation rates for Fe-doped TiO_2 prepared by hydrothermal treatment as compared to undoped TiO_2 in the photodegradation of active yellow XRG. Tong et al. [53] and Ambrus et al. [55] reported an improved photocatalytic performance for the optimum Fe dopant concentration. Beyond the optimum concentration of dopant, the photodegradation rate decreased.

On the other hand, noble metals such as Pt, Au, and Pd are always advantageous to the photocatalytic degradation process. Sakthivel et al. [57] studied the effect of dopant concentration on the photocatalytic degradation of acid green 16 using doped TiO_2. In their research, the optimum dopant loading concentration enhanced the photocatalytic activity by increasing the photonic efficiency and inhibiting the electron-hole pair recombination. However, any further increase in dopant content exert is negative effect on the photocatalytic activity of the photocatalyst. When in excess, the existence of dopant on the TiO_2 surface blocks the active sites of TiO_2, lessens the adsorption of reactant, and, thereby, reduces the photodegradation efficiency. Huang et al. [58] also studied the decolorization performance of methyl orange using Pt-doped TiO_2. They observed that there was a great enhancement in the decolorization by doping TiO_2 with different amount of wt% Pt. Their report showed that a doping level beyond the optimum doping level (1.5 wt% Pt) seemed to affect adversely the photocatalytic activity. Any further increase in dopant concentration could notably induce the photogenerated hole and electron recombination and decrease the photocatalytic efficiency.

The effect of halogen doping on the photocatalytic degradation of organic pollutants in TiO_2 aqueous solutions has been investigated [77]. They have concluded that F has a strong enhancing effect on the photocatalytic activity, by altering the properties of TiO_2 such as crystallite size, crystallinity, and phase structure. They noted that the addition of F^- ions promotes the formation of anatase phase by suppressing the formation of brookite phase, subsequently forms ≡Ti-F groups, and hence, enhances the free $^\bullet$OH radicals production and reduces the photogenerated electron-hole recombination.

Yu et al. [79] studied the effect of sulfur dopant amount in the photocatalytic activity of S-doped TiO_2. The photocatalytic degradation of methyl orange was studied in the presence of S-doped TiO_2. In their research, they have found that the optimum loading of S dopants could produce TiO_2 with smaller particle size and larger surface area, which increases the formation of photogenerated electrons and thus increases the photocatalytic activity.

The foregoing notwithstanding, there are other researchers who are of the view that the presence of dopant

Table 9: Effect of dopant amount on the photocatalytic activity of nano-doped-TiO_2 in the photocatalytic degradation of various organic pollutants.

Type of dopant	Doped TiO_2 preparation method	Range of dopant amount (wt%)	Optimum dopant concentration (wt%)	Organic pollutant	Initial reactant concentration (mg/L)	Light source	Irradiation time (h)	Degradation efficiency (%)	Reference
Fe	Sol gel	0.0–1.0	0.500	Methyl orange	20.0	UV-vis	3.0	99.7	[46]
	Hydrothermal	0.00–0.12	0.090	XRG	100.0	UV	7.0	42	[50]
	Controlled hydrolysis	0.00–0.20	0.200	Methyl orange	20.0	UV	6.0	72	[53]
	Co-precipitation	0.0–10..0	0.017	Phenol	18.8	Visible	3.1	20	[55]
	Hydrothermal	0.0–5.0	0.001	Methylene blue	100.0	UV	1.0	72	[51]
Pt	Impregnation	0.0–1.6	0.800	Acid green 16	122.0	UV	1.0	94	[57]
	Photochemical reduction	0.0–3.0	1.500	Methyl orange	20.0	UV	0.5	88	[58]
Pd	Impregnation	0.0–2.0	0.050	Acid green 16	122.0	UV	1.0	80	[57]
Au	Impregnation	0.0–1.6	0.800	Acid green 16	122.0	UV	1.0	98	[57]
S	Hydrothermal	0.0–2.0	0.012	Methyl orange	20.0	UV	0.7	96	[79]
Ce	Hydrothermal	0.0–5.0	0.017	Rhodamine B	24.0	UV	2.0	90	[62]

is not requisite for the improvement of the photocatalytic activity of TiO_2. Li et al. [51] investigated the photocatalytic performance of Fe-doped TiO_2 in the degradation of methylene blue. In their research, they have found that the presence of Fe has a suppressing influence on the photocatalytic performance of TiO_2. The inhibition effect can be explained as the insertion of Fe^{3+} ions into the TiO_2 interior matrix, which behaved as charge carrier scavengers. Probably the isolated Fe^{3+} ions from the surface lower the chances of trapped charge carriers and increases the recombination rate of the photogenerated electron-hole pairs. Also, Xiao et al. [63] found that undoped TiO_2 showed better photocatalytic activity as compared to that Ce-doped TiO_2 in the Rhodamine B degradation. They have found that the presence of Ce has a suppressing influence on the photocatalytic performance of TiO_2. It can be explained that the partial blockage of the TiO_2 active sites lowered the activation of the TiO_2 catalyst particle and the collision between the active molecules and ground state molecules of TiO_2, and thus, decreasing the photocatalytic activity.

Table 9 shows the effect of dopant amount on the photocatalytic degradation of various organic pollutants.

6. Conclusions

A comprehensive series of nano-doped-TiO_2 photocatalysts are discussed in this paper. There are three main sections included: (a) the presence of various dopants (metal dopants, nonmetal dopants, halogen dopants, metalloid dopants, and co-dopants) in the formation of nano-doped-TiO_2 photocatalysts, (b) the effect of the presence of dopants on the photocatalytic degradation of organic pollutants, and (c) the effects of various operating parameters on the photocatalytic degradation of organic pollutants in the presence of nano-doped-TiO_2 photocatalysts. Judging from the referenced literatures, doping techniques are simple procedures used to enhance photocatalysis by TiO_2. Desirable characteristics such as small crystallite size, high specific surface area, and the presence of the anatase phase are easily achieved by doping techniques. Nevertheless, the mechanisms underlying doped TiO_2 are still unclear. The relationship between the photocatalytic activity and physical properties of TiO_2 requires further study to arrive at optimal conditions for the photocatalytic degradation of various organic pollutants.

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