



Review

TiO₂ photocatalyst for water treatment applications

Seul-Yi Lee, Soo-Jin Park*

Department of Chemistry, Inha University, 100 Inharo, Incheon 402-751, Korea

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ABSTRACT

Recently, many water treatment technologies, such as biological treatment, coagulation/precipitation techniques, Fenton oxidation treatments, and advanced oxidation techniques, have been assessed to address the worsening clean water shortage. This review summarizes these technologies and provides the background and principle of photocatalysis for advanced oxidation technology. In particular, this paper focuses on semiconductor TiO₂ photocatalysts as well as the latest modifications of TiO₂ photocatalyst, such as the introduction of metals or heteroatoms onto TiO₂, physical modification of TiO₂ for a variety of morphologies, and hybrid TiO₂/nanocarbon composites, to improve the photocatalytic activities for an advanced oxidation process. This review provides useful information to scientists and engineers in this field.

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1. Introduction

Recently, water shortages are becoming an increasing problem due to scientific advances following rapid industrial growth, environmental pollution, depleted water resources, global warming causing abnormal climate changes, and uncontrolled ground-water development [1,2]. The rapid development of manufacturing technology after the industrial revolution has improved the standards of living significantly but it is becoming a factor that is threatening human health and the environment. Pollutants are changing both quantitatively and qualitatively, and the number of chemicals currently in circulation is 38,000 with more than 300

new materials being synthesized every year due to the diversification of industrial structures and high-tech industry [3–5].

In line with national development, growth and policy, industrial wastewater is becoming more contaminated and difficult to process. In particular, there are few effective and economic treatment methods for livestock manure and litter leachate. Organic compounds and toxic pesticides, and manure emission from each industry are polluting drinking water and rivers, which is becoming a worldwide contamination with increased severity. The wide area of water pollution, diversification and non-biodegradable problems has become a problem that cannot be solved by the natural cleansing cycle [6–8].

Moreover, in the case of water treatment technology, which includes non-biodegradable organic compounds, it is very difficult to remove pollutants completely with existing biological treatment technology, which includes coagulation/precipitation

* Corresponding author.

E-mail address: sjpark@inha.ac.kr (S.-J. Park).

techniques, and Fenton oxidation treatment technology. Biological treatment technologies use the microbial metabolism [9–11]. The methods are reliable, economical and safe, but the process efficacy for removing suspended solids is low highlighting the need for better operation management. The coagulation and precipitation technique is a method that precipitates suspended solids by forming flocs after the addition of a polymer coagulator or inorganic coagulants (Fe, Al, etc.), which can coagulate with pollutants to be moved by adding a water-soluble metal salt and adjusting the pH or adding polymer coagulant to form sludge flocs to precipitate or separate suspended or dissolved solids from waste water [12–15]. This has high treatment efficiency but the use of chemicals, environmental problems and biological sludge causes pipe blockages and water deterioration. Fenton oxidation treatment technology breaks down organic matter by the strong oxidation power of the Fenton's reagent because it generates OH radicals (OH•) via a reaction of hydrogen peroxide and iron salts, which are the Fenton's reagents [16–20]. This process involves a coagulation process to remove the iron salts, neutralization, and oxidative reactions due to Fenton's reagent. Therefore, additive devices are not used excessively compared to other high-level oxidation methods or photooxidation method, and the process is easy to apply. On the other hand, its disadvantages include the amount of sludge produced, and the excessive operating expense for secondary processing. Table 1 lists the advantages and disadvantages of a photocatalytic system and existing water treatment methods.

A strong water treatment technology that can treat water rapidly is needed to handle the large quantities of water by effectively removing these new contaminants.

Compared to the typical chemical treatments, Advanced Oxidation Technology (AOT) is a method that uses a range of technologies to the increase oxidation power. For effective water treatments, a range of pollutants need to be removed economically at room temperature and under atmospheric pressure [21–23]. As shown in Table 2, AOT produces OH•, which has stronger oxidation power than ordinary oxidants normally used in the oxidation process, in water (oxidation potential: 2.80 eV) and decomposes the organic compounds into relatively harmless compounds, such as CO₂, H₂O, or HCl [24].

In these advanced oxidation technologies, a variety of advanced oxidation technologies exist according to the methods to generate

Table 2

Redox potential of major oxidizing agents that are used in water treatment technology.

Oxidizing agent	Oxidation potential (V)	Relative oxidation power ^a
OH radical	2.80	2.06
Ozone	2.07	1.52
Hydrogen peroxide	1.77	1.30
Perhydroxyl radical	1.70	1.25
Permanganate	1.68	1.24
Chlorine dioxide	1.57	1.15
Chlorine	1.36	1
Oxygen	1.20	0.88

^a Relative oxidizing power when chlorine's oxidation power is 1.

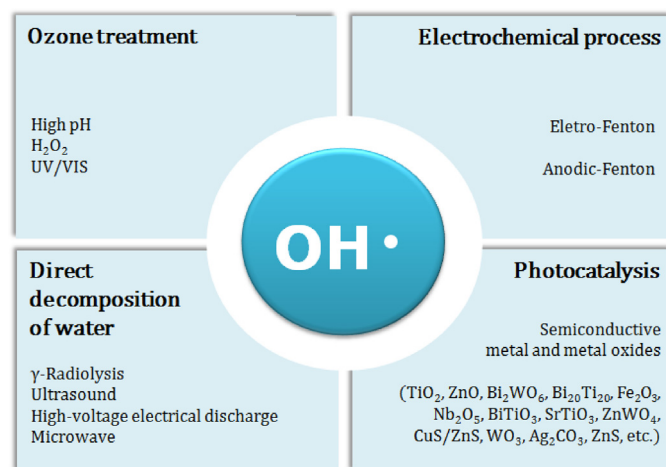


Fig. 1. Hydroxyl radicals formed according to advanced oxidation technologies.

OH•. The following techniques are used in AOT (Fig. 1): (i) technology that uses ozone [25–28], (ii) Fenton technology that uses electrochemical activity [29–31], (iii) decomposing water directly using external energy sources, such as an electromagnetic beam [32], ultrasound [33] and microwave [34], and (iv) photochemical techniques that uses the catalytic activity of semiconducting metal oxides [35,36].

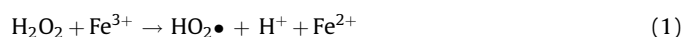
Table 1

Comparing the advantages and disadvantages of photocatalytic system and existing water treatment methods.

	Advantage	Disadvantage
Biological treatment technique	<ul style="list-style-type: none"> - High reliability of the method - High load operation can be processed 	<ul style="list-style-type: none"> - Efficiency of processing difficulty securing stable - High level of sludge - Operating management requires expertise
Coagulation/precipitation	<ul style="list-style-type: none"> - High efficiency of processing - Low sites 	<ul style="list-style-type: none"> - Excessive sludge - Difficult to maintain
Fenton technology	<ul style="list-style-type: none"> - Wide coverage - Treatment process is simple and easy to manage - Effective colored discoloration of wastewater 	<ul style="list-style-type: none"> - High operating costs over the use of the Fenton's reagent - Remove the equipment needed iron salts
Photocatalytic advanced oxidation technology	<ul style="list-style-type: none"> - Non-biodegradable waste water treatment is possible - Low operational and installation cost - Sludge treatment costs do not occur, no burden of costs - Unprofessional and unmanned operation is possible - Simple pre-processing is directly to the wastewater treatment - Less area is linked with the existing treatment facilities - Changes in water quality and quantity can give partial installation selection for operation 	<ul style="list-style-type: none"> - Limited lamp life when UV-Lamp is used - Photocatalyst recovery facility when using powder

AOT with ozone is used worldwide. This technology inserts ozone gas directly into contaminated water [37]. One method is to make the organic contaminants react directly with ozone, and another is to effectively cause oxidative decomposition through an indirect reaction with OH•, which is generated by decomposed ozone. On the other hand, the mechanism of ozone decomposition depends on the properties of the organic pollutants in polluted water. Hence, the organic pollutants in contaminated water can either promote or inhibit ozone decomposition. Therefore, the advanced technology using ozone can treat a range of organic pollutants that are difficult to decompose by a direct reaction with ozone, but the treatment efficiency for those pollutants that are highly reactive with ozone can deteriorate [38,39].

Fenton oxidation technology that uses the Fenton reaction is a method to generate OH• in a Fe²⁺ and H₂O₂ mixture [40,41]. This can decompose H₂O₂ by Fe²⁺ in the liquid phase without light irradiation, and generate OH•. In the case where light is irradiated, the faster decomposition of H₂O₂ is possible due to ferrous or ferric ions and rapid OH• generation is possible. These reactions can be performed under UV radiation and visible light, and the range can be expanded. On the other hand, the rate of OH• generation decreases sharply when the initially injected Fe²⁺ is consumed completely. This is because a reduction reaction is much slower than the Fenton reaction, in which Fe²⁺ is oxidized by H₂O₂. In addition, the Fenton oxidation reaction is only applicable under the acidic conditions, *i.e.*, pH < 4. Therefore, the process has disadvantages of high cost of operation due to the additional cost of the acid/base for pH adjustments [42,43]. Fenton reaction can be express as:



OH• can be generated by directly decomposing water using an external energy source, such as an electromagnetic beam, ultrasound and microwave [44]. When water is irradiated with an electromagnetic beam (gamma rays), water molecules are decomposed to OH•, H⁺, and aqueous electrons. Water molecules can also be decomposed by a high-voltage discharge in water. When high voltage pulses of approximately 10 kV, which has a fast voltage rise time in nanoseconds, are added between two electrodes installed with a narrow gap (a few centimeters) between them, a flame is generated as water discharge is caused. This generates localized high concentrations of OH•. OH• can also be generated by ultrasound or microwaves [45]. When these energy sources pass through water, localized pressure differences with time generate microbubbles, which acquire vibration energy and become unstable. These bubbles generate strong energy at high temperatures and high pressures, and the water molecule is broken down to OH• and H⁺.

Technology that uses the catalytic activity of semiconducting metal oxides, such as TiO₂, ZnO, Bi₂WO₆, Bi₂₀Ti₂₀, Fe₂O₃, Nb₂O₅, BiTiO₃, SrTiO₃, ZnWO₄, CuS/ZnS, WO₃, Ag₂CO₃, ZnS, *etc.* [24,46], has been researched actively with particular focus on TiO₂ photocatalytic technology [47]. The advanced technology that uses TiO₂ photocatalysis is attracting the most attention for generating OH• semi-permanently using only photoenergy without additional chemicals. In addition, the operating cost for the process can be reduced dramatically when solar energy is used. On the other hand, the low luminous efficiency of TiO₂ is an obstacle to the practical use of this technology in water treatment [48].

Therefore, this paper reviews the literature on improving the photocatalytic activity of TiO₂ for applications to AOT.

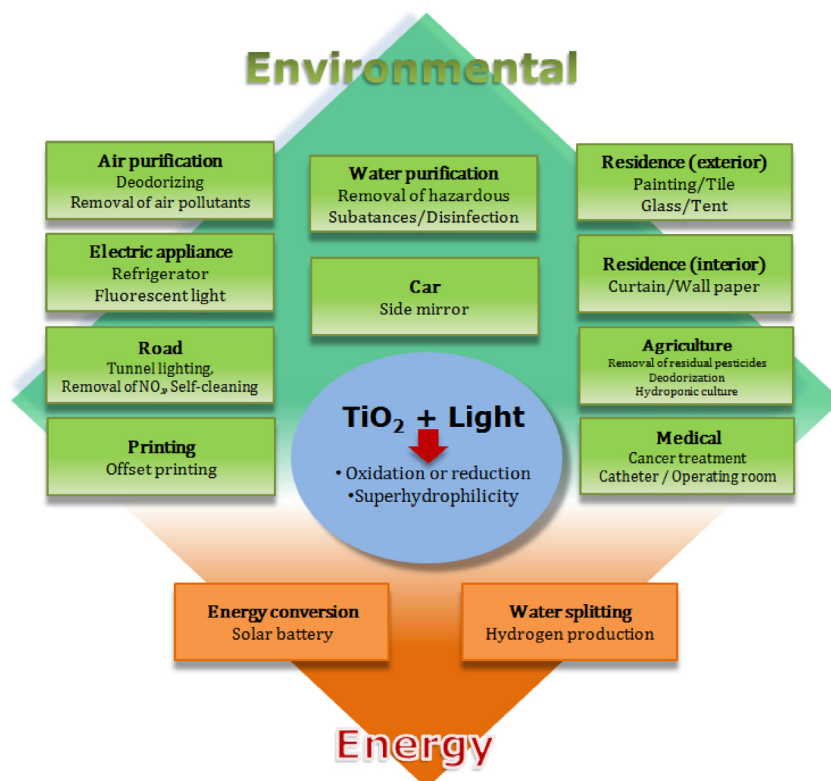


Fig. 2. Various applications of TiO₂ photocatalysis in environment and energy fields.

2. Background of TiO₂ photocatalysis

Photocatalytic research is basically related to the development of solar energy use. The use of solar energy technology can be divided into solar batteries [49,50], solar heat [51] and photocatalysis [52]. The core technology among them is to convert solar energy into chemical energy. This conversion refers to the synthesis of chemical energy to induce a chemical reaction.

In the early 1970s, Formenti *et al.* [53] and Fujishima and Honda [54] revealed the possibility of hydrogen production through water decomposition by photocatalysis and solar energy, and explosive research began. Afterwards, the interest in TiO₂ photocatalysis has been growing in the academic and industrial fields, and has been applied actively to hydrogen production [55,56], air cleaning [57], metal anti-corrosion [58,59] and hydrophilic [60,61], self-purification [62,63], and antibacterial activity [64,65]. Some of these technologies have been released on the market. Fig. 2 shows the various applications of TiO₂ catalysis in a recent.

A photocatalyst refers to a “catalyst that accelerates the solar photo reaction”, and to become photocatalyst, the following conditions need to be fulfilled: (i) the photocatalyst should not participate directly in the reaction or be consumed; and (ii) needs to provide other mechanism routes from existing photo reactions and accelerated reaction rate.

Semiconductor molecules contain a valence band (VB) occupied with stable energy electrons and empty higher energy conduction bands (CB). As shown in Fig. 3, the band gap of the semiconductor with higher energy is used to emit light inside the semiconductor to induce a reaction with the absorbent material on its surface *via* a redox reaction. This is called the photocatalytic reaction [66]. Photocatalytic reactions are based on solar energy absorption in the bad gap of the semiconductor and the following photo-generated electron transfer. Therefore, all semiconductor materials can be used in photocatalysis. On the other hand, there are few effective semiconductors as photocatalysts, and TiO₂ is the most widely used among them.

3. Characteristics of TiO₂ photocatalysis for advanced oxidation technology

To apply semiconductor photocatalysts for water treatment, the following needs to be fulfilled; the operation needs to be performed at room temperature or pressure, complete mineralization without secondary pollution, repetitive cycles and low costs for operations. TiO₂ photocatalysis is a photo-induced charge separation phenomenon that occurs on the TiO₂ surface, and very

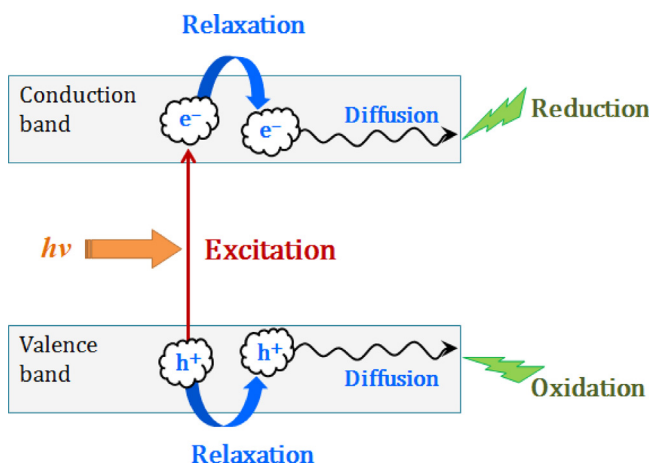


Fig. 3. Schematic illustration of the formation of photoinduced charge carriers (e^-/h^+) on absorption of UV light.

high reactive oxygen species can cause microbial inactivation and organic mineralization without secondary pollution [67,68].

In addition, other characteristics of TiO₂ have attracted attention as environment purifying catalysts, and the contents are as follows. First, the decomposition reaction of polluted materials is mostly an oxidative reaction, and is dependent on the VB of the photocatalyst. Therefore, the oxidation reaction improves when the VB holes have higher oxidative power and there is a more positive electrochemical potential with respect to the normal hydrogen electrode (NHE) potential. The band gap of TiO₂ is generally a range of 3.0–3.2 eV, wavelength is about 400 nm. This means that UV light irradiation with a wavelength lower than 400 nm begins a photo-reaction [69]. The characteristics of TiO₂ are the more powerful oxidative power of the VB holes than the reducibility of photo-induced electrons. TiO₂ has very strong oxidation power, *i.e.*, 3.2 eV for anatase TiO₂ and 3.0 eV for rutile TiO₂, considering the approximately 3.0 eV from the hydrogen reference potential and approximately 1.2 eV from oxidation potential of water [70]. The photon energy of 400 nm corresponds to more than 30,000 °C of thermal energy. Therefore, when TiO₂ is irradiated with UV light below 400 nm, its surface is likely to achieve heat higher than 30,000 °C, and this extremely high temperature oxidizes all materials. Therefore, organic compounds are decomposed completely into water and carbon dioxide [71]. This schematic illustration on removal of pollutants by the formation of photoinduced charge carriers (e^-/h^+) in a semiconductor TiO₂ particle surfaces is presented in Fig. 4.

In other words, when surface of the TiO₂ catalysts suspended in water are irradiated with UV light, the photo-induced electrons in the CB participate in the reduction processes, which typically react with dissolved oxygen in air to produce superoxide radical anions ($O_2^{\bullet-}$). The photo-induced holes in the VB diffuse to the TiO₂ surface and react with adsorbed water molecules, forming OH^{\bullet} . Actually, the OH^{\bullet} is very important as a major active species during the photocatalytic oxidation reaction [72,73]. This photo-induced formation mechanism of the electron–hole pair in the TiO₂ photocatalyst by the following equation is widely assumed [74]:

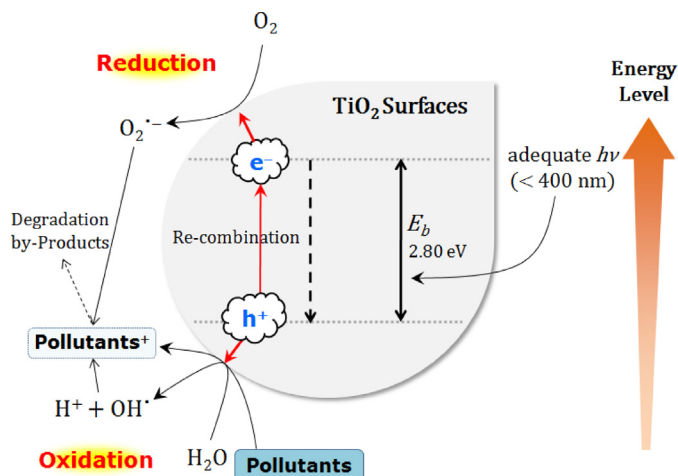
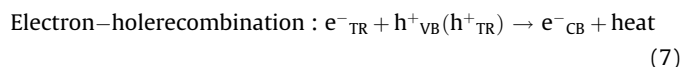
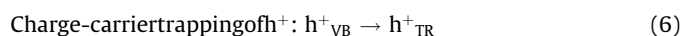
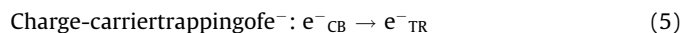
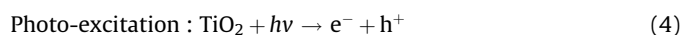
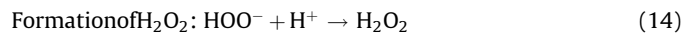
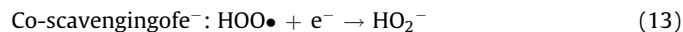
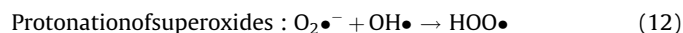
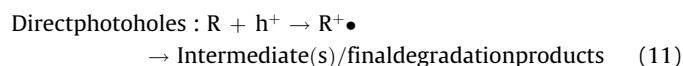
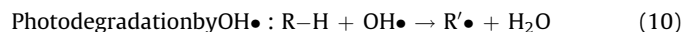
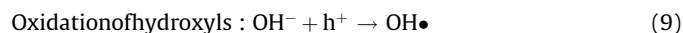
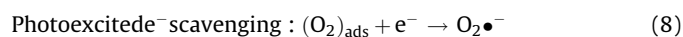


Fig. 4. Schematic illustration on removal of pollutants by the formation of photoinduced charge carriers (e^-/h^+) in a semiconductor TiO₂ particle surfaces.



where e^-_{TR} and h^+_{TR} represent the surface trapped VB electron and CB hole, respectively.

Second, TiO_2 is an industrially mass-produced material that is easy to obtain, inexpensive, and can be synthesized easily in a laboratory. Often white TiO_2 powder or a colloidal dispersion in a liquid phase is obtained. A thin film on a substrate by coating can also be used. Therefore, the ease of applying these forms highlights their potential applications in TiO_2 photocatalytic technology [75,76].

Third, TiO_2 photocatalyst is very stable, both chemically and photochemically, and safe and non-toxic. The materials can maintain the water solubility and self-degradable performance. In addition, it does not undergo photo-corrosion degradation itself because the charge-pair on the TiO_2 surface reacts with the solid lattice ions directly under irradiation. TiO_2 also has a strong resistance against acids and alkalis [77,78].

TiO_2 catalyst is used in the photocatalytic purification of the environment as well as additives in foods or medicines [79,80]. In contrast, some other semiconductors, including CdS, GaP and ZnO, cannot be used for environmental purification as well as food or medicine, because they can dissolve and produce toxic by-products in solution during the photocatalysis of semiconductors [81].

The TiO_2 photocatalytic system is being certified by the appropriate techniques owing to its strong oxidation power that can decompose recalcitrant substances, and because it is much more economical and environmentally friendly in the water purification process compared to chlorine. Table 3 lists the non-biodegradable organic pollutants degraded by the TiO_2 photocatalytic system. Therefore, the TiO_2 photocatalytic system is considered as a promising technology for the degradation of organic pollutants in groundwater and industrial wastewater.

In applying the TiO_2 photocatalytic system for the AOT for water treatment, TiO_2 has a very fast response and has a great advantage in good photo-efficiency even in weak light. Nevertheless, it is inactive in visible light and is unsuitable for a mass processing

system [82]. In addition, the TiO_2 photocatalytic system needs to solve these problems because it requires an additional recovery/separation process from the slurry after the water treatment and an artificial light source suitable for TiO_2 photocatalysis.

Until recently, metal and non-metal doped TiO_2 and the synthesis of unique structures and properties of TiO_2 have been investigated to obtain a broad spectrum in the range of visible light. Hybrid TiO_2 composites with carbon materials, zeolites [83–85], ceramics [86], glasses [87], and fibers [88] have studied widely as a support for anchoring TiO_2 powder.

4. Advancements in TiO_2 photocatalysis for advanced oxidation technology

4.1. Introduction of metals or heteroatoms onto TiO_2

The photocatalytic activity of TiO_2 is observed under UV irradiation, but it can only use 5% of the solar energy that actually reaches the Earth [89,90]. Therefore, increasing the activity of TiO_2 under the visible irradiation through the introduction of metals or heteroatoms onto the TiO_2 surfaces is a major research focus.

Metallic nanoparticles including Pt [91], Pd [92,93], Au [94], Ag [95–99], Ru [100], and Fe [101–105] have been used to enhance the photocatalytic activity on the TiO_2 surfaces by suppressing the e^-/h^+ (electron-hole) recombination behaviors. The photo-induced electrons migrate to the metal due to the relatively low Fermi level of metals, which make the photo-induced holes stable on the TiO_2 surfaces by increasing the lifetime of the charge carrier [106,107]. Therefore, more $\text{OH}\bullet$ and superoxide radicals ($\text{O}_2^{\bullet-}$) are generated as an enhanced redox reaction.

In addition to the characteristics discussed above, Fe^{3+} -doped TiO_2 show greatly improved photocatalytic activity compared to crude TiO_2 . Fe^{3+} can be suitably inserted into the TiO_2 lattice structures, because the ionic radius of Fe^{3+} and Ti^{4+} is similar [108,109].

Moreover, the photocatalytic activities of TiO_2 may be facilitated by creating the relatively high activity of the crystallographic facets. Of these processes, the reactive crystallographic facets of TiO_2 have increased quantitatively, the photocatalytic activities of TiO_2 promote the production of $\text{OH}\bullet$, and the degradation of organic pollutants can be achieved [110,111].

In addition to metals, the O in the TiO_2 lattice can be substituted with a range of heteroatoms, including B [112–114], N [115–117], F [118–120], P [121,122], S [123–126], and co-doping of N–S [127] and B–C [128], etc., to take advantage of visible light in the TiO_2 photocatalysis. Furthermore, both metals and anions are introduced simultaneously to decompose organic contaminants by enhancing the photocatalytic activity of modified TiO_2 [129,130].

Table 3

Non-biodegradable organic pollutants degradable by TiO_2 photocatalytic system.

CH_3CHO , Acetaldehyde	CCl_4 , Carbon tetrachloride	$(\text{HO}_2\text{CCH}_2)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CO}_2\text{H})_2$, Ethylenediaminetetraacetic acid (EDTA)	$\text{C}_6\text{H}_5\text{NO}_2$, Nitrobenzene
CH_3COOH Acetic acid	CHCl_3 Chloroform	HCHO Formaldehyde	$\text{C}_3\text{H}_5(\text{NO}_3)_3$ Nitroglycerine
CH_3COCH_3 Acetone	CH_3Cl Chloromethane	HCOOH Formic acid	H_2NNO_2 Nitroamine
$\text{C}_3\text{H}_4\text{O}$ Acrolein	$\text{C}_{10}\text{H}_7\text{Cl}$ Chloronaphthalene	C_6Cl_6 Hexachlorobenzene	$\text{C}_{12}\text{Cl}_x\text{H}_{10-x}$ Polychlorinated biphenyl (PCBs)
$\text{C}_3\text{H}_4\text{O}_2$ Acrylic acid	$\text{C}_6\text{H}_4(\text{CH}_3)\text{OH}$ Cresol	N_2H_4 Hydrazine	$\text{C}_{14}\text{H}_{10}$ Phenanthrene
C_6H_6 Benzene	$\text{Cl}_2\text{C}_6\text{H}_3\text{OH}$ Dichlorophenol	$\text{C}_8\text{H}_6\text{O}_4$ Isophthalic acid	$\text{C}_6\text{H}_5\text{OH}$ Phenol
$\text{C}_6\text{H}_5\text{COOH}$ Benzoic acid	$\text{C}_{12}\text{H}_{10}\text{Cl}_2\text{N}_2$ Dichlorobenzidine	CH_2Cl_2 Methylene Chloride	$\text{Cl}_2\text{C}=\text{CCl}_2$ Tetrachloroethylene
$\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$ Butyric acid	$(\text{CH}_3)_2\text{NNO}$ Dimethylnitrosamine	C_{10}H_8 Naphthalene	$\text{C}_6\text{H}_5\text{CH}_3$ Toluene
	$\text{C}_{12}\text{H}_4\text{Cl}_4\text{O}_2$ Dioxin		$\text{C}_6\text{H}_4(\text{CH}_3)_2$ Xylene

4.2. Physical modification of TiO₂

Many studies have focused on modifying the morphology of TiO₂ to improve the photocatalytic activity. Fig. 5 shows the various dimensions of the structure of TiO₂. TiO₂ can exist in a range of morphologies; zero-dimensional TiO₂ spheres [131–135], one-dimensional with TiO₂ fibers [136–138], rods [139–142], and tubes [143–146], two-dimensional with TiO₂ nanosheets [147,148], and three-dimensional with interconnected architectures [149–151].

TiO₂ nanoscales by optimizing the size and shape of TiO₂ particles can maximize the photocatalytic activities [152–154]. This can enhance the photocatalytic activities during the water treatment process by maximizing the active surface area of TiO₂ with nanoscales. In addition, the modification of TiO₂ surfaces according to the morphologies or scales enables an improvement in the adsorption capacity of the contaminants, which is useful in AOT for water treatment.

In particular, compared to the unmodified TiO₂ (commercially available P25, Degussa Co.), TiO₂ with a modified morphology including nanotubes [143,155], foams [156,157], mesoporous phases [158,159], etc. has shown a variety of photoactive characteristics as well as improved photocatalytic behaviors.

In particular, with decreasing size of TiO₂ nanoparticles, the e⁻/h⁺ recombination behaviors decreased due to the enhanced interfacial charge carrier transfer on the TiO₂ surfaces [160]. In addition, the TiO₂ crystalline structure of a well-formed rutile (tetragonal) structure is quite stable in nanoparticles larger than 35 nm; and the anatase (tetragonal) structure for the production of reactive oxygen species is more efficient and stable than 11 nm nanoparticles [161,162]. On the other hand, the photocatalytic activities of small TiO₂ nanoparticles of less than several nm are decreased due to the dominant e⁻/h⁺ recombination on the TiO₂ surfaces.

The well-defined mesoporous TiO₂ with a large specific surface area that will help increase their photocatalytic efficiency has been considered because of the unique mesoporous structure itself, where a mesopore channel can facilitate the intraparticle molecular transfers of ions [163–166]. TiO₂ nanotubes were reported to be more efficient in the adsorption and decomposition of non-biodegradable organic compounds compared to TiO₂ particles, which was attributed to the tube walls of the TiO₂ nanotubes exhibiting a shorter carrier-diffusion pathway and

faster mass transfer of organic compounds on the nanotube surfaces and between the nanotubes [167].

These TiO₂ materials with various morphologies do not themselves improve the photocatalytic activities under visible light irradiation without a photosensitizer. Many studies have been conducted to broaden the range of the solar absorption band by incorporating novel metals, transition metals, and anions to TiO₂ with a range of morphologies, maximizing the efficiency of the photocatalysts [168,169].

4.3. Hybrid TiO₂/nanocarbon composites

Nano-dimensional TiO₂ has a highly specific surface area (large surface area-to-volume ratio), which promotes efficient charge separation and charge trapping of ions on the TiO₂ surfaces [170]. The nano-sized TiO₂ shows increased oxidative power with opacity of the aqueous phase (suspended phenomenon) compared to the bulk-sized TiO₂ [171]. On the other hand, the nano-dimensional TiO₂ photocatalysts cannot be applied directly to water treatment because they tend to aggregate during the advanced oxidation processes due to the size and morphology, and physical and chemical properties [172].

Recently, to solve these problems, many attempts have been made to enhance the photocatalytic activity of TiO₂ and anchor the TiO₂ onto carbon materials. The hybrid composites between TiO₂ and a range of carbon materials including activated carbon or activated carbon nanofibers [173–176], carbon nanotubes [177–181], and graphene [182–187], are considered a promising technology in many areas. Carbon materials are considered to be suitable as a support for TiO₂ owing to their excellent thermal [188–190], optical [191–193], mechanical [194–196], electrical [197–199] characteristics, chemical resistance [200], and the design of an optimized pore structure and surface properties [201–203], resulting in rapid charge transfer on hybrid TiO₂/carbon composites [204,205].

TiO₂/nanocarbon composites are used not only for the removal of organic pollutants in aqueous solutions [206,207], but also in the removal of contaminants from vapors including NO_x, CO, and acetaldehyde [208,209], decomposition of biological pollutants [210,211], hydrogen production by photocatalytic splitting from water [212–214], and the photo-electrochemical electrode (in particular, dye-sensitized solar cells) [215–221], and an antibiotic catalyst [222] has been widely applied.

Recently, hybrid composites of TiO₂ with CNT and graphene have attracted increasing attention. CNT and graphene have the potential to contribute to the routes of enhancing photocatalytic activities, due to the large specific surface area, high quality active sites, retardation of e⁻/h⁺ recombination, and visible light catalysis by tuning the band gap.

In particular, some mechanisms of photocatalytic activities of TiO₂/CNT composites have been proposed, e.g., CNTs can act as extremely effective electron sinks, which is a p-type semiconductor [223]. CNTs can create a Schottky barrier at the TiO₂/CNT interface (a space charge region). TiO₂ acts as an n-type semiconductor, but in the presence of CNT, photo-induced electrons may migrate freely in the direction to the CNT surfaces, which might have a lower Fermi level like a metal. Another possible mechanism is that CNTs may act as a photosensitizer, transferring electrons to the TiO₂ surfaces. This might be responsible for extending the TiO₂ photocatalytic activity to the visible light range [224,225]. In addition to the above-mentioned two mechanisms, a range of hypotheses have also been proposed [226,227].

Graphene is used as a two-dimensional photocatalyst mat owing to its excellent redox properties [228]. High quality graphene makes the electrons travel without scattering at a

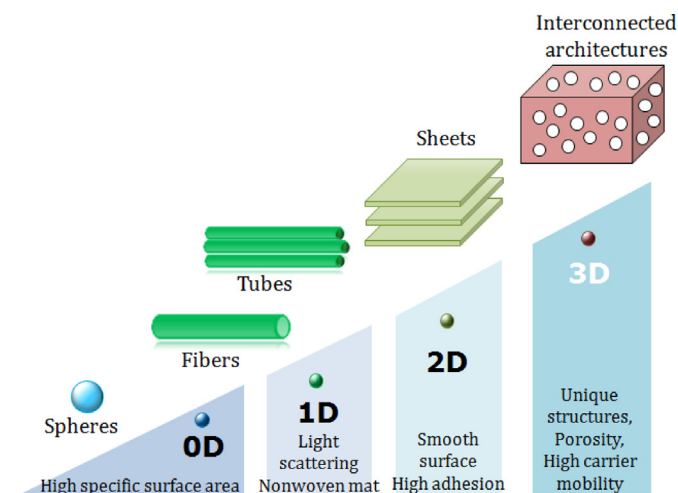


Fig. 5. TiO₂ structures according to the structural dimensionality and expected property.

mobility higher than 15,000 m²/V/s at room temperature [229], meaning that it acts as an ideal electron sinks and electron transfer bridge.

This is possible because the electron delocalized behaviors in the conjugated π - π interaction of TiO₂/nanocarbon composites affect the conductivity, resulting in rapid photo-induced charge separation and slow charge recombination in the electron transfer process [230,231]. The band gap behavior of TiO₂/graphene composites has a wide range (2.66–3.18 eV), according to the graphene content from 0.25 to 10 wt.% [232]. This suggests that the newly formed Ti–O–C bands of TiO₂/nanocarbon composites can extend to the absorption edge, which can absorb the long-wavelength light of the visible region [233].

Combining TiO₂ with various nanocarbon materials is being investigated as a promising material for photocatalysts due to the enhanced photocatalytic activities through control of the band gap to photosensitization, mineralization of e⁻/h⁺ recombination, etc. In addition, the fundamental benefit of nanocarbon materials is that it provides a high-surface area structure and high conductivity pathway, in which TiO₂ particles might be distributed and immobilized, resulting in greater sensitivity, improved selectivity, and a faster response time of TiO₂/nanocarbon materials [234,235].

TiO₂/nanocarbon composites have good effects on self-purification compared to ozonation and UV irradiation when applied to advanced oxidation technologies for water treatments. These composites are expected to be industrially effective in AOT for water treatment because these nanocarbon materials can be used as a support for tight immobilization by preventing the loss of TiO₂ particles in a flowing fluid stream (vortex effect) [236,237].

5. Conclusion

TiO₂ photocatalyst under either UV light or solar irradiation has become more prominent owing to its low cost, safety, high photocatalytic activity, etc., and as an advanced oxidation technology for the water treatment industry. In addition to the degradation of organic contaminants, the photocatalytic activity of TiO₂ has potential use as an additive in foods or medicines, electrodes of solar cells, etc. On the other hand, the utilization of solar energy is currently limited by the photo-inefficiency of the TiO₂ catalyst (only 5% of the solar spectrum can be used). Therefore, the development of an innovative TiO₂ photocatalyst and its optimization are needed this photocatalyst can be used commercially in photocatalytic water treatment technology.

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