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Review

Recent Advances in TiO_2 Films Prepared by Sol-Gel Methods for Photocatalytic Degradation of Organic Pollutants and Antibacterial Activities

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Abstract: Photocatalysis has recently emerged as an advanced, green, and eco-friendly process for the treatment of wastewater and air, and antimicrobial disinfection applications. In this context, TiO_2 nanostructures have been shown to be the prominent photocatalyst candidates due to their low cost, non-toxicity, and ease of fabrication. This review highlights the investigation and development of TiO_2 photocatalyst film by sol-gel method with special emphasis on the photodecolorization of synthetic dyes and antibacterial activities. Furthermore, various synthesis methods for the preparation of TiO_2 films and their advantages, as well as limitations, are summarized. Finally, recent advances in TiO_2 films by sol-gel method for dye degradation and antibacterial activities, challenges, and future perspective are discussed.

Keywords: TiO_2 film; sol-gel; photocatalysis; organic pollutant; dye degradation; antibacterial

1. Semiconductor Photocatalysis

Energy, environment, and health are serious challenges that the modern world faces today. Besides several benefits to mankind, industrialization has resulted in adverse impacts on ecosystems. Among the most critical contemporary global issues, environmental pollution has gained extensive interest. One of the main pollution sources comes from wastewater containing dyes discharged from textile, foodstuff, and leather industries [1,2]. Water pollution is caused by both synthetic and biological contaminants and can, among other things, be damaging for aquatic environments. The prevention of toxic chemical and biological contamination through environmentally green techniques is an important issue.

In recent decades, semiconductor photocatalysis has been intensively studied for water and air treatment [3,4]. The semiconductors possess a band gap that separates the valence band (VB) and conduction band (CB). When the photocatalyst is illuminated by light with an appropriate wavelength with energy equal to or greater than its band gap, the electrons are excited from the VB to the CB, thereby producing an electron (e-) in the CB and leaving a positive hole (h+) in the VB. If the as-produced electron and hole migrate to the surface of the semiconductor photocatalyst without recombination, they facilitate redox reactions with the compounds adsorbed on the catalyst. The positive hole at the valence band oxidizes pollutants either directly or through a reaction with water to produce powerful hydroxyl radicals (OH). Similarly, the electrons at the conduction band reduce the oxygen atoms adsorbed on the photocatalyst. During the photocatalytic process, superoxide radicals (O_2-) and other reactive groups are produced, resulting from reactions with moisture oxygen (O_2). These oxidation and reduction reactions are the fundamental mechanism of photocatalysis [5–7].

2. TiO_2 Photocatalyst

TiO_2 powders have, since ancient times, been commonly used as a paint additive to obtain white pigments [8]. Since the discovery of the photocatalytic activity of TiO_2 [9], it has been known as one of the most efficient photocatalytic materials. TiO_2 is known for its various properties such as high photoactivity, good stability, low cost, and low toxicity [10,11]. In the last few decades, TiO_2-based nanostructures have been widely studied in academic research and used in a variety of applications such as photovoltaics, sensors, removal of organic pollutants and pathogens, and energy storage [1,10,12–16].

TiO_2 nanomaterials have a bandgap of 3.0–3.2 eV and can be excited by UV light. Due to this reason, the use of TiO_2 is limited as less than 5% of the solar spectrum falls within the UV range [17–19]. TiO_2 exists in three crystalline structures: (i) rutile, (ii) anatase, and (iii) brookite [20]. Anatase and rutile are preferred for photocatalysis, whereas brookite is considered as the least stable phase and is generally not used in photocatalysis [21,22]. The bandgaps of bulk anatase and rutile are 3.2 and 3.0 eV, which correspond to the wavelengths of 388 and 414 nm, respectively [23]. As compared to rutile, the anatase phase is considered as photocatalytically more active due to its ability to adsorb water and hydroxyl groups [24]. Studies have shown that the synergistic effect between anatase and rutile is helpful in enhancing the photocatalytic activity of the TiO_2 structures [21].

In TiO_2-based photocatalysis, when a photon (with energy equal to or greater than the bandgap of TiO_2) illuminates the TiO_2 particles or film, the electrons are activated from the valance band to the conduction band and produce electron–hole pairs. The formed charge carriers migrate towards the surface and react with the adsorbed chemicals, thereby degrading organic pollutants. The process of formation of the advanced oxidant and the degradation of the pollutant is given in Figure 1.

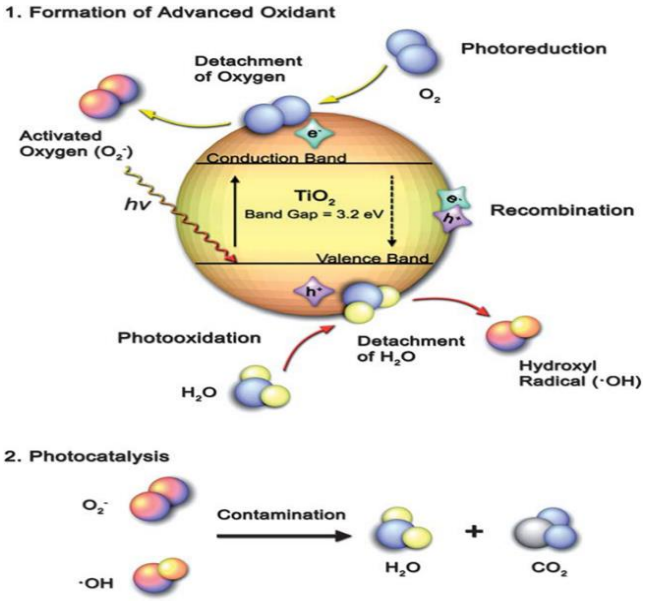

Figure 1. Schematic diagram showing the TiO_2 photocatalysis. Adapted with permission from [7]; Copyright 2011 The Royal Society of Chemistry.

Limitations of TiO_2 as a Photocatalyst

Although TiO_2 is the most studied photocatalyst for the degradation of organic pollutants, there are lots of limitations to overcome for its widespread application (Figure 2). The main drawback of TiO_2 is its poor ability to absorb solar irradiation [6,25]. Its wide bandgap (3.2 eV) limits the use of visible light as the light source. Fast recombination of photogenerated charge carriers is also a limitation of TiO_2 in photocatalysis, which decreases the quantum efficiency of the overall reaction. Since photocatalytic degradation occurs on the surface of photocatalysts, adsorption is prerequisite

for good performance [26]. However, the adsorption capacity of TiO_2 is relatively low, which results in slow photocatalytic degradation rates [27]. Reducing the size of the TiO_2 particles in nanoscale can enhance the surface area; however, aggregation may appear as a problem that hampers the light incidence on the active center, thereby reducing the catalytic activity [14]. In addition, separation, recovery, and reuse of the nanostructured TiO_2 may be a key obstacle in its practical application [14,28]. Another limitation of TiO_2 is the poor thermal stability of its most effective anatase phase. Anatase is a highly active polymorph and is normally less stable and transforms to rutile phase at a higher temperature (above ~700 °C) [13,27].

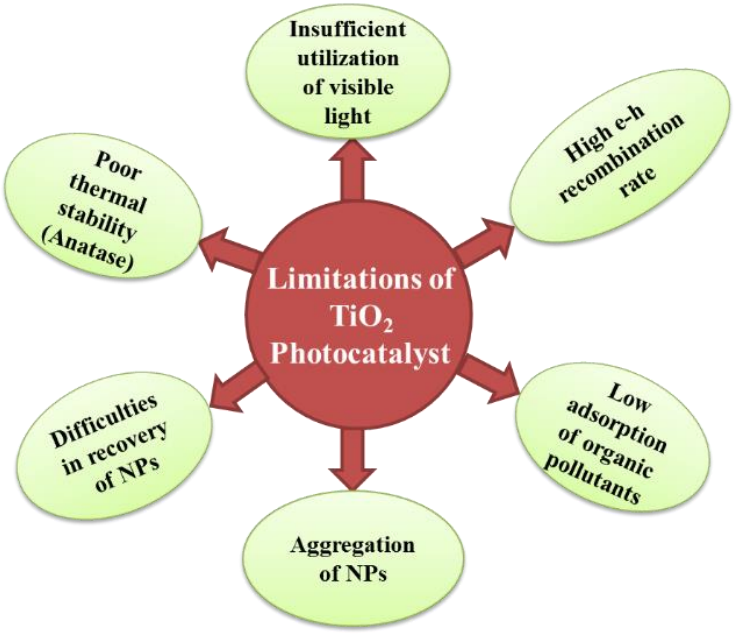

Figure 2. A schematic diagram showing the limitations of TiO_2 photocatalysts.

3. TiO_2 Films

TiO_2-based photocatalytic thin films and nanostructures are now being used extensively for a variety of applications such as environmental remediation, self-cleaning windows, water splitting, hydrogen release, and antibacterial material due to their interesting chemical, electrical, and optical properties [19,29–33]. The thin films can be applied to various substrates and are used instead of bulk materials that result in substantial cost savings. Engineering thin films at nanoscale enables distinct mechanical, chemical, and physical surface functionalities including higher surface area and enhanced photocatalytic performance [34]. TiO_2 thin films can contain anatase, rutile, or a combination of both of these phases. Mostly, photocatalytic thin TiO_2 films have been used for the decomposition of organic contaminants and antibacterial applications [34].

3.1. Preparation of TiO_2 Film

TiO_2 thin films have been synthesized by several sophisticated techniques such as chemical vapor deposition (CVD) [35,36], hydrothermal synthesis [37,38], metal organic chemical vapor deposition (MOCVD) [39,40], sputtering [41,42], liquid phase deposition (LPD) [43,44], electrophoretic deposition [45], physical vapor deposition (PVD) [46], pulsed laser deposition [47,48], sol-gel [5,49,50], electrochemical deposition [51], atomic layer deposition (ALD) [52], etc. Most of the synthesis processes require a high temperature and pressure. The method of synthesis and processing conditions play an important role in the properties of the materials. Since the microstructure and physical properties of TiO_2 affect its photocatalytic activity, the choice of a proper method is important in order to achieve

good results. Table 1 summarizes some of the common techniques along with their advantages and limitations.

Table 1. Common techniques for TiO_2 coating and their advantages as well as limitations.

Method	Description	Advantages	Limitations	Ref.
Sputter deposition	An ionizing plasma sputters the target in a vacuum chamber and the ionized atoms are deposited on the substrate.	—High quality and uniform deposition —Good adhesion	—Risk of substrate damage due to ionic bombardment —Grain size of the sputtered films is typically smaller	[34,53,54]
Chemical vapor deposition	A thin film of metal oxide is formed on a heated substrate from a gaseous phase in a closed chamber at a relatively higher temperature.	—Produce uniform, films at low or high rates —Flexible with regards to the shape of the substrate —Compatibility with good adhesion —Simultaneously coat multiple components —Control structure of crystal and generate uniform films with pure materials and high density	—High cost —High reaction temperature —Low deposition rates —Cannot control the stoichiometry of films using more than one material	[53–55]
Physical Vapor Deposition	It involves the transfer of material on an atomic level onto a solid substrate. This is a physical process such as high temperature vacuum evaporation followed by condensation rather than a chemical reaction among precursors.	—Suitable for any type of inorganic materials —Safer than other methods	—High cost	[54,55]
Sol-gel synthesis	This is a wet chemical method that involves hydrolysis and condensation of metallo-organic alkoxide precursors for gel formation followed by dip/spin/spray coating or screen printing.	—Simple, homogeneity, low cost, reliability, reproducibility, controllability —Films are easily anchored on the substrate bearing complicated shapes and a large surface area. —Suitable for deposition on various substrates —Easy method	—Long period of deposition —High temperature —Not possible to attach a thick layer of nanoparticles on the substrate	[34,53,55]
Spray pyrolysis	A solution containing a precursor is sprayed by a nanoporous nebulizer onto the hot substrate in the furnace.	—Cost-effective and can be easily performed —Substrates with complex geometries can be coated. —Uniform and high-quality coatings —Low processing temperature —Multilayer fabrication capability	—Coatings are not uniform in thickness.	[34,56]
Electrophoretic deposition	Formation of coating on the charged surface takes place by the movement of charge particles in suspension under an appropriate electric field	—Simple and cheap —Uniform coating —Size and shape of nanoparticles can be controlled —High-quality coatings	—Volatile, toxic —Flammability —Costly —High electric field strengths are required.	[53]

Table 1. *Cont.*

Method	Description	Advantages	Limitations	Ref.
Hydrothermal	Includes either a single or heterogeneous phase reactions in aqueous solution at elevated temperatures and pressures to crystallize materials directly from solution	—Simple to operate —Ability to grow large, high-quality crystals, maintaining a good control of their chemical composition	—Expensive autoclaves are required —Impossibility of observing the crystal as it grows	[34,55]
Doctor-blade	A slurry is placed on a substrate, and the unidirectional shear force is applied by a blade over the substrate.	—Simple and economic —Easy to control film thickness and homogeneity —Suitable for mass production of electro-ceramic thick films	—Slow evaporation —Tendency to aggregate or crystallize at high solution/paste concentration	[34]
Plasma-enhanced chemical vapor deposition (CVD)	This method utilizes a plasma to deeply fragment organic precursor molecules, which subsequently deposit onto solid substrates within the reaction chamber, such as nanoparticles.	—Requires much lower temperatures —Good for deposition on multilayer films —Good adhesion and uniformity —High deposition rate —Good mechanical properties —Controllable coating thickness	—Chemical and particle contamination —High cost —Toxic byproducts	[54]
Spray coating	The solvent is evaporated during the spraying process.	—Simple —Low-cost —Scalable film forming technique	—The thickness is not uniform.	[57,58]

3.2. *Preparation of TiO_2 Film by Sol-gel Method*

Among the various methods, the sol-gel method is one of the most used methods to prepare thin film or a powder catalyst for various applications such as catalysis, sensors, membranes, electrochemical devices, etc. [5,34]. The sol-gel method has become the most common and simple approach to prepare TiO_2 films due to its effectiveness, homogeneity, and reliability [34]. In this process, TiO_2 colloidal suspension is formed from the involvement of hydrolysis and polycondensation reactions of the precursor (metal alkoxides or inorganic metal salts), and the film with the desired thickness can be deposited onto the substrate either by dip coating or spin coating techniques [59]. By controlling the sol-to-gel transition and thereby the sol viscosity, a variety of shapes with desired porosity and texture can be obtained [60]. Most importantly, the sol-gel coating can be carried out at room temperature without special expensive instruments [34]. The sol-gel route combined with deep or spin coating has been widely applied to coat metallic film in different substrates. In this section, we discuss the sol-gel-assisted synthesis of TiO_2 or doped-TiO_2 films and their photocatalytic performance in the degradation of organic pollutants and antibacterial activities. Figure 3 shows a process flow chart for the preparation of TiO_2 film by sol-gel method.

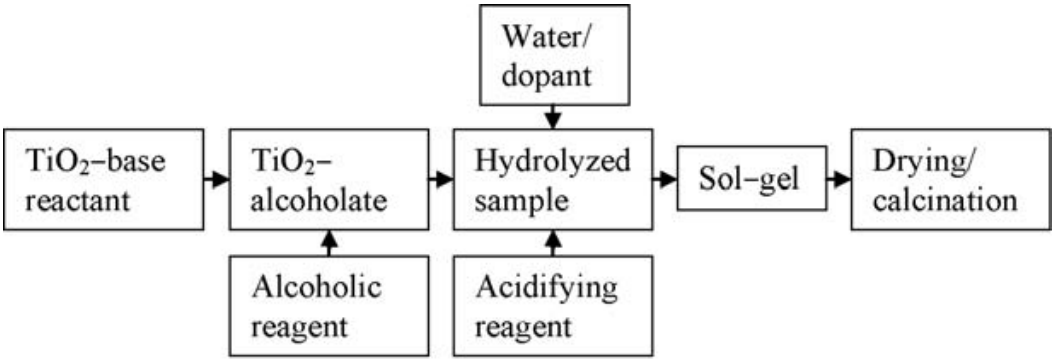

Figure 3. Schematic diagram showing the process flow chart for the preparation of TiO_2-based film by sol-gel method. Adapted with permission from [5]; Copyright 2010 Elsevier B.V.

3.3. TiO_2 Film for Organic Dye Removal Application

Among the most critical contemporary global issues, environmental pollution related to water pollution has gained extensive interest. One of the main pollution sources comes from wastewater containing dyes discharged from textile, foodstuff, and leather industries. TiO_2 films have been shown to be promising materials for removing organic dyes from water. In recent years, pure or modified TiO_2 films have been developed for organic dye removal applications [5,34,61,62]. Table 2 presents some examples of TiO_2-based film for organic dye removal applications.

3.3.1. Undoped TiO_2 Films

Guillard el al. [63] employed several sol-gel methods for depositing TiO_2 films on various substrates such as silicon wafers, soda lime glass, and Pyrex glass and studied their effectiveness in water treatment. The photocatalytic efficiency of synthesized films was tested by degrading malic acid. It was found that several factors such as TiO_2 loadings, the thickness, the number of coatings, and the calcination temperature influenced the photocatalytic activity of the film. The optimal calcination temperature was 400 °C.

Chen et al. [64] synthesized a series of mesoporous ultrafine anatase nanocrystallite TiO_2 films onto a borosilicate glass substrate via the sol-gel preparation route. The synthesis process involved the use of nonionic surfactant Tween 20 as a template through a self-assembly pathway. After calcination at 500 °C, crystalline structure, thickness, morphology, optical properties, and porous structures were investigated. The photocatalytic property was investigated by creatinine degradation test. The study revealed that the high calcination temperature was beneficial to get good crystallinity and adhesion between the film and substrate. The obtained results showed that the photocatalytic activity could be remarkably improved by increasing the Tween 20 loading in the sol.

The anatase phase of TiO_2 is normally found in the sol-gel synthesis, although brookite is often observed. Pure brookite without anatase or rutile is difficult to prepare [22]. Recently, Komaraiah et al. [65] employed a sol-gel spinning technique in order to deposit TiO_2 thin film onto a glass substrate. After annealing at different temperatures, the authors studied the photocatalytic degradation of a methylene blue aqueous solution under visible light irradiation. It was confirmed from the XRD that the thin film was of a single phase orthorhombic brookite structure. SEM analysis showed highly uniform, crack-free, and spherical nanoparticles with around a 68 nm diameter. The as-synthesized film showed 92% methylene blue (MB) degradation efficiency within 240 min under visible light irradiation.

Dulian et al. [60] studied the influence of coating thickness on the photocatalytic performance of TiO_2 films. In their study, the authors prepared transparent anatase TiO_2 film by sol-gel method in alcoholic solution. The thin films were deposited on the borosilicate glass substrate and a multiple dip coating technique was employed to prepare different layers of coating for up to 12 dip-coating cycles. It was observed that with an increasing number of coatings, the roughness and optical band gaps were

decreased. Furthermore, the photocatalytic degradation of MB was strongly related to the thickness of the layer, the number of the layer, and its morphology. The thicker oxide layers showed faster MB degradation properties.

In recent years, various supporting media such as glass, ITO, textile, etc. have been applied for TiO_2 coating. Among different substrates, textile has attracted increasing interest due to the durability and good affinity of inorganic nanostructures with fabrics [66]. In this regards, Costa and coworkers have developed TiO_2-supported textile media with self-cleaning properties [67]. Their study revealed that the photocatalytic efficiency is correlated to the surface hydrophilicity, which promotes the formation of a higher amount of OH radicals.

3.3.2. Modified TiO_2 Films

One important approach to overcome the quick recombination of photogenerated charge carriers is the doping technique. The doping strategy can suppress the electron–hole pair recombination rate and shift the activity of TiO_2 from UV to the visible light region, thereby enhancing the photocatalytic efficiency in visible light [68]. In past decades, several approaches have been adopted for TiO_2 modification, for example, metal-doped TiO_2 (such as Pt, Pd, Ag, Sr, Au, Ce, V, Fe) [34,69], non-metal doped TiO_2 (such as N, S, C, B, F) [34,69], composite of TiO_2 with a lower semiconductor bandgap energy than that of TiO_2 [18,69].

Metal-Doped TiO_2 Films

Sonawane et al. [70] prepared Fe-doped TiO_2 thin films on a variety of substrates (glass, silica rings, glass-helix) using a Ti-peroxy sol-gel dip coating method. Fe and polyethylene glycol (PEG) were incorporated in titanium peroxide sol, and after drying and calcination at 500 °C, the PEG was removed and crystalline Fe-doped TiO_2 film was obtained. The photocatalytic activity of the Fe–TiO_2 film was studied by methyl orange degradation under sunlight. As compared to undoped TiO_2 film, the degradation capacity was enhanced by 2–2.5 times in the Fe-doped TiO_2 film.

Gultekin et al. [71] prepared gold nanoparticle-doped TiO_2 film by sol-gel method and studied the effect of Au doping on the optical, structural, and morphological properties. From their study, the authors conclude that Au doping can modify the optical, structural, and morphological properties of TiO_2 film.

Yu et al. [72] investigated the photocatalytic activity of sol-gel-derived Pb-doped TiO_2 film by degrading dimethyl-2,2-dichlorovinyl phosphate (DDVP) under sunlight irradiation. The Pb dopant reduced the bandgap of the photocatalyst and extended the wavelength response towards the visible region, thereby improving the photocatalytic activity under solar light.

Rapsomanikis et al. [73] synthesized cerium (Ce)-modified TiO_2 film via the sol-gel route at 500 °C on glass substrate with a varying content of Ce. The presence of Ce caused a decrease in the size of TiO_2 NPs, and the films were formed without cracks. The authors examined the photocatalytic behavior of the Ce-modified TiO_2 films for the decoloration of Basic Blue 41 in water under both UV and visible light. It was found that the cerium-modified TiO_2 films effectively extend the spectral response to the visible region, exhibiting enhanced photocatalytic decoloration of BB-41 in water under visible light.

Guillén-Santiago's group [74] prepared Ag-doped TiO_2 thin films by sol-gel method and compared their photocatalytic properties with undoped TiO_2 film. The author also studied the effect of ageing time of the starting solution, as well as the number of coatings, on the photocatalytic degradation of MB. It was found that the film thickness and ageing time of the solution play an important role in the degradation of MB. An optimal photocatalytic activity (35% under UV irradiation) was achieved in 5-immersion Ag-doped TiO_2 thin films that were deposited from 7- and 14-day-old solutions. Solís-Casados and coworkers [75] synthesized Bi-doped TiO_2 film with different Bi contents by sol-gel method. The material was characterized with various techniques. It was found that the addition of bismuth promotes the formation of bismuth titanate. Malachite green was selected as a representative

pollutant, and the degradation test was carried out under simulated solar light. The TiO_2 film with bismuth showed better photocatalytic activity as compared to pure TiO_2 film.

MB is one of the most commonly used substances for dyeing cotton, wood, paper, and silk [26,76]. It has been widely used in medicine for several therapeutic and diagnostic purpose. Due to its complex aromatic structure, hydrophilic nature, and stability against light, temperature, and chemicals, it is difficult to degrade MB completely through the conventional water treatment process. For decades, semiconductor photocatalysis has been considered as an advanced technique for the complete degradation of MB. MB is one of the most commonly used dyes to study the photocatalytic performance of TiO_2 films. Generally, brookite is considered as a less effective phase of TiO_2 as compared to rutile and anatase. Komaraiah et al. [65] employed the sol-gel spinning technique in order to deposit TiO_2 thin film onto a glass substrate. After annealing at different temperatures, the photocatalytic degradation of MB in aqueous solution was carried out under visible light irradiation. It was confirmed from the XRD that the thin film was of a single-phase orthorhombic brookite structure. SEM analysis showed highly uniform, crack-free, and spherical nanoparticles around 68 nm in diameter. The as-synthesized film showed 92% MB degradation efficiency within 240 min under visible light irradiation.

Non-Metal Doped TiO_2 Film

Although metal doping has been widely applied for enhancing the photocatalytic activity of TiO_2 film, the metal dopants tend to suffer from thermal instability, which causes an increase in photoinduced carrier recombination centers, thereby decreasing the lifetime of the electron–hole pairs. In this regard, non-metal doping seems to be a more promising technique for enhancing the photocatalytic activity of TiO_2 film in the visible light region due to the presence of impurity states that are near the valence band edge. Several non-metal (such as C, F, S, N)-doped TiO_2 films have been prepared.

Lin et al. [77] prepared C-doped mesoporous TiO_2 film by combined sol-gel and hydrothermal processes, using glucose as a carbon source and structure-directing agent. Their study indicated that the oxygen sites in the TiO_2 lattice were substituted by carbon-atom-forming O–Ti–C bonds, and the film was composed of mainly anatase TiO_2. The C-doped TiO_2 film exhibited a significant red shift to the visible region, showing visible light active photocatalytic properties. The photocatalytic activity of C-doped TiO_2 film for the degradation of X-3B was higher than that of undoped TiO_2 film under both UV and the visible region.

Rajendra et al. [59] employed a sol-gel dip coating method to prepare immobilized activated carbon-doped TiO_2 film by sol-gel method using titanium tetraisopropoxide. It was observed that the type and concentration of the doping agents and the operating temperature influenced the properties of TiO_2 film. Hassan et al. have reported that the presence of carbon influences the crystallinity of TiO_2, which controls the photocatalytic sites and activity [78].

Han et al. [31] prepared visible-light-activated S-doped TiO_2 film by sol-gel method based on a self-assembly technique for a water treatment application. In this work, borosilicate glass was used as a substrate and the films were calcined to remove the organic content. The results showed that the calcination temperature influenced the physiochemical properties of the film. S-doped TiO_2 film with a smooth surface and minimum roughness was obtained at 350 °C calcination and was the most effective for the degradation of hypatotoxin microcystin-LR (MC-LR), compared to other films obtained at 400 and 500 °C.

Nitrogen is known for enhancing the photoresponding range of TiO_2 into the visible region [79]. Among all the non-metal dopants, nitrogen has been applied most for visible-light-active photocatalytic TiO_2 systems. Introducing nitrogen into the TiO_2 lattice is effective and straightforward due to the atomic size, low ionization potential, and high stability of nitrogen. Nitrogen atoms either occupy interstitial sites (possibly with N–O bonding) or substitutional sites (replacement of O with N atoms) in TiO_2. Mekprasart et al. [80] prepared nitrogen-doped TiO_2 films on glass substrate by spin coating technique and studied the effect of nitrogen doping on the optical and photocatalytic properties. They found that after doping with nitrogen, the absorption spectrum of the TiO_2 film shifted to the

visible region, clearly suggesting photocatalytic activity under visible light. Compared to undoped TiO_2, the N-doped TiO_2 film showed better photocatalytic performance for the degradation of Rhodamine B under solar light irradiation.

Binary Composite

Preparation of a binary or ternary semiconductor system is another approach to modify the TiO_2 film photocatalyst and can improve the charge separation system and enhance the photocatalytic activity. In this regards, Pérez-González et al. [81] synthesized TiO_2–ZnO composite thin films by sol-gel method and studied their optical, structural, and morphological properties. The photocatalytic efficiency was evaluated by degradation of MB. The result indicated better photocatalytic properties than single metal oxide films. Photocatalytic properties were further enhanced with the addition of Ag NPs on the film [82].

Weerachai Sangchay [83] deposited SnO_2-doped TiO_2 film on a glass substrate and calcined it at 700 °C for 2 h. The photocatalytic decolorization of the aqueous MB solution revealed enhanced performance as compared to the pristine TiO_2 film. Furthermore, the TiO_2 film doped with 1 mol% of SnO_2 showed the highest photocatalytic properties.

Hernández-Torres and coworkers [84] prepared CdS/TiO_2 composite films on glass substrate by chemical bath deposition and the sol-gel /dip coating method. They examined the influence of CdS deposition on the morphology and optical and photocatalytic properties of TiO_2 films and found that the CdS deposition time influences the absorbance of the composite, with the absorption edges being shifted to the visible region. The photocatalytic study was carried out by degrading methyl blue under visible light, and the composite showed enhanced photocatalytic properties as compared to CdS-free TiO_2 film. Stoyanov et al. [85] studied the photocatalytic performance of mixed TiO_2/V_2O_5 films and found that the composite film showed better photocatalytic decomposition of methylene blue in water as compared to TiO_2 films.

Composites of TiO_2 with silicon dioxide (SiO_2) have been prepared for enhancing the performance of TiO_2 photocatalysts [86,87]. SiO_2 is employed as an additive to TiO_2 due to its interesting properties such as chemical inertness, thermal stability, and low refractive index [88]. In this regard, Pakdel and Daoud [87] employed a sol-gel method to prepare titania and silica sols. The TiO_2/SiO_2 composite was loaded in the cotton fabrics. The authors evaluated the self-cleaning properties of the composite sample by studying the decomposition rate of MB under UV irradiation and observed that the sample coated with TiO_2/SiO_2 showed an enhanced photocatalytic performance [87].

Table 2. Photocatalytic dye degradation performance of various TiO_2 films prepared by sol-gel method.

Catalyst	TiO_2 Precursor	Substrate	Light Source	Pollutant	Initial Concentration of the Pollutant	Degradation Performance	Ref.
TiO_2 nanocrystalline thin film	titanium (IV) butoxide and Degussa P25 TiO_2	glass	UV	3,5-dichlorophenol (3,5-DCP)	5 ppm	1600 min	[89]
TiO_2 film	titanium tetraisopropoxide and Degussa P25	soda lime glass, pyrex glass	UV	2-hydroxybutanedioic acid	50 ppm	200 min	[63]
Fe-doped TiO_2 film	titanium tetraisopropoxide	soda lime glass, silica rings, glass helix	sunlight	methyl orange	100 ppm	95% in 3 h	[70]
TiO_2 film	titanium isopropoxide	glass	solar light	4- chlorophenol and carbaryl	20 mg/L	4-chlorophenol: 75% degradation in 3 h, and carbaryl: 65% for degradation in 3 h	[90]
Mesoporous TiO_2 film	titanium isopropoxide	Tween 20 as template	UV	creatinine	19.5 mg/L	-	[64]
Au-doped TiO_2 film	titanium isopropoxide	quartz glass	UV	methylene blue	1.63×10^{-5} M	180 min	[91]
S-doped TiO_2 film	titanium isopropoxide	borosilicate glass	visible light	hepatotoxin microcystin-LR (MC-LR)	500 μg L^{-1}	~50% degradation was observed in 5 h	[31]
Cr-doped TiO_2 film	butyl titanate	glass or silicon	visible light	methyl orange	–	90% within 5 h	[92]
Nb-doped TiO_2 film	titanium (IV) butoxide	glazed porcelain	UV	methylene blue	5 ppm	76.2% within 120 min	[93]
Ag-doped TiO_2 film,	titanium butoxide	ITO plates	visible light	methanol and basic orange II (BOII)	60×10^{-3} mol L^{-1}	80% of total organic carbon in 5 h	[94]
P-doped TiO_2 film	titanium tetrabutyl titanate	glass plates	visible light	butyl benzyl phthalate (BBP)	20 mg/L	98% in 240 min	[95]
Fe, Ni, and Cu –ion implanted TiO_2 film,	tetrabutylorthotitanate	glass	UV, visible, sunlight	methyl orange	–		[96]
Ag/TiO_2 films	tetrabutylorthotitanate	glass	UV, visible light	methyl orange	5×10^{-5} mol/L	UV365 (73%) and visible light (3.8 times) enhanced.	[97]
Bi-modified TiO_2 film	titanium isopropoxide	borosilicate glass	simulated sunlight	malachite green	10 μmol/L	67% 180 min	[75]
TiO_2 thin films	titanium tetraisopropoxide	glass	visible light	methylene blue	1×10^{-6} M	92% 4 h	[65]
Pb-doped TiO_2 film	titanium (IV) butoxide	soda-lime glass	sunlight	dimethyl-2,2-dichlorovinyl phosphate	10^{-4} M	~30% 6 h	[72]
Ce-modified TiO_2 film	titanium tetraisopropoxide	glass	UV and visible light	basic blue 41	2.5×10^{-5} M	~85% in 180 min	[73]

Several factors influence the photocatalytic behavior of TiO_2 films, such as the initial concentration of dye, catalyst amount, pH, presence of inorganic anions, temperature, light source, light intensity, and configuration of the photocatalytic reactor [26,98]. In recent years, pilot plant studies for different reactor configurations have been carried out and compared to select the optimal configuration for scale-up [99,100].

3.4. TiO_2 Film for Antibacterial Application

TiO_2 is considered a promising antibacterial agent due to its good antibacterial behavior and biocompatibility [1,101]. In addition, TiO_2 nanostructures have been found to be effective for the inactivation of both Gram-positive and Gram-negative bacteria [102]. Table 3 represents the antibacterial performances of various TiO_2 films prepared by sol-gel method. TiO_2 kills the microorganisms upon illumination of light mainly due to its photocatalytic properties [103]. Currently, there are three different mechanisms suggested for the antibacterial action of TiO_2-based materials [103]: i) reactive oxygen species (ROS) generation, ii) cell wall damage and lipid peroxidation of the cell membrane, iii) cytoplasmic flow due to cell membrane damage. Several studies have indicated that ROS formation is the main mechanism responsible for the antibacterial activities of TiO_2-based materials [104–107].

The bactericidal activity of ROS is attributed to its high reactivity and oxidizing properties. ROS are generated continuously by aerobic cells during metabolism and include the superoxide anion (UO_2-), hydrogen peroxide (H_2O_2), the hydroxyl anion (OH−), and hydroxyl radical (UOH). The generated species are capable of destroying cell membrane constituents directly, damage the integrity of the membrane, and even cross the bacterial membrane. The destruction of cellular components such as lipids, DNA, and proteins leads to loss of function and ultimately to the death of cells [14,103,108,109]. A schematic diagram showing the antibacterial mechanism of TiO_2 is given in Figure 4.

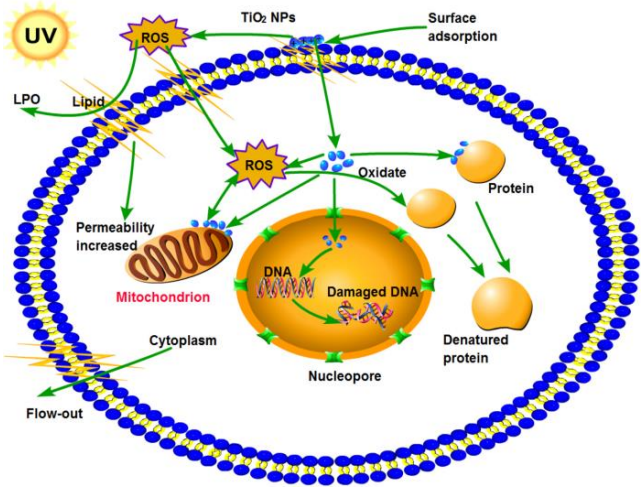

Figure 4. Schematic diagram showing the toxicity of TiO_2 NPs to microorganisms [103]. Reprinted with permission from [103]; Copyright 2018 The Research Centre for Eco-Environmental Sciences, Chinese Academy of Sciences. Published by Elsevier B.V.

In order to investigate antibacterial performance against *Eschericia coli* (*E. coli)* under visible light, Arellano et al. [110] prepared Fe-doped TiO_2 film deposited on a sodium glass substrate. The precursor was treated at 400 and 800 °C to give the anatase and rutile phase of TiO_2, respectively. The antibacterial study showed that the Fe–TiO_2 film containing 5% of Fe and treated at 800 °C eliminated *E. coli* completely after 60 min. This is attributed to the higher contact area for the adherence of bacteria and smaller energy band gap.

Kiwi et al. [111] present a design, characterization, and antibacterial evaluation of TiO_2 and TiO_2-doped films (polyethylene–TiO_2, TiO_2–In_2O_3, and TiO_2–polyester) against *E. coli*. The authors suggest bacterial cell wall damage to be the main bactericidal action of the films.

Pleskova and coworkers [102] prepared TiO_2 films on glass substrate using tetrabutyl oxytitan as a TiO_2 precursor. The bactericidal activity of TiO_2 films was studied against both Gram-negative and Gram-positive bacteria under UV irradiation at a wavelength of 380 nm. After 12 min of exposure to UV light, a 29, 45, and 47% decrease in viability was recorded for *Staphylococcus aureus* (*S. aureus*), *Staphylococcus epidermidis* (*S. epidermidis*), and *E. coli*. Furthermore, the authors reported that the sterilization activity was only observed in a single use; however, photoinduced bactericidal activity can be restored by annealing the TiO_2 at a temperature higher than 400 °C.

Sunada and researchers [106] prepared TiO_2 films on silica coated soda-lime glass plates using titanium isopropoxide as a precursor and studied their photokilling acidity against *E. coli* cells. The authors found that the photocatalytic reaction affected cell survival by causing damage from the outside of the cell. They concluded that the TiO_2 film photocatalyst decomposes the lipopolysaccharide of *E. coli*'s cell wall. The AFM photographs of *E. coli* cell on TiO_2 films after different time of UV illumination is given in Figure 5. The AFM image showed that the outer membrane decomposed first, and upon further UV illumination, the bacterial cell completely decomposed.

Pleskova et al. [112] used TiO_2 films as a self-sterilization surface, which killed several bacteria by reactive oxygen species upon irradiation with UV light. The authors presented a new way to

enhance the antibacterial action of TiO_2 films by the forming of nanopores on the surface of the film. They studied the bactericidal activities of TiO_2 films against both Gram-positive and Gram-negative bacteria and observed that the modified surface possesses significantly higher antibacterial activity as compared to the conventional TiO_2 surface film, due to the increased surface area as well as possible changes in the microstructure of TiO_2 induced by laser exposure. The morphological changes in the bacteria after the incubation was examined by atomic force microscopy and indicated cell wall damage caused by the exposure to UV and/or ROS.

In the literature, most antibacterial investigations have been carried out against *E.coli.* bacteria, which is a member of the coliform group. However, there have been few studies of the photocatalytic destruction of other bacteria. Recently, Pleskova et al. [112] studied the antibacterial properties of TiO_2 film against various bacteria such as *E. coli*, *S. aureus*, *Staphylococcus epidermidid* (*S. epidermidis*), *Enterococcus faecium* (*E. faecium*), *Klebsiella oxytoca* (*K. oxytoca*), *Kelbsiella penumoniae* (*K. pneumoniae*), *Proteus vulgaris* (*P. vulgaris*), and *Micrococcus spp*. Their study suggested that the vast majority of the strains used were sensitive to the bactericidal property of TiO_2 film under UV irradiation. However, the degree of antibacterial efficacy was bacteria-dependent. As can be seen in Figure 6, *P. aeruginosa* 9691 and *S. epidermidis* 1061 showed the most sensitivity when treated with TiO_2 film under UV irradiation. On the other hand, *P. vulgaris* 1212 and *K. pneumonia* 527 showed the least sensitivity.

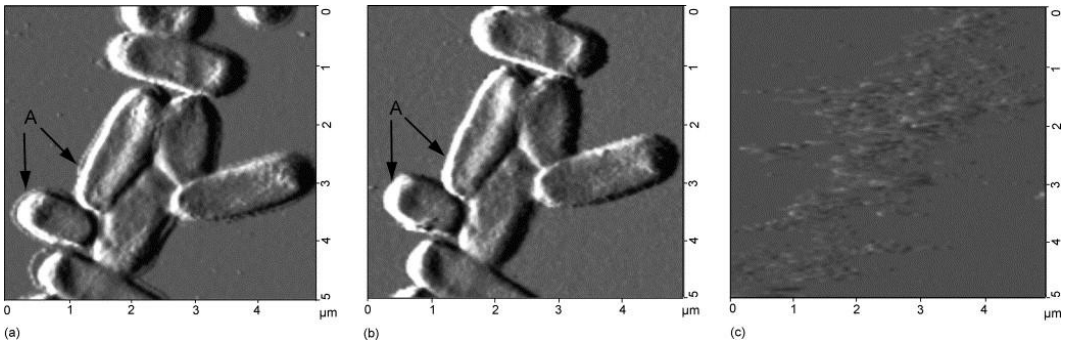

Figure 5. AFM images of *E. coli* cells on the TiO_2 film: (**a**) no illumination; (**b**) illumination for 1 day; (**c**) illumination for 6 days. Light intensity was 1.0 mW/cm^2. Adapted with permission from [106]; Copyright 2003 Elsevier Science B.V.

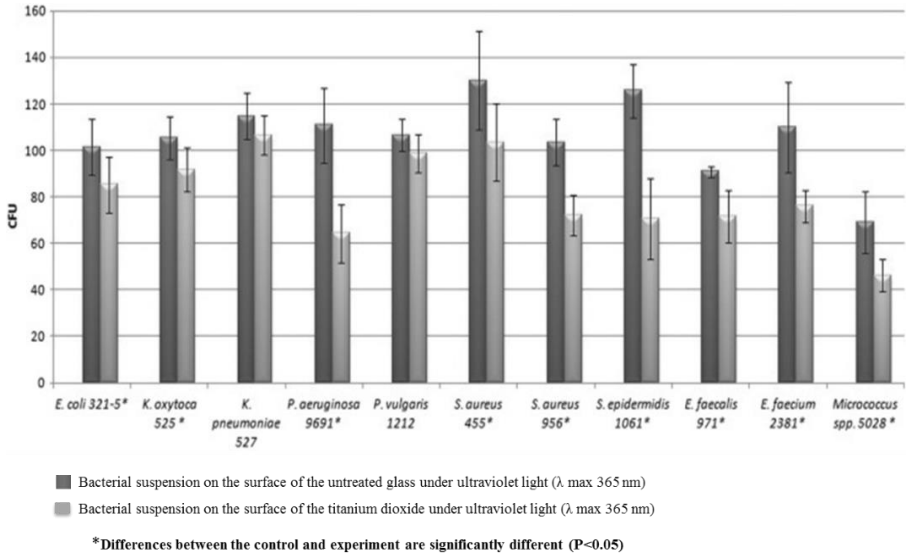

Figure 6. Colony forming units (CFUs) of various bacteria strains after incubation under UV for 15 min on the surface of sterile glass (control) and TiO_2. Reprinted with the permission from [113]; Copyright 2015 Elsevier B.V.

Table 3. Antibacterial performance of various TiO_2 films prepared by the sol-gel method.

Catalyst	Substrate	Bacteria	Concentration of Bacteria	Incubation Time	Light Source	Inhibition %	Ref.
Fe–TiO_2 thin film	sodium glass	*E. coli*	-	1 h	Visible light	100	[110]
Multi-Layered TiO_2 film	glass plates	*E. coli*	2.59×10^7 CFU/ml	8 h	Sunlight	91.9	[113]
nano-TiO_2 (anatase)-based thin films	Silicon	*E. coli*	10^8 CFU/mL	20 min	UV	100	[101]
SiO_2–TiO_2 film	glass slides	*E. coli*	10^6–10^8 per ml	1 h	Artificial solar radiation	50	[114]
Cu-doped TiO_2 film	glass	*E. coli*	103 CFU/ml	4 h	UV	100	[115]
TiO_2 film	glass plate	*S. aureus*, *S. epidermidis*, *E. coli*	200 CFU	15 min	UV	50	[102]
TiO_2 thin film	silica- coated soda-lime glass	*E. coli*	2×10^5 CFU/ml	90 min	UV	100	[106]
Ag ion-implanted TiO_2 thin films		*E. coli*	4.46×10^8 CFU/mL	24 h	fluorescent lamp and in the dark	100	[116]
Ag-doped TiO_2 film	glass fiber	*P. aeruginosa*	1×10^3 CFU/ml	10 min	UV	100	[117]
Mesoporous TiO_2 film	glass	*E. coli*	10^6 cells mL^{-1}	60 min	UV	99.99	[118]
GO nanosheets on TO_2 film	glass	*E. coli*	10^6 CFU/mL	24 h	Solar light	–	[119]

4. Conclusions, Challenges and Future Perspectives

TiO_2-based photocatalytic systems, including films, have shown promising results for the removal of organic pollutants and the destruction of pathogens in water. TiO_2 films are mainly prepared by chemical, physical, and sputter-based approaches, among which sol-gel coating is the most simple, low-cost, and suitable method for laboratory studies. Despite several advantages of TiO_2, such as low cost, non-toxicity, and ease of fabrication, a poor ability to absorb solar irradiation is the main drawback to widening its application in photocatalysis. In recent years, pristine TiO_2 films as well as modified (or doped) TiO_2 films have been developed by sol-gel technique for photocatalytic dye degradation and antibacterial applications. Although there is great progress in designing and synthesizing TiO_2 films with enhanced photocatalytic efficiency, challenges remain in developing a cheap, low-toxicity, and reproducible synthetic approach. Control over the thickness of the coating, pore size, surface area, uniform morphology, and crystallinity also need to be addressed for better results. Another challenge associated with the use of TiO_2 film for photocatalytic dye removal and antibacterial applications is stability and durability. It is expected that continued research in this field will lead to a better understanding and uncover the way to overcome existing limitations.

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