



## Use of TiO<sub>2</sub> in Photocatalysis for Air Purification and Wastewater Treatment: A Review

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### HIGHLIGHTS

- The advantages of TiO<sub>2</sub> -based as photocatalyst are reviewed in this study.
- The development of the group gap in photocatalyst (TiO<sub>2</sub>) by different doping was investigated.
- Modification in the structure across the photocatalytic activity of TiO<sub>2</sub> is reviewed.
- Different preparation methods and applications of the Methodology of photocatalysts were also reviewed.

### ARTICLE INFO

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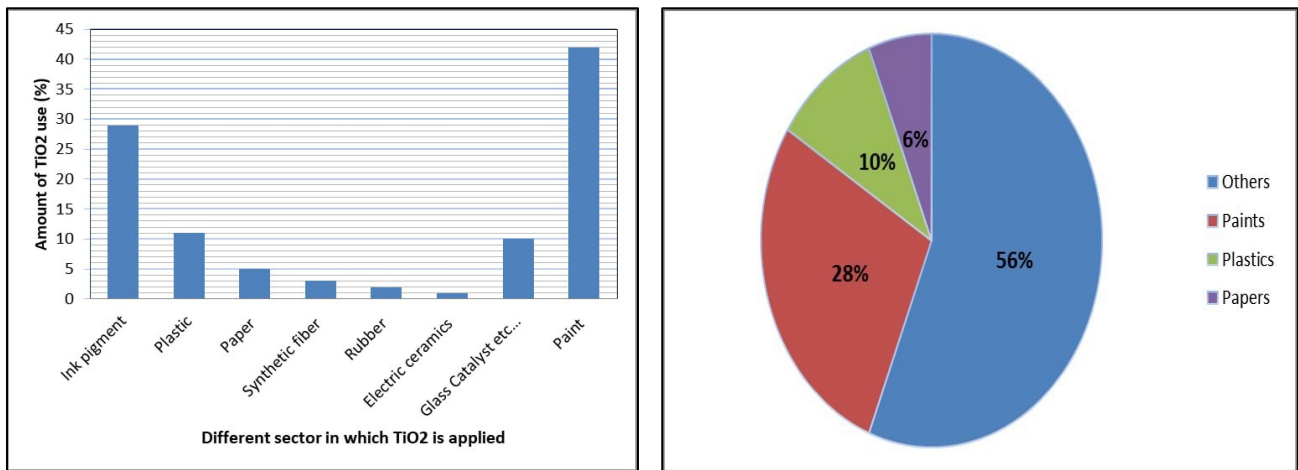
### ABSTRACT

This study reviews recent research on the synthesis and application of titanium dioxide (TiO<sub>2</sub>)-based photocatalysts for environmental applications. The principles of non-homogenous photo-catalysis include utilizing a solid semiconductor, such as titanium dioxide Nano or macro, to form a stable suspension (heterogeneous phase) at the impact of irradiation to elevate a reaction at the surface interface of the different phases in the system. Recently, titanium dioxide has been considered the better semiconductor in non-homogenous photoinduced treatment. TiO<sub>2</sub>-based photocatalysts have broad applications for industrial processes because of their exceptional physicochemical properties. Nevertheless, having a narrow band near the ultraviolet region limits its applications within visible radiation. As a result of this, there have been considerable research efforts to improve the visible light tendency of TiO<sub>2</sub> through modifications of its optical and electronic properties. Several strategies, such as coupling TiO<sub>2</sub> tightly and incorporating other metallic components during synthesis, have increased the bandgap of TiO<sub>2</sub> for visible light applications. Moreover, an overview of nanotechnology that could enhance the properties of TiO<sub>2</sub>-based catalysts in an environmentally friendly way to decompose pollutants is also presented. The various TiO<sub>2</sub>-based photocatalysts have wide applications in degrading recalcitrant pollutants in the air, water, and wastewater treatment under visible light.

## 1. Introduction

The past decades' successes in research and innovations have resulted in astronomical growth in industrial activities to meet the ever-increasing human demands. These anthropogenic activities from the various industries have adversely affected air and water quality through the discharge of industrial wastes, produce wastewater from oil refineries, and emissions of gaseous pollutants [1-3]. Of all the various types of pollution, using petroleum fuel for mobility has resulted in a severe emission of toxic gaseous pollutants and particulate matters into the environment, adversely affecting human health [4-6]. The most significant impact of these pollutions is often experienced among the populace living in the urban area or cities [7]. The high concentration of these pollutants in the environment, which has resulted in various chronic diseases, has been a significant concern for environmentalists and researchers [3, 8]. For instance, studies have shown that high human exposure to nitrogen oxide (NO<sub>x</sub>) often results in asthma [9]. Hence, it is expedient to strategically reduce vehicular emissions, which will invariably lead to NO<sub>x</sub> reduction and minimize its effect on human health [10]. Several methods have been explored and reported in the literature to mitigate the effects of NO<sub>x</sub> from vehicular emissions on the environment.

One of the emerging techniques for mitigating gaseous pollutants is using heterogeneous photo-oxidation (HPO) [11- 12]. The HPO techniques entail using photocatalysts, mostly semiconductors, to degrade these recalcitrant organic pollutants in the presence of an active radiation source and an oxidizing agent. The radiation source could be solar ultraviolet or simulated light [13]. Enormous light irradiation is usually produced from the sun, estimated to be 0.2-0.3 moles of photons per hour in the range of 300-400 nm with a UV flux of 20-30 W/m<sup>2</sup> [14]. Hence, from the economic and environmental point of view, the sun has a great potential to be used as an irradiation source for photocatalytic degradation of organic pollutants [15]. Furthermore,



**Figure 1:** Application and Proportions of TiO<sub>2</sub> used in various sectors (Data for 2013, Merchant Research and Consulting, 2015 [22])

The HPO techniques have been reported to have a promising route for mitigating the impact of NO<sub>x</sub> and other gaseous substances released into the environment [16].

The oxidant used during the NO<sub>x</sub> process is often based on very powerful oxidants, often referred to as hydroxyl radicals, that are usually generated during the photocatalytic process [17]. The hydroxyl radicals can oxidize a wide range of organic pollutants by converting them to harmless inorganic products [18]. Therefore, the HPO process has stimulated the interest in developing an effective electro-catalytic process that can be applied for air purification and treatment of wastes containing recalcitrant organic pollutants. These innovations have also resulted in introducing smart products into the markets that can be deployed to combat environmental pollutants in the past three decades [19].

Semiconductor-based photocatalysts such as titanium dioxide (TiO<sub>2</sub>), tungsten trioxide (WO<sub>3</sub>), and zinc oxide (ZnO) have been widely used for various applications in buildings, paving roads, vehicles side mirrors, lamps, and textiles [20- 21]. Specifically, TiO<sub>2</sub> has been widely applied for various industrial applications, as represented in Figure 1. For example, TiO<sub>2</sub> has been applied in ink pigment production, plastic paper, synthetic fiber, rubber, electric ceramics, paints, glass, and catalysts. In addition, a large proportion of the TiO<sub>2</sub> is applied in paint manufacturing. The annual global consumption of TiO<sub>2</sub> is increasing due to these numerous applications.

## 2. An Overview of Photocatalytic Semiconductors

The increasing interest in removing recalcitrant pollutants from polluted wastewater has led to the development of various inexpensive absorbents that can be easily applied [42]. Also, absorbents have been developed from alternative sources to make them accessible [44]. However, advancement in wastewater treatment has resulted in development of semiconductor materials that are very effective in cleaning up hazardous waste sites, pollution treatment, desalination, and environmental pollution awareness and control [45- 46]. Semiconductors, mostly metal oxides in nanostructures, have been employed in photocatalytic applications due to their excellent physicochemical properties such as band-gap, desired band edge position, large surface area, perfect morphology, and chemical stability, and reusability capability [24]. Table 1 shows that various semi-conductor-based metal oxide is similar in photocatalytic properties and capable of photoactivity under visible light, ultraviolet (UV) light, or a combination of visible and UV light irradiation with a band gap. TiO<sub>2</sub> and ZnO have been used as excellent photocatalysts to degrade numerous environmental contaminants. The increasing interest in TiO<sub>2</sub> and ZnO is due to their high photosensitivity, stability, and large band gap.

### 2.1 General Types and Characteristics of Titanium Dioxide

TiO<sub>2</sub> is abundant in nature as the fourth most easily found material and exists in three phases, namely anatase, rutile, and brookite [48]. The most stable crystalline phase-out of the three is anatase. Rutile, on the other hand, is commonly available, whereas brookite is very rare and often has scanty application. The properties of TiO<sub>2</sub> and ZnO are summarized in Table 2.

Amongst the various semiconductors, TiO<sub>2</sub> has the most comprehensive applications as a photocatalyst [23]. ZnO, which could be a viable alternative to TiO<sub>2</sub>, has received less attention. Because of the large bandgap of ZnO compared to TiO<sub>2</sub>, poor reactivity to visible light, the high recombination ratio of photoinduced electron-hole pairs, and photo corrosion, ZnO has hampered its use in photocatalysis [24]. The discovery of TiO<sub>2</sub> for electrochemical decomposition of water was reported in 1972 by Fujishima and Honda [25]. The authors reported that water was electrochemically decomposed to hydrogen and oxygen using connected TiO<sub>2</sub> and platinum electrodes under ultraviolet light. The platinum electrodes absorbed the ultraviolet light while the electron generated flows from the TiO<sub>2</sub> electrode onto the platinum electrode. The reduction reaction during which hydrogen was produced occurs at the cathode [26]. Later in 1977, it was reported that integrating noble metals such as platinum and gold into the electrochemical photolysis process may enhance the photoactivity of the TiO<sub>2</sub> [27]. Also, studies have shown that hydrogen can be produced by photogeneration on SrTiO<sub>3</sub> photocatalyst and the production of hydrogen and methane by photolysis of ethanol over TiO<sub>2</sub> and PtO<sub>2</sub> [28,29]. photocatalytic applications targeting only the adsorbed

substances on water or air have been published by several authors [30-35]. The abundance of UV irradiation from the sun could be exploited for photocatalytic degradation [29]. A novel concept whereby a light source was employed for maintaining the TiO<sub>2</sub> surface as a cleaning material and photocatalysts were discovered to initiate the change in the water wettability of the TiO<sub>2</sub> surface before and after UV irradiation. The innovation has broadened the application of TiO<sub>2</sub> with a highly hydrophilic having a stable and semi-permanent property. Fujishima and Honda, Fujishima et al., and Yamaguti and Sato [25, 26, 36] investigated the potential of electrochemical photolysis of water to identify the potential challenge of creating a photoelectrochemical tandem cell that is cost-effective, energy-efficient, and imitates natural photosynthesis. The various studies reported the application of TiO<sub>2</sub> in the photolysis of water. However, there is a going interest in the multifunctional capabilities of TiO<sub>2</sub> in photolysis applications. Obtaining intelligent and multifunctional TiO<sub>2</sub> materials requires designing the appropriate composition, incorporating new functional components, and modifying the pristine microstructure [20]. As a result of the large surface area of photocatalytic piers and their nearness to exhaust gases from cars, nobles metal modified photocatalysts have been reported to have a great potential to reduce poisonous gaseous emissions such as sulfur dioxide, nitrogen oxides, carbon dioxide, and so on [30, 35, 37]. As a result of the excellent photocatalytic properties, several studies have reported promising findings in the degradation of the various gaseous organic pollutants from vehicular emissions [32, 35, 38]. These photocatalysts can be categorized as self-cleaning materials with suitable physicochemical properties that can remove the products of oxidation of gaseous pollution from the surface with the help of water. In other words, the surface of TiO<sub>2</sub> can self-renew [39]. Moreover, TiO<sub>2</sub> nanoparticles possess some characteristics in terms of their nano-size, specific surface area, pore-volume, exposed surface facets, and crystalline phase content that could enhance their efficiency in photodegradation of gaseous pollutants in the air, thereby purifying it [40]. TiO<sub>2</sub>-based catalysts have been reported mounted on asphalt pavement for air purification. Besides, Pone and Cheung (2006) reported using paving blocks that make use of NO and TiO<sub>2</sub> to remove waste generated. Moreover, TiO<sub>2</sub> nanoparticles have been reportedly used as an embedded spray for existing pavements in Italy. In another study, Hung et al. (2007) conducted a comparative analysis of the performance of different photocatalysts used in the treatment of waste obtained from cement production under ideal laboratory conditions [41]. In a similar study by Chan et al. (2009), nano-TiO<sub>2</sub> asphalt was applied as an environmental protection material using a permeability technique [42]. The application of modified N-doped TiO<sub>2</sub> photocatalysts prepared and used by spraying onto sample bituminous has been reported by Yan Hua (2010). The effectiveness of photocatalytic materials in removing pollutants such as NO<sub>x</sub> from the atmosphere has been reported by Hassan [43]. This study, therefore, aims at delving into the various properties of TiO<sub>2</sub> nanoparticles and other related photocatalysts, as well as their reaction mechanisms. Besides, their applications in Civil engineering as related to asphalt mixture applications are also reviewed. The various applications of photocatalytic materials in chemical engineering were also reviewed. The various modification strategies employed to enhance the photocatalytic efficacy in the various applications were also explored in the literature and reported. Finally, the modeling of optical pavements and the influence of modifications on the fundamental properties of asphalt mixture were analyzed and reported.

Both anatase and crystallized rutile exist in quadrangular form, whereas brookite possesses a rhomboid shape. In the anatase phase of TiO<sub>2</sub>, there exists a hierarchical symmetry of four units in every primacy cell. The rutile phase has quadrangular symmetry, possessing two equivalent units for every primary cell [50]. However, crystal symmetry has a similar form for both rutile and anatase. Due to structural constraints resulting from high thermodynamic stability, the rutile form of TiO<sub>2</sub> is not usually used for photocatalytic applications [51].

On the contrary, the anatase phase of TiO<sub>2</sub> was widely investigated for potential applications as photocatalysts due to its excellent physicochemical properties and photoactivity. The anatase phase of TiO<sub>2</sub> photocatalysts is highly stable in a photovoltaic reaction using an aqueous system. The anatase phase has a bandgap of 3.23 eV compared to the rutile phase with a bandgap of 2.02 eV, making the anatase TiO<sub>2</sub> to be widely applied in photocatalytic oxidation reactions [24]. Besides, anatase has a more suitable conduction domain for driving the photocatalytic oxidation reaction. During the photocatalytic oxidation reaction, electrons form and highly stable surface peroxide groups over the anatase.

In contrast, the rutile phase is hardly used for the photocatalytic oxidation reaction [52]. In a 1a situation, where there is a combination of both rutile and anatase in a ratio of 0.25 to 0.75, respectively, the combined phase will result in the formation of clusters or a thin rutile layer on the surface of the anatase nanoparticles. This might also lead to the formation of heterojunctions of the two crystalline phases [53]. Studies have shown that when both rutile and anatase are combined, an improvement in the photocatalytic efficiency exists compared to pristine rutile and anatase [54]. TiO<sub>2</sub> has been adjudged as an "ideal" semiconductor for photocatalytic processes due to its numerous advantages in degrading recalcitrant gaseous pollutants. Besides, it is inexpensive, not toxic, and very effective at low concentration and flow rate, high flow rates, high stability, excellent activity, and high removal efficiency [55-56]. These excellent properties have motivated several researchers to be involved in the use of TiO<sub>2</sub> for photocatalytic wastewater treatment.

**Table 1:** Energy band-gap (E<sub>bg</sub>) with a corresponding wavelength (λ<sub>Ebg</sub>) required for activation of various semiconductors [47]

Photocatalysts	Band gap(eV)	(λ <sub>Ebg</sub> )	Photocatalysts	Band gap(eV)	(λ <sub>Ebg</sub> )
Si	1.1	1127	α-Fe <sub>2</sub> O <sub>3</sub>	3.1	400
WSe <sub>2</sub>	1.2	1033	ZnO	3.2	388
Fe <sub>2</sub> O <sub>3</sub>	2.2	564	TiO <sub>2</sub> (Anatase)	3.2	388
CdS	2.4	517	SrTiO <sub>3</sub>	3.4	365
WO <sub>3</sub>	2.7	459	SNO <sub>2</sub>	3.5	354
TiO <sub>2</sub> (rutile)	3.0	413	ZnS	3.7	335

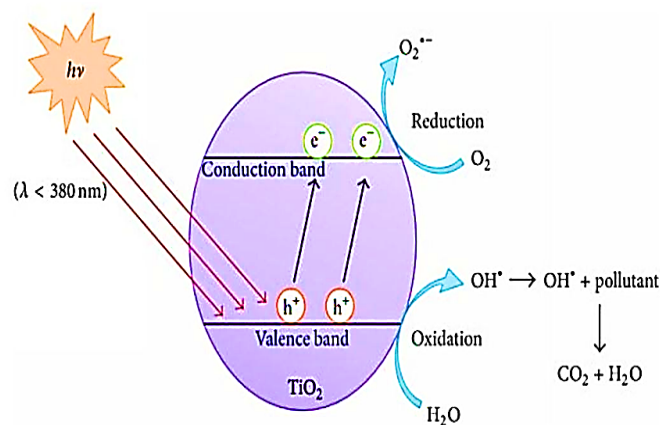
**Table 2:** Summary of selected Properties of TiO<sub>2</sub> and ZnO [47, 49]

Properties at 25 °C	TiO <sub>2</sub> (Rutile)	TiO <sub>2</sub> (Anatase)	ZnO
Density (g/cm <sup>3</sup> )	4.250	3.894	5.606
Volume (nm <sup>3</sup> /molecule)	0.0312	0.0341	0.0241
Specific heat (J/Kmol)	55.06	55.52	43.90
Mohs hardness	7.0-7.5	5.5-6.0	4.5
Melting point (°C)	1840 (decomp.)	Trans. to. Rutile	1970 (decomp.)
Refractive index E//c	2.616	2.554	2.020
(@nD, 589nm) E c	2.903	2.493	2.02
Relative permittivity, ε (0)	167(//c)		7.4 ( c)
Bandgap energy (eV)	3.0 (direct)	3.8 (direct)	3.4
		3.2 (indirect)	
Effective mass (hole)	20	0.8	0.24
Mobility (cm <sup>2</sup> /Vs)	0.1	4-20	130-205
Isoelectric point	5.6	6.1	10.3

### 3. Principle and Mechanism of Photocatalysis

The photocatalytic reaction can be grouped into four different stages. These stages include (i) the photo-excitation process, (ii) the reduction process, (iii) the oxidation process (iv) the recombination process. As shown in Figure 2, the whole process can be explained in detail. During the photo-excitation process, there is the generation of conduction band electrons and valence band holes by the absorption of light that often corresponds to the generation rate of the conduction band and valence band holes onto the photocatalysts. In the second stage, the conduction band electrons trapping on the photocatalysts' surface. The adsorbed molecules are reduced using the trapped electrons. During the oxidation stage, the adsorbed molecules are oxidized by the valence band holes. Trapped holes are formed by the trapping of valence band holes on the photocatalysts' surface. During the recombination stage, there is a conduction band of electrons with the valence band holes. The trapped holes are also recombined with the conduction band electrons. There is also recombination of the valence band holes with the trapped electrons. And finally, the trapped holes are recombined with the trapped electrons.

During the decomposition of organic pollutants, the pathways for the primary reaction in the oxidation stage are often the reaction that occurs directly on the surface of TiO<sub>2</sub> with valence bands holes or trapped holes [48]. The presence of oxygen in the process generally speeds up the photocatalytic reaction. In the photocatalytic reaction, hydroxyl radicals and superoxides are responsible for oxidizing and reducing environmental contaminants [57]. There are four distinct pathways in oxidative decomposition to form OH radicals in the photocatalytic reaction. First, electrons are extracted directly through the valence band slots from the adsorbing molecules to oxidize them. In the second stage, valence band holes are superimposed on the surface of TiO<sub>2</sub>, often resulting in trapping holes that are used to oxidize molecules on the surface of the photocatalyst. During the third stage, the surface hydroxyl groups or the water adsorbed are oxidized by the valence band openings, resulting in the generation of adsorbed hydroxyl radicals. The molecules adsorbed by OH radicals on the surface of the photocatalyst are then oxidized, causing the material to break down to form carbon dioxide and inorganic ions such as NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, and SO<sub>4</sub><sup>2-</sup> [53, 58]. Lastly, the generated OH radicals are released from the surface to the atmosphere or into the solution. The released OH radical can then be used to oxidize the compounds far away from the photocatalyst surface. As the irradiation time increases, there is often a corresponding increase in the formation of OH radicals, leading to complete degradation of the organic pollutant as time progresses [59]. For example, consider NO<sub>x</sub> degradation, as illustrated by Equations (1-6) [60]. The end products of the photocatalytic process are usually water-soluble nitrates [61]. These water-soluble nitrates undergo a reaction to form soluble mineral salts, which are harmless to the environment [57].

**Figure 2:** Schematic representation of the photocatalysis in a semiconductor material [62]



## 4. Application of Semiconductor-Titanium Dioxide

TiO<sub>2</sub> as a heterogeneous photocatalyst has been demonstrated to have a great potential for various applications, most especially for wastewater treatment, hydrogen production from water splitting, and photo-reforming. In addition, several studies have demonstrated the robustness of TiO<sub>2</sub> in the degradation of recalcitrant organic pollutants present in pharmaceutical wastewater.

### 4.1 General Application of Titanium Dioxide

Generally, TiO<sub>2</sub> is found in several industries for wide applications, such as paper production, plastic, pharmaceuticals, and sunscreen. This is due to its transparent and UV-absorbing properties. Using TiO<sub>2</sub> in a smart building could help in energy saving as a result of its light-reflecting qualities, which drastically reduce the amount of heat absorbed by the building. Hence, researchers (Hashimoto et al. 2005; Chen & Poon 2009) have shown dramatic energy savings through the reduction in air conditioners [63, 64]. In addition, there is an increasing research interest in the use of TiO<sub>2</sub> for the promotion or improvement of some properties like self-cleaning, the degradation of air and water organic pollutants, anti-fogging, anti-microbial, anti-aging, and surface cooling.

### 4.2 Application of Titanium Dioxide in Water Purification

Due to its interesting properties, photocatalytic degradation has been widely used to treat industrial wastewater from pharmaceuticals, refineries, and agro-allied industries. As summarized in Table 3, various modified TiO<sub>2</sub> have been employed to treat pharmaceutical wastewater containing organic pollutants such as chloramphenicol, metronidazole, amoxicillin trihydrate, bisphenol A, naproxen sodium, and malathion. The various studies revealed that the modified TiO<sub>2</sub> photocatalysts used under various conditions, such as varying irradiation time, degraded the organic pollutants to a large extent, except for Sn-TiO<sub>2</sub>, which performed poorly in percentage removal of the organic pollutants.

### 4.3 Application of Titanium Dioxide in Air Purification

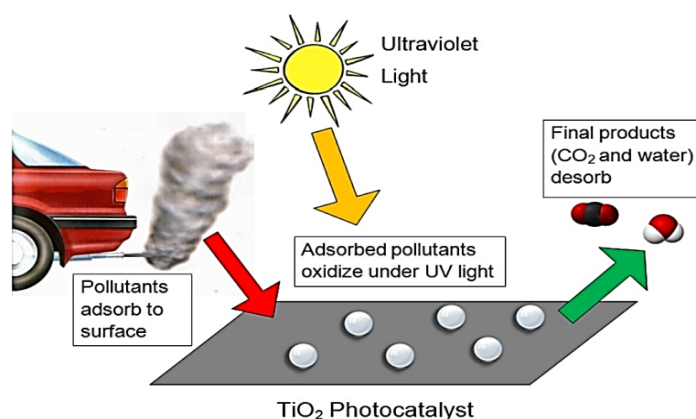
The various industrial activities and vehicular mobility often result in the emissions of gaseous pollutants to the environment. Among these various organic pollutants are formaldehyde, naphthalene, polycyclic aromatic hydrocarbons, trichloroethylene, tetrachloroethylene, carbon monoxide, and nitrogen dioxides have been identified as the most important air pollutants. Hence, researchers and environmentalists have focused on various strategies to reduce the impacts of these organic air pollutants on the environment. Table 4 summarizes research efforts in the last decades whereby different modified TiO<sub>2</sub> were applied for degrading the various organic and inorganic pollutants. The various studies revealed that the photocatalysts effectively removed over 80% of the organic pollutants from the air. The TiO<sub>2</sub>-based photocatalysts' activities were largely dependent on several factors such as the organic pollutants concentration, air humidity and flow rate, the pollutants' nature and source of light radiation, and the physicochemical properties of the photocatalysts. As shown in Figure 3, the ultraviolet light source facilitates the degradation of the organic pollutants, thereby assisting in the decontamination of the air.

**Table 3:** Summary of the application of TiO<sub>2</sub>-based photocatalysts for wastewater treatment

TiO <sub>2</sub> -based photocatalysts	Organic pollutants	Irradiation time (min)	Percentage removal (%)	References
Ag-TiO <sub>2</sub>	Chloramphenicol (20 mg/L)	30	~100	[65]
Fe <sub>2</sub> O <sub>3</sub> -TiO <sub>2</sub>	Bisphenol	120	97	[66]
Sn-TiO <sub>2</sub>	Amoxicillin trihydrate (10–40 mg/L)	30	0.25	[67]
Zr-TiO <sub>2</sub>	Bisphenol A (15–60 mg/L)	80	100	[68]
Ni-TiO <sub>2</sub>	Naproxen sodium (10 mg/L)	360	84	[69]
Cu-TiO <sub>2</sub>	Mefenamic Acid (10 mg/L)	90	97	[70]
Fe-TiO <sub>2</sub>	Naproxen sodium (10 mg/L)	360	99	[69]
N-TiO <sub>2</sub>	Malathion (15 mg/L)	150	97	[71]
Fe-TiO <sub>2</sub>	4-nitrophenol (10 mg/L)	300	92	[72]
Ag-TiO <sub>2</sub>	Metronidazole (15–30) mg/L	120	96.55	[73]
Ag-TiO <sub>2</sub>	Amoxicillin (20 mg/L)	300	63.48	[74]
Cr-TiO <sub>2</sub>	2,4dichlorophenol (100mg/L)	480	83	[75]
Ni-TiO <sub>2</sub>	Bisphenol A (10 mg/L)	120	93	[76]
S-TiO <sub>2</sub>	Diclofenac (10 mg/L)	240	93	[77]
N-TiO <sub>2</sub>	4-chlorophenoxyacetic acid (0.01–0.1 mM)	360	100	[78]
C-TiO <sub>2</sub>	2,4,6-trichlorophenol (10–40 mg/L)	90	98	[79]

**Table 4:** Summary of the application of TiO<sub>2</sub>-based photocatalysts

TiO <sub>2</sub> -based photocatalysts	Organic pollutants in air	Preparation method	References	Removal efficiency
N-Ni-TiO <sub>2</sub>	Formaldehyde	Sol-gel	[80]	Not mentioned
Graphene-TiO <sub>2</sub>	Acetone	Hydrothermal	[81]	Not mentioned
CNT/TiO <sub>2</sub>	Benzene	Mixing	[82]	Not mentioned
Pt/TiO <sub>2</sub>	Toluene	Photo-deposition	[83]	Not mentioned
Ag/TiO <sub>2</sub>	Toluene	Photo-deposition	[83]	Not mentioned
TiO <sub>2</sub> P25	Ethylbenzene	Commercial	[84]	Not mentioned
TiO <sub>2</sub> P25	o-Xylene	Commercial	[84]	Not mentioned
TiO <sub>2</sub>	Hexane	Sol-gel	[85]	Not mentioned
TiO <sub>2</sub>	Dichloromethane	Sol-gel	[41]	44%
Fe-TiO <sub>2</sub>	Dichloromethane	Sol-gel	[41]	65%
Pt/TiO <sub>2</sub>	Trichloroethylene	Photo-deposition	[83]	improving mineralization by a 3.5 time
Ag/TiO <sub>2</sub>	Trichloroethylene	Photo-deposition	[83]	deterredTCE photodegradation
TiO <sub>2</sub>	Tetrachloroethylene	Sol-gel	[86]	Not mentioned
TiO <sub>2</sub> P25	2-Propanol	Commercial	[87]	Not mentioned
Pt/TiO <sub>2</sub>	Carbon monoxide	Mixing	[88]	Not mentioned
CdS/TiO <sub>2</sub>	Nitrogen oxide	Sol-gel	[47]	80%

**Figure 3:** Photocatalytic asphalt mixture [89]

The use of TiO<sub>2</sub> for environmental radiation has been reported to increase the span of materials and facilitate the decontamination of some industrial processes, especially in the petroleum, textile, and pharmaceutical industries. Advanced oxidation photocatalytic degradation has gained increasing interest due to its efficiency and ease of handling of the process. Besides wastewater treatment and air purification, one key application of TiO<sub>2</sub>-based photocatalysts is the decontamination of harmful pathogens in the air. Due to the high level of contamination by pathogens, it is expedient to decontaminate indoor environments like residences and hospitals [90]. Most often, pathogens such as bacteria, viruses, and fungi are present in the air, thereby reducing the air quality, which can endanger human health. Studies have shown that TiO<sub>2</sub>-based photocatalysts are highly efficient in photo-disinfection the various pathogen investigated.

## 5. Synthesis of TiO<sub>2</sub>-Based Photocatalysts Using Different Methods

The need to expand the application of TiO<sub>2</sub> in various fields of photocatalysis has increased research interest in increasing the threshold wavelength of 388nm to the wavelength range within the visible light spectrum. Modifying TiO<sub>2</sub> photocatalysts to enhance their activities within the visible light region would enable a wider application in terms of degrading the recalcitrant organic pollutants in wastewater and air. Furthermore, the modifications of TiO<sub>2</sub> could further help restrain electron-hole recombination, which invariably improves photosensitivity. One major strategy to achieve this is by doping the TiO<sub>2</sub> with metals or non-metals. The doping of TiO<sub>2</sub> with metals or non-metals could be achieved either by chemical or physical ion implantation methods. Hence, the doping strategy facilitates shifting the TiO<sub>2</sub> absorption band toward the visible region, which can be used under natural solar irradiation [91]. The doping of TiO<sub>2</sub> can effectively be achieved using different synthesis methods. Various techniques have been employed for the synthesis of TiO<sub>2</sub>-based photocatalysts that is used for various

photodegradation applications. These techniques are summarized in Table 5. These techniques include sol-gel, reverse micelle mediated sol-gel, wet impregnation, chemical reduction, microemulsion, hydrothermal, microwave mediated sol-gel, and sol-gel & hydrothermal. To increase the photoactivity of TiO<sub>2</sub> and enhance its ability to function effectively under visible light, various metal dopants have been employed for the synthesis. The metal dopants that have been employed include Ag, Au, Fe, Cu, Ni, Co, Mn, Zn, and Mo.

The use of the sol-gel method for the synthesis of modified TiO<sub>2</sub> photocatalysts has been reported by several authors such as [89, 91 - 93] used Ti (OCH(CH<sub>3</sub>)<sub>2</sub>)<sub>4</sub>, FeCl<sub>3</sub> as the precursor materials for synthesizing Au-TiO<sub>2</sub> using sol-gel. Au composition of 0.25, 0.5, 1.0, 2.0, 4.0, and 5.0 atomic% were employed for the modification of the Au-TiO<sub>2</sub>. Also, [94] employed TiCl<sub>4</sub>, C<sub>2</sub>MnO<sub>4</sub>, TiCl<sub>4</sub>, C<sub>2</sub>ZnO<sub>4</sub>, and Ni (NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O as precursor materials for synthesizing Mn-TiO<sub>2</sub> and Zn-TiO<sub>2</sub>, and Ni-TiO<sub>2</sub> photocatalysts by sol-gel method. The effect of varying the concentration of the Mn, Zn, and Ni dopants on the photoactivity of the TiO<sub>2</sub> was also investigated. Similarly, [91] also used Ti(OCH(CH<sub>3</sub>)<sub>2</sub>)<sub>4</sub>, Cu(CO<sub>2</sub>CH<sub>3</sub>)<sub>2</sub> as precursors materials for the synthesis of Cu-TiO<sub>2</sub> using the sol-gel method. The Cu dopant's concentration of 5.9 and 13 mol% was used to determine its effect on the TiO<sub>2</sub> photoactivity. Ali et al. (2018) employed Titanium tetra-isopropoxide, silver nitrate, glacial acetic acid, and absolute ethanol to prepare TiO<sub>2</sub> and Ag-TiO<sub>2</sub> photocatalysts. The concentration of 2, 4, 6, and 8 mol% was used for the Ag synthesis to determine the photoactivity effect [92]. Modified forms of sol-gel, such as reverse micelle-mediated sol-gel, microwave-mediated sol-gel, and combined sol-gel-hydrothermal methods, have also been employed to synthesize Ag-TiO<sub>2</sub> Cu-TiO<sub>2</sub> and Bi-TiO<sub>2</sub> photocatalysts. Precursors such as Ti{OCH(CH<sub>3</sub>)<sub>2</sub>}<sub>4</sub>, AgNO<sub>3</sub>, TiCl<sub>4</sub>, C<sub>2</sub>NiO<sub>4</sub>, Ti (OCH(CH<sub>3</sub>)<sub>2</sub>)<sub>4</sub>, Bi (NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O were employed for the synthesis of the photocatalysts with varying concentrations of dopants.

Besides the sol-gel method, wet-impregnation of the metal precursors into the TiO<sub>2</sub> has been reported by Tayade et al. (2006) for the synthesis of Ag-TiO<sub>2</sub>, Fe-TiO<sub>2</sub>, and Ni-TiO<sub>2</sub> using Ti{OCH(CH<sub>3</sub>)<sub>2</sub>}<sub>4</sub>, AgNO<sub>3</sub>, TiO<sub>2</sub> (Degussa P25), Cu(NO<sub>3</sub>)<sub>2</sub>, and CoSO<sub>4</sub>, TiOSO<sub>4</sub> as precursors. Furthermore, the effect of varying the Ag, Fe, and Cu dopants on the TiO<sub>2</sub> photoactivity was also investigated [93].

**Table 5:** Summary of synthesis techniques employed for TiO<sub>2</sub>-based photocatalysts

TiO <sub>2</sub> -based photocatalyst	Preparation methods	Chemicals	References
Ag-TiO <sub>2</sub>	Sol-gel	Ti{OCH(CH <sub>3</sub> ) <sub>2</sub> } <sub>4</sub> , AgNO <sub>3</sub>	[92]
Ag-TiO <sub>2</sub>	Reverse micelle mediated sol-gel	Ti{OCH(CH <sub>3</sub> ) <sub>2</sub> } <sub>4</sub> , AgNO <sub>3</sub>	[95]
Ag-TiO <sub>2</sub>	Wet impregnation	Ti{OCH(CH <sub>3</sub> ) <sub>2</sub> } <sub>4</sub> , AgNO <sub>3</sub>	[8]
Ag-TiO <sub>2</sub>	Chemical reduction	TiO <sub>2</sub> powder, AgNO <sub>3</sub>	[96]
Ag-TiO <sub>2</sub>	Microemulsion	(Ti(OC <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> ), HAuCl <sub>4</sub> ·4H <sub>2</sub> O	[97]
Au-TiO <sub>2</sub>	Photolysis	Ti{OCH(CH <sub>3</sub> ) <sub>2</sub> } <sub>4</sub> , FeCl <sub>3</sub>	[98]
Fe-TiO <sub>2</sub>	Wet impregnation	Ti{OCH(CH <sub>3</sub> ) <sub>2</sub> } <sub>4</sub> , Fe (NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	[8]
Fe-TiO <sub>2</sub>	Hydrothermal	Ti{OCH(CH <sub>3</sub> ) <sub>2</sub> } <sub>4</sub> , CuCl <sub>2</sub>	[99]
Cu-TiO <sub>2</sub>	Sol-gel	Ti{OCH(CH <sub>3</sub> ) <sub>2</sub> } <sub>4</sub> , Cu(CO <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub>	[91]
Cu-TiO <sub>2</sub>	Wet impregnation	TiO <sub>2</sub> (Degussa P25), Cu(NO <sub>3</sub> ) <sub>2</sub>	[8]
Cu-TiO <sub>2</sub>	Microwave mediated sol-gel	TiCl <sub>4</sub> , C <sub>2</sub> NiO <sub>4</sub>	[100]
Ni-TiO <sub>2</sub>	Sol-gel	Commercial TiO <sub>2</sub> , Ni(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	[94]
Ni-TiO <sub>2</sub>	Hydrothermal	Ti{OCH(CH <sub>3</sub> ) <sub>2</sub> } <sub>4</sub> , Ni(OCOCH <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	[101]
Ni-TiO <sub>2</sub>	Wet impregnation	CoSO <sub>4</sub> , TiOSO <sub>4</sub>	[8]
Co-TiO <sub>2</sub>	Hydrothermal	Ti{OCH(CH <sub>3</sub> ) <sub>2</sub> } <sub>4</sub> , CoCl <sub>2</sub>	[102]
Co-TiO <sub>2</sub>	Wet impregnation	CoSO <sub>4</sub> , TiOSO <sub>4</sub>	[8]
Bi-TiO <sub>2</sub>	Sol-gel & hydrothermal	Ti{OCH(CH <sub>3</sub> ) <sub>2</sub> } <sub>4</sub> , Bi (NO <sub>3</sub> ) <sub>3</sub> ·5H <sub>2</sub> O	[103]
Mn-TiO <sub>2</sub>	Sol-gel	TiCl <sub>4</sub> , C <sub>2</sub> MnO <sub>4</sub>	[94]
Zn-TiO <sub>2</sub>	Sol-gel	TiCl <sub>4</sub> , C <sub>2</sub> ZnO <sub>4</sub>	[94]



**Figure 4:** (a) The TiO<sub>2</sub> solution spraying process (b) the painting process of TiO<sub>2</sub> solution [43]

## 6. Conclusions

The study has presented an overview of the modification of TiO<sub>2</sub> photocatalysts used for various applications such as air purification and wastewater treatment. The distinctive properties of TiO<sub>2</sub> and modified TiO<sub>2</sub> make it suitable for air purification and wastewater treatment application. The various studies have revealed that TiO<sub>2</sub> has been modified with different metals and non-metals. The physicochemical properties of the modified TiO<sub>2</sub> strongly depend on the composition of the photocatalysts, the type of synthesis methods, and the nature of dopants. Out of the various synthesis methods used for synthesizing the modified TiO<sub>2</sub>, the sol-gel was commonly used and found effective compared to other methods such as wet impregnation, hydrothermal, and chemical reduction. On the other hand, the TiO<sub>2</sub> doped with noble metals was very effective in degrading the air and water pollutants. This can be attributed to the distinctive physicochemical and photo properties of the TiO<sub>2</sub>-based catalysts. Although the various modified TiO<sub>2</sub> has been proven effective for degrading the various air and water pollutant, there is a need for continuous strategies to improve the properties of TiO<sub>2</sub>-based catalysts for effective mitigations of environmental pollutants from the environment.

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### Author contribution

All authors contributed equally to this work.

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### Data availability statement

The data that support the findings of this study are available on request from the corresponding author.

### Conflicts of interest

Authors declare that their present work has no conflict of interest with other published works.

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