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Review

A Review of the Use of Semiconductors as Catalysts in the Photocatalytic Inactivation of Microorganisms

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Abstract: Obtaining clean and high-quality water free of pathogenic microorganisms is a worldwide challenge. Various techniques have been investigated for achieving an effective removal or inactivation of these pathogenic microorganisms. One of those promising techniques is photocatalysis. In recent years, photocatalytic processes used semiconductors as photocatalysts. They were widely studied as a green and safe technology for water disinfection due to their high efficiency, being non-toxic and inexpensive, and their ability to disinfect a wide range of microorganisms under UV or visible light. In this review, we summarized the inactivation mechanisms of different waterborne pathogenic microorganisms by semiconductor photocatalysts. However, the photocatalytic efficiency of semiconductors photocatalysts, especially titanium dioxide, under visible light is limited and hence needs further improvements. Several strategies have been studied to improve their efficiencies which are briefly discussed in this review. With the developing of nanotechnology, doping with nanomaterials can increase and promote the semiconductor's photocatalytic efficiency, which can enhance the deactivation or damage of a large number of waterborne pathogenic microorganisms. Here, we present an overview of antimicrobial effects for a wide range of nano-photocatalysts, including titanium dioxide-based, other metal-containing, and metal-free photocatalysts. Promising future directions and challenges for materials research in photocatalytic water disinfection are also concluded in this review.

Keywords: photocatalysis; semiconductor; waterborne microorganism; inactivation; nanotechnology



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1. Introduction

Water is one of the most vital pillars for sustaining all life forms on our planet. Not only is it essential for drinking and cooking, but it is also required for other purposes such as agriculture, food production, sanitation, industrial processes and ecosystems. Although water covers 71% of the Earth's surface, oceans account for 96.5% of the total surface water but are unsuitable for human consumption [1–4]. While freshwater constitutes about 2.5% of the full hydrosphere water, about 30.1% is present as groundwater, and 68.7% is stored in glaciers and permanent snow cover [5]. This leaves only 1.2% freshwater in swamps, lakes, rivers, soil moisture, and other sources [6]. Technological advances, population growth, agricultural discharge, inappropriate sanitation, water treatment plants, and rapid industrialization cause water pollution, which have adverse effects on human health and the environment [7–9]. Therefore, water pollutants can be classified as biological

(pathogens) or chemical contaminants [10]. Pathogens are microorganisms (such as bacteria, viruses, and protozoa) that can cause or spread various diseases to human beings, plants, or even animals through water [7].

According to the World Health Organization (WHO) 2016 report, it is estimated that about 0.84 million deaths in 2012 were related to water pollution [11]. Water contaminated with pathogenic microorganisms can lead to the spread of numerous diseases (such as hepatitis, malaria, dysentery, cholera, and typhoid fever), which vary in their severity and can be fatal as *Norovirus*, *Echo* viruses, *E. coli*, and *Salmonella* [7,12]. Furthermore, the global public health was threatened by the first Severe Acute Respiratory Syndrome Coronavirus (SARS-CoV-1) outbreak in 2002 followed by the Middle East Respiratory Syndrome Coronavirus (MERS-CoV) and Severe Acute Respiratory Syndrome Coronavirus 2 (SARS-CoV-2, also known as COVID-19 pandemic) outbreaks in 2012 and 2020, respectively [13]. SARS-CoV-1 was reported to exist in hospital wastewater for 2 days and 14 days at 20 °C and 4 °C, respectively. COVID-19 is also RNA positive in hospital wastewater, meaning that these viruses could infect drainage systems. Accordingly, the coronavirus inactivation and disinfection techniques of sewage discharged from hospitals and biomedical laboratories have gained significant attention from the scientific community [14,15].

Obviously, acquiring clean and safe water free of pathogenic microorganisms is a critical global issue for sustaining human health and ecosystems. This can be achieved by removing, inactivating, or killing these pathogens. Therefore, cheap, green, and effective water disinfection or sterilization methods are urgently required [16]. Chlorination, ozone, and ultraviolet irradiation are the traditional technologies used in water/wastewater disinfection. Although the chlorination technique has high efficiency, hazardous mutagenic, and carcinogenic disinfection by-products are generated from the chlorine that reacts with the organic materials present in microorganisms. Some waterborne pathogens are reported to be resistant to chlorine disinfection, such as viruses, specific bacteria as *Legionella*, and protozoans as *Cryptosporidium* and *Giardia lamblia* cysts. Unlike chlorination techniques, ozone and ultraviolet irradiation treatments do not leave any residues in treated water/wastewater leading to no water recontamination. However, the high operating costs of the ozone disinfection process, the complexity of its operations, and the production of toxic disinfection by-products such as bromates are the main limitations of this disinfection technique. Despite the low costs of ultraviolet irradiation, it has some drawbacks, including: (i) certain viral types are highly resistant to UV radiation, such as rotaviruses and adenoviruses, and (ii) the inadequate penetration power that inactivates surface wastewater pathogens resulting in regrowth of the treated bacterial cells after irradiation removal [14,16–18]. Accordingly, new techniques are needed to overcome the limitations of the traditional disinfection methods.

Over the last decades, the Advanced Oxidation Processes (AOPs) have been considered efficient environmental remediation techniques. These processes involve hydroxyl radicals and other strong oxidants to eliminate the hazardous organic pollutants efficiently through direct or indirect methods. Due to the high standard potential of these radicals ($E^\circ = 2.80 \text{ V/SHE}$), they are classified as one of the strongest oxidizing agents. They can react with a vast range of pollutants producing hydroxylated or dehydrogenated products leading to mineralization (conversion into CO_2 , water, and inorganic ions) [19].

Photocatalysis, as one of the AOPs techniques, has greatly attracted the scientific community's concern. In 1985, the photocatalysis technique was used for the first time by Matsunaga and his group as an effective water disinfection process [20], where Pt-loaded TiO_2 photocatalyst deactivated various microorganisms, such as *Lactobacillus acidophilus*, *Saccharomyces cerevisiae*, and *Escherichia coli* [16]. Since then, the photocatalysis technique is widely used in water disinfection because of its high efficiency, low cost, being safe and non-toxic, its ability to disinfect a wide range of microorganisms without hazardous by-products, and ability to inactivate different resistant microbial forms, such as fungal spores and bacterial endospores. In addition, the photocatalyst remains unchanged during reaction leading to less chemical consumption; the photocatalyst can also be used for

multiple cycles without losing its activity and can work at deficient concentrations because the contaminant is strongly attracted to the catalyst surface [21–24].

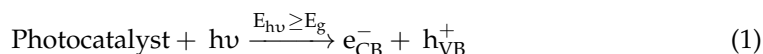
Based on photocatalytic process technique advantages, heterogeneous photocatalysis using semiconductors is more efficient than conventional methods for contaminant control in water because semiconductors have different convenient properties suitable for the photocatalytic reaction as light absorption properties, ability to produce charge carriers when activated with light photons, and their electronic structure [19,25].

This review provides a concise summary of recent advances in photocatalytic water disinfection, with a focus on bacteria and virus disinfection. The following are the key issues that have been addressed in this review:

- (i) The different water disinfection methods.
- (ii) Semiconductors photocatalytic mechanism.
- (iii) Photocatalytic mechanisms for inactivation of various microorganisms in water and the limitations facing the usage of TiO₂ as photocatalyst.
- (iv) Recent strategies for enhancing the photocatalytic efficiency for water disinfection.

2. Fundamental Mechanism for Photocatalytic Processes

The photocatalytic reaction is initiated when the semiconductor photocatalyst is excited by photons after irradiation by the light source. These photons cause the electrons (e^-) on the surface photocatalyst to become 'excited' in the valance band if the energy of the photons ($E_{h\nu}$) is greater than or equal to the bandgap (E_g) [26–28]; this causes the e^- to jump into the conduction band. Once the e^- have absorbed to the conduction band (e_{CB}^-), a positive hole is formed on the valence band (h_{VB}^+), according to the following equation:



This process lasts for a few femtoseconds and is then followed by recombination of the excited negative electrons in the conduction band (CB) with the previously generated positive holes at the valence band (VB) either on the surface or in the bulk of the particle releasing heat energy [29–31]. Otherwise, these produced charge carriers (e^- and h^+) can migrate to the surface of the photocatalyst and initiate further redox or oxidation reactions with adsorbed or reactant molecules on the surface if they have sufficient time or energy, as illustrated in Figure 1, which is inspired from a previous article [16]. The oxidation potential of the reaction between the holes and the reactant molecules should be higher than that of the valence band. Generally, in an aqueous environment, the positive holes (h^+) can oxidize water adsorbed at the surface producing hydroxyl radicals ($\cdot\text{OH}$), which can oxidize organic pollutants producing carbon dioxide, water, and mineral salts. Otherwise, the excited electrons (e^-) can rapidly reduce the absorbed oxygen on the surface producing superoxide anion radical ($\text{O}_2^{\cdot-}$). This superoxide anion radical can react with (H^+), forming a hydroxyl radical ($\cdot\text{OH}$), which in turn can undergo further oxidation reaction [32–36].

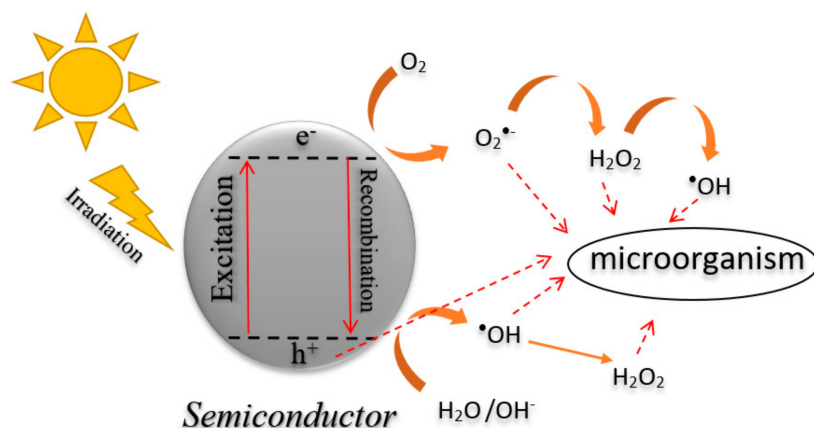
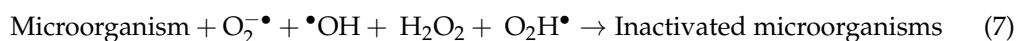
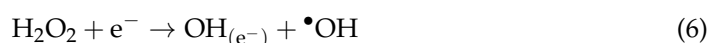
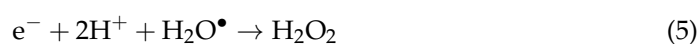


Figure 1. Schematic diagram for the photocatalytic mechanism of a semiconductor.

3. Photocatalytic Water Disinfection

Since about 99 wt% of the pathogenic microorganisms consist of organic compounds, such as proteins, lipids, lipopolysaccharides, polysaccharides, sugars, amino acids, nucleotides, and nucleic acid (DNA and RNA) that can be degraded by photocatalytic materials [37]. The photocatalyst forms reactive oxygen species (ROS), including $\bullet\text{OH}$, $\text{O}_2^{\bullet-}$, $\text{O}_2\text{H}^{\bullet}$, and H_2O_2 [38], that have a powerful oxidizing ability for inactivation and/or death of various waterborne pathogenic microorganisms under ambient conditions [18,21]. The ROS can efficiently oxidize the unwanted contaminants present in the water besides water disinfection [39]. This process can be summarized by the next relations (Equations (2)–(7)) [40,41].



In the case of bacteria, the oxidizing ability of ROS can be achieved by one of three photocatalytic mechanisms that have been proposed in the literature (see Figure 2, which is inspired from an article [21]). In the first mechanism, the cell membrane is attacked by reactive oxygen species (ROS), causing damage to the cell membrane coenzyme A, which inhibits respiration on the cell membrane [40]. This reduces or prevents cellular respiration activity, causing cell lysis [21]. In the second one, the ROS attacks the cell membrane. they enter the bacterial cell causing further oxidation to the internal cellular macromolecular components, such as nucleic acids (as DNA and RNA) and proteins [40]. Eventually, cell lysis occurs. In the last mechanism, the ROS damage the cell membrane and the cell wall; then the internal cellular components (nucleic acids as DNA and RNA, proteins, and some cations) leak out, leading to inactivation and finally to bacterial cell death [21].

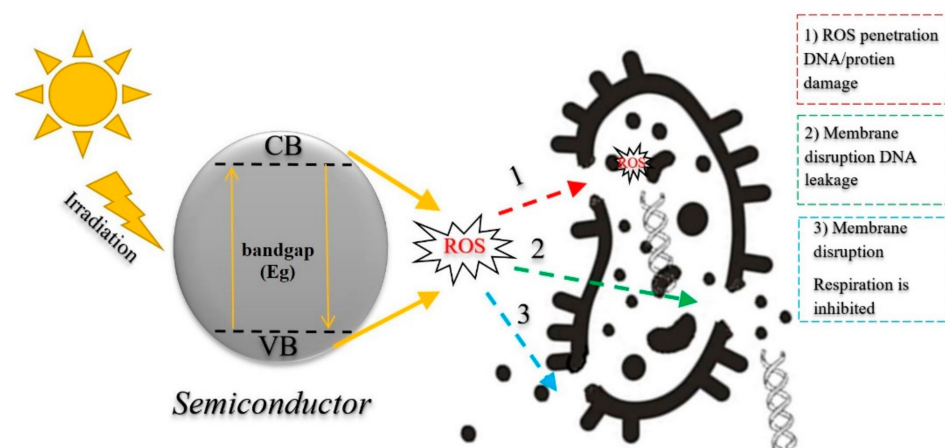


Figure 2. Proposed photocatalytic water disinfection mechanisms.

4. Photocatalysts Used in Water Disinfection

Based on previous studies, photocatalysis has been used successfully to inactivate various types of bacteria in wastewater. Table 1 summarizes a list of bibliographical references dealing with the implementation of photocatalytic processes using different catalysts for the bacteria inactivation.

Table 1. Semiconductors for bacteria inactivation.

Catalyst	Target Bacteria	Operating Conditions	Inactivation Rate	Ref.
TiO ₂	<i>Escherichia coli</i>	Catalyst dosage: 1.5 g/L; pH: 10; reaction time: 60 min; Initial bacterial cells: 10 ⁸ CFU/mL; Temperature: 32 °C; Irradiation: ultraviolet (UV) irradiation at 254 (UV254)	100%	[42]
	<i>Methicillin-resistant Staphylococcus aureus</i>	Fixed TiO ₂ ; Reaction time: 10 min; Initial bacterial cells: 10 ⁷ CFU/mL; Temperature: 37 °C; Irradiation: ultraviolet (UV)	98.0%	[43]
	<i>Salmonella typhimurium</i>	Catalyst dosage: 100 mg/L; Reaction time: 45 min; Initial bacterial cells: 10 ⁹ CFU/mL; Temperature: 30 °C; Irradiation: ultraviolet (UV)	100%	[44]
	<i>Erwinia amylovora</i> , <i>Xanthomonas arboricola</i> pv. <i>juglandis</i> , <i>Pseudomonas syringae</i> pv. <i>tomato</i> and <i>Allorhizobium vitis</i> .	Catalyst dosage: 0.5 g/L; Reaction time: 30 min; Initial bacterial cells: 10 ⁸ CFU/mL; Temperature: 30 °C; Irradiation: ultraviolet (UV 15 W),	−5 log ₁₀ , −4 log ₁₀ , 100%, 100%, respectively	[45]
ZnO	<i>Escherichia coli</i>	Catalyst dosage: 1.5 g/L; pH: 5; reaction time: 180 min; Optical density: 1 ZnO film 12.2 mJ/cm ² ; Reaction time: 35 min; Initial bacterial cells: 10 ⁷ CFU/mL; Temperature: 82 °C; Turbidity 100 NTU; Irradiation: ultraviolet (UV)	94%	[46]
	Coliforms	Catalyst Dose: 0.01 g/L, Reaction time: 120 min for strains of fungi, 40 min for other strains, Initial bacterial cells: 10 ⁵ CFU/mL, Temperature: 37 °C, Irradiation: ultraviolet (UV)	100%	[47]
TiO ₂ and ZnO	<i>Saccharomyces cerevisiae</i> , <i>Candida albicans</i> and <i>Aspergillus niger</i>	Catalyst dosage: 500 mg/L; Reaction time: 210 min; Initial bacterial cells: 10 ⁷ CFU/mL; Temperature: 37 °C	100%	[48]
Ag/SnO ₂ /ZnO	<i>Bacillus species</i>	Catalyst dosage: 0.2 g/L; Initial bacterial cells: 2 × 10 ⁶ CFU/mL and light intensity: 48 mW/cm ² ; Reaction time: 4 h; Irradiation: visible light.	100%	[49]
Bi ₂ WO ₆	<i>Escherichia coli</i>	Catalyst dosage: 1 g/L; Initial bacterial cells: 10 ⁶ CFU/mL; Reaction time: 120 min; Irradiation: artificial solar simulator (light intensity of ~120,000 Lux)	100%	[50]
Pd-Ag/rGO	<i>Escherichia coli</i>	Catalyst dosage: 5 mg/mL, Reaction time: 360 min, Initial bacterial cells: 10 ⁷ CFU/mL	96%	[51]
NiMoO ₄	<i>Methicillin-resistant Staphylococcus aureus</i>	Catalyst: 2 wt % Pd/BiFeO ₃ , Dose: 1 g/L, Reaction time: 240 min, Initial bacterial cells: 10 ⁷ CFU/mL Temperature: 37 °C	100%	[38]
Pd-BiFeO ₃	<i>Enterococcus faecalis</i>		98%–100%	[52]

Table 1 shows several bacteria strains successfully inactivated by several kinds of photocatalytic materials (TiO₂, Ag-TiO₂, ZnO, and others), which demonstrate the beneficence of the photocatalytic process in the disinfection of water from several types of bacteria. Another observation can be derived from this table, the most widely used semiconductor in the literature is TiO₂, due to its effectiveness as it shows complete inactivation of various types of bacteria (*Escherichia coli*, *methicillin-resistant Staphylococcus aureus*, and *Salmonella*

typhimurium). Because semiconductors have shown to be effective in inactivating bacteria, it is worth looking into how they can be used to inactivate viruses.

In the case of viruses, only a few studies on photocatalytic viral disinfection can be found in the literature. The first viral photocatalytic disinfection was conducted in 1994 using TiO₂ as a photocatalyst for the inactivation of phage MS2 [53]. This work sparked further research into TiO₂ and TiO₂-based photocatalysts' antiviral activity in water and wastewater disinfection and sterilization.

However, viruses have simpler structures than bacteria, as most viruses cover their central genetic material (RNA or DNA) by a protein shell (capsid); they are challenging to be removed due to their small size, unique surface properties, and ability to repair and regrowth under suitable conditions. The ROS oxidative ability can damage the protein shell leading to serious leakage and/or destruction of the virus genes, which results in virus inactivation and/or definite viral death [18,21].

Over the last two decades, there have been many appealing photocatalytic applications for viral disinfection, in which the process led to the inactivation of viruses. Bibliographic references related to studies of photocatalytic processes for the inactivation of viruses are listed in Table 2.

Table 2. Semiconductors for viruses' inactivation.

Catalyst	Target Viruses	Operating Conditions	Inactivation Rate	Ref.
TiO ₂	<i>A/H1N1 Influenza virus</i>	Reaction time: 8 h; Initial viral cells: 1 × 10 ⁸ TCID ₅₀ /mL; Irradiation: ultraviolet light	4-log ₁₀ (99%)	[54]
	<i>Bacteriophage f2</i>	Catalyst dose of 25 mg/L; Reaction time: 1 h; Initial viral cells: 5.22 log PFU/g, Irradiation: ultraviolet light	95.79%	[55]
	<i>Bacteriophages (MS2, PRD1, phi-X174, and fr)</i>	Catalyst dosage: 1 g/L; UV dose of 8 mJ/cm ² ; pH: 7; initial concentration: 4 log PFU/g	85%, 81%, 94%, and 100%	[56]
	<i>Hepatitis B virus (HBsAg)</i>	Catalyst dosage: 0.5 g/L; pH: 7.2; Reaction time: 4 h, Irradiation: ultraviolet light	97%	[57]
	<i>Norovirus (HuNoV)</i>	Reaction time: 20 min; Initial viral cells: 6.1 log PFU/g, Irradiation: ultraviolet light	2,9 log ₁₀ 99%	[58]
Tungsten Trioxide-Based (WO ₃)	<i>Rotavirus (Odelia, SA11), Astrovirus, and Feline calicivirus (FCV)</i>	Reaction time: 24 h; pH: 6, T: 30 °C; Initial viral cells: 3.4–5.19 log TCID ₅₀ ; Irradiation: ultraviolet light	1.5–3 log ₁₀	[59]
	<i>Coronavirus 2 (SARS-CoV-2)</i>	Reaction time: 30 min; Initial viral cells: 1.7 × 10 ⁴ PFU/mL	1.5 log ₁₀ 100%	[60]
Pt-WO ₃	<i>Influenza virus H1N1</i>	The catalyst was used as glass plate; Initial viral cells: 10 ^{7.0} TCID ₅₀ /mL; Temperature (25 °C); Reaction time: 6 h; Irradiation: ultraviolet light	>3.0 log ₁₀ 99.9%	[61]
Ag–AgI/Al ₂ O ₃	<i>human rotavirus (and Shigella dysenteriae and Escherichia coli)</i>	pH 4.5; Initial viral cells: 10 ⁸ CFU/mL; catalyst dose (0.2 g/L); Temperature (25 °C); Reaction time: less than 1 h	100%	[62]
MIL-125 (Ti)-NH ₂	<i>Coronavirus 2 (SARS-CoV-2)</i>	pH: 6; Reaction time: 30 min; Initial viral cells: 1 × 10 ⁵ TCID ₅₀ /mL	100 TCID ₅₀ /mL 99%	[63]
O-g-C ₃ N ₄ /HTCC-2	<i>Adenovirus (HAdV-2)</i>	Photocatalyst dose of 0.15 g/L; pH: 5, Temperature: 37 °C Reaction time: 120 min; Initial viral cells: 10 ⁵ MPN/mL	100%	[64]

Table 2 shows that semiconductors also have excellent photocatalytic performance in the viral disinfection of water besides bacteria. It shows also that lot of viruses such as *A/H1N1 Influenza virus*, *Bacteriophage f2*, *Hepatitis B virus*, *Coronavirus 2 (SARS-CoV-2)*,

Shigella dysenteriae, *Escherichia coli*, human rotavirus, Adenovirus (HAdV-2), and Norovirus (HuNoV) has completely inactivated and disinfected from water by various catalysts, this demonstrates the photocatalytic process' efficacy in the viral disinfection. It can be seen in the tables that Titanium dioxide TiO₂ is the most used and efficient catalyst among those semiconductors, as it shows efficient inactivation for all of *A/H1N1 Influenza virus*, *Bacteriophages (MS2, PRD1, phi-X174, and fr)*, *Hepatitis B virus (HBsAg)*, *Rotavirus (Odelia, SA11)*, *Astrovirus*, and *Feline calicivirus (FCV)*. As a result, it is critical to concentrate on Titanium dioxide TiO₂ as a topical catalyst for microorganism inactivation and to look for ways to improve its photocatalytic effectiveness for water disinfection.

5. Titanium Dioxide as a Photocatalyst

Among the various semiconductor materials, TiO₂ is the most widely used as a photocatalyst. This is attributed to its strong oxidizing ability, chemical stability, highly reactive, ease of preparation, abundant, reduced cost, low toxicity, chemical inertness, and long-term photostability [65,66]. In addition, titanium dioxide photocatalysts are widely employed in many research fields, such as organic pollutants degradation and mineralization, selective organic synthesis, solar fuels production as hydrogen and methane, the annihilation of pathogenic microorganisms (as bacteria, fungi, parasites), and utilization in anticancer therapies [67,68].

Titanium dioxide belongs to the transition metal oxides family, which can be extracted from various natural ores present throughout the world. It is a well-known n-type semiconductor due to the presence of oxygen vacancies in its structure. In TiO₂, the crystalline phase, the composition and the surface states strongly affect the electronic structure and the charge properties. There are three crystalline forms of TiO₂: anatase (tetragonal structure), rutile (tetragonal structure), and brookite (orthorhombic structure). The main building unit consists of a titanium atom surrounded by six oxygen atoms forming a distorted octahedral configuration. The rutile phase is stable at most temperatures and pressures in comparison to the other phases. However, both anatase and brookite phases with particle size greater than 14 nm can turnover to rutile at high temperatures [69,70]. The photocatalytic activity of TiO₂ depends on its present phase. The anatase phase is metastable with a bandgap of 3.2 eV, but it has a more efficient photocatalytic activity compared to the other phases (rutile and brookite). While rutile has a bandgap of about 3.02 eV with high chemical stability but it is less photo-active than anatase. Although brookite is metastable and its bandgap is about 3.4 eV, the experimental data on TiO₂ brookite as a photocatalyst is limited due to its rareness, higher density, and the difficulty of preparation. The high photocatalytic activity of anatase can be attributed to its lower density, its higher electron mobility and the longer lifetime of the photo-activated electrons and holes due to the lower oxygen adsorption and higher hydroxylation degree by electrons and holes, respectively, which reduces the charge carriers' recombination rate in anatase than in the other two phases [71–73].

Unfortunately, natural TiO₂ is activated only by the near-UV photons of the solar spectrum ($\lambda < 390$ nm) due to its wide bandgap. While solar light is made up of only 4% of UV but visible light counts for approximately 42% of solar light [32]. This wide-bandgap hinders its usage in environmental applications. Therefore, increasing the photocatalytic activity of TiO₂ is a challenging issue [74,75].

Various strategies have been used to improve the photocatalytic efficiency of TiO₂ under visible light, which includes the following: (i) Bulk or surface doping with metal ions (using transition or noble metals like Cu, Cr, Fe, Ru, Au, Ag, and Pt) or non-metals (as N, S, C, and F) [66,76–78]; (ii) Composite formation, coupling photocatalyst with different bandgap materials like conjugated carbon as carbon nanotubes, or small bandgap semiconductors such as CdS nanoparticles, or polymeric materials [77,79–81]; and (iii) Sensitization with organic dyes, which involves ionic or covalent bonds formed between photocatalyst surface and dye molecules [82–85].

6. Strategies to Improve the Photocatalytic Activity of Titanium Dioxide

Nanotechnology can provide different solutions for water/wastewater treatment by adding or applying different forms of nanomaterials (such as nanoparticles, nanotubes, nanowires, nanofilms, and quantum dots) to the photocatalyst. This can result in more enhanced efficiency on pathogens disinfection due to their large specific surface area, high activity and an increased degree of functionalization, antipathogenic properties, and ability to deactivate various microorganisms, either photothermally or via photocatalysis by the induced reactive oxygen species (ROS) [86–89]. The high surface area to volume ratio of nanomaterials gives a high contact area for reacting with pathogenic microorganisms [80].

With the development of photocatalytic disinfection techniques, semiconductor nano-photocatalysts showed high efficiency in the deactivation or killing a large number of bacteria, either Gram-positive or negative, filamentous and single-cell fungi, algae, protozoa, mammalian viruses, and phages, showing that it can be a promising technology for water and wastewater treatments [21].

The Ag-doped TiO₂ nano-photocatalyst showed the highest bacterial inactivation efficiency compared to Cu and Fe doped TiO₂ and bare TiO₂ when applied on waterborne bacterial pathogens (*Escherichia coli*, *Salmonella enterica*, *Shigella flexneri*, and *Vibrio cholera*) in real and synthetic wastewater. A 100% disinfection efficiency was achieved without any bacteria regrowth after 60 min and 180 min under UV and solar irradiation, respectively [12]. Additionally, the Ag-loaded TiO₂ nano-photocatalyst caused complete disinfection of the parasitic cysts, *Giardia intestinalis* and *Acanthamoeba castellanii*, in water under UV light after 30 min, which is higher than the impact of bare TiO₂. Cell viability tests showed that the cysts cell walls were irreversibly damaged by the photocatalyst ROS and do not regrow again [90]. In another study, the Cu-doped TiO₂ nanofibers exhibited high antiviral activity against bacteriophage f2 and complete inactivation of its host bacteria *E. coli* 285 under visible light [91].

The addition of metal chalcogenides nanoparticles on TiO₂ nanoparticles facilitated the visible light absorption and increased photocatalytic activity under visible irradiation, as mentioned by Nazir and her group [68]. The presence of PbS and CdS quantum dots on P25-TiO₂ to prepare nanocomposites exhibited high antibacterial disinfection activity against *Bacillus subtilis* due to the generation of ROS, which penetrates the bacterial cell membrane leading to membrane lipid oxidation and consequently bacterial inactivation. The highest antibacterial activity was for CdS-Titanium based nanocomposite. This is due to the lethal effect of the Cd atom, which binds to proteins' sulfhydryl groups, causing protein denaturation, membrane damage, and thiol binding, thereby destroying the pathogenic microorganism's protective functions [80].

P25-TiO₂/sodium-Y-zeolite composite prepared via solid-state dispersion method exhibited antibacterial properties against *E. coli* and *S. aureus*. For 20% composite maximum growth reduction of bacterial cells was achieved under sunlight for 1 h at room temperature [92]. While TiO₂/C Heterojunctions (Carbon-doped anatase: brookite (80:20) nano-heterojunction) and Degussa P25 suspension attained a significant increase in photocatalysis and antibacterial properties against *S. aureus* under polychromatic visible-light and *Legionella pneumophila* under UV irradiation, respectively [93,94].

The metal-free semiconductor graphite carbon nitride (g-C₃N₄) based photocatalysts showed antibacterial properties. In addition, it was reported that it has antiviral activity as it inactivated the phage MS2 under visible light irradiation. The best disinfection performances were attained after 6 h irradiation with 150 mg/L g-C₃N₄ with no virus regrowth recorded due to the shape distortion and RNA damage by the ROS [21]. While employing AgVO₃/g-C₃N₄ and BiVO₄ photocatalysts inactivated the *Salmonella* and *E. coli* bacteria, respectively [21]. Additionally, in water disinfection under visible light irradiation, metal-containing photocatalysts such as Ag-AgI/Al₂O₃ and Pt-WO₃ inactivated human rotavirus (type 2 wa) after 40 min and Influenza virus H1N1 after 120 min, respectively [61,62].

Besides, bacterial inactivation, TiO₂ based photocatalysts exhibited antimicrobial properties for various types of fungi (such as *Aspergillus niger*, *Candida famata*, *Penicillium citrinum*,

and *Trichoderma asperellum*), protozoa (such as *Cryptosporidium parvum*, *Giardia* species, *Giardia lamblia*, and *Acanthamoeba castellanii*) and algae (such as *Cladophora*, *Chroococcus*, *Oedogonium*, and *Melosira* species) [16].

Furthermore, titanium dioxide-based nano-photocatalysts exhibited antiviral properties for a broad spectrum of viruses, including *Polio virus*1, *Phage* (as MS2, T4, and f2), *Hepatitis B virus*, *Murine norovirus*, *Human adenovirus 40*, *influenza viruses* (as H9N2, H1N1, H3N2, and H5N2), *Herpes simplex virus*, and *SARS coronaviruses* [16,18]. Employing a photocatalytic titanium apatite filter led to an effective inactivation of *SARS-CoV-1* coronavirus (which is a large lipid-enveloped and single-stranded RNA virus) under UV irradiation for 6 h. Indeed, the generated ROS damaged the spike proteins leading to the decrease of the viral infectious capacity with 99.99% inactivation efficiency [89,95]. Due to the genome similarities between *SARS-CoV-1* and *SARS-CoV-2*, this latter can be sensitive and affected by disinfectants, like *SARS-CoV-1*. Thus, titanium dioxide-based photocatalysts might be promising against coronaviruses in water/wastewater treatments [14].

The next table (Table 3) shows the improvements of photocatalytic performance of titania with the different strategies (doping, coupling semiconductors or others) in photocatalytic disinfection applications for both bacteria and viruses.

As can be seen from this table, all improved catalysts have given an almost complete disinfection of water for various types of microorganisms, from bacteria to viruses. This proves the advantage of enhancing the activity of a semiconductor by different strategies such as doping and coupling the catalyst.

Table 3. Improved semiconductors for water disinfection.

Catalyst	Target Bacteria	Operating Conditions	Inactivation Rate	Ref.
TiO ₂ -Ag	<i>Mycobacterium kansasii</i> and <i>Mycobacterium avium</i>	Catalyst: Ti/TiO ₂ eAg nanotube electrode (5 cm × 5 cm); Reaction time: 240 min; initial bacterial cells: 5 × 10 ⁸ CFU/mL; Temperature: 35 °C; Irradiation: ultraviolet (UV)	99.9%	[96]
1%Cu-N-TiO ₂	<i>Escherichia coli</i>	Catalyst dosage: 100 mg/L; Initial cell concentration of 1 × 10 ⁷ CFU/mL; Irradiation time: 100 min; Irradiation: LED light	100%	[97]
0.1Fe-0.4Zn- TiO ₂	<i>Staphylococcus aureus</i> and <i>Escherichia coli</i>	Catalyst dosage: 1 mg/L; Reaction time: 90 min; Initial bacterial cells: 10 ⁴ CFU/mL; Temperature: 37 °C	100%	[98]
B-Doped TiO ₂ -CNT	<i>Escherichia coli</i>	Catalyst Dose: 2 g/L; Reaction time: 240 min; Initial bacterial cells: 10 ⁶ CFU/mL; Irradiation: ultraviolet (UV)	100%	[99]
Co-doped TiO ₂	<i>Campylobacter jejuni</i> , <i>Salmonella Typhimurium</i> , <i>E. coli</i> , <i>Yersinia enterocolitica</i> , <i>Shewanella putrefaciens</i> , <i>Listeria monocytogenes</i> and <i>Staphylococcus aureus</i>	Catalyst dosage: 500 µg/mL; Initial bacterial cells: 10 ⁶ CFU/mL; Reaction time: 3–6 h; Irradiation: UVA irradiation	100%, 100%, ~4 log ₁₀ , ~3 log ₁₀ , ~5 log ₁₀ , ~2.5 log ₁₀ , respectively	[100]
C-doped TiO ₂	<i>Salmonella typhimurium</i>	Catalyst dosage: 1 g/10 mL; Initial bacterial cells: 3 × 10 ⁹ CFU/mL; pH 7.4; temperature: 37 °C; Reaction time: 1 h; Irradiation: UV-B lamp 5 mW/cm ²	100%	[101]
Fe ³⁺ Doped TiO ₂ /3S _n O ₂	<i>Salmonella typhimurium</i>	Catalyst dosage: 250 mg/L, reaction time: 60 min, Initial bacterial cells: 10 ⁶ CFU/mL, Temperature: 37 °C	100%	[102]

Table 3. Cont.

Catalyst	Target Viruses	Operating Conditions	Inactivation Rate	Ref.
N-doped TiO ₂ -coated Al ₂ O ₃	<i>MS2 bacteriophage</i>	In the presence of 120 mg L ⁻¹ Ca ²⁺ ; Reaction time: 120 min; pH: 6; Initial viral cells: 10 ¹¹ PFU/mL	4.9 log ₁₀ (99.99%)	[103]
TiO ₂ -coated ceramic	Aerosol-Associated <i>Influenza</i>	Reaction time: 30 min; Initial viral cells: 10 ⁵ PFU/mL	99%	[104]
Cu-doped TiO ₂	<i>Norovirus (HuNoV)</i>	UVA-LED wavelength: 365 nm; Cu:TiO ₂ ratio: 5.5; Reaction time: 60 min; Initial viral cells: 6.7 log PFU/g	2.89 log ₁₀ 99%	[105]

7. Conclusions and Outlook

Considering the fact that waterborne pathogenic microorganisms can threaten human health, their removal or inactivation in water/wastewater is an essential concern for sustainable human life. The photocatalysis technique using semiconductors offers a practical and sustainable strategy for dealing with this problem. Accordingly, semiconductors photocatalytic water disinfection has received great attention recently. TiO₂ is the widest semiconductor used as a photocatalyst due to its strong oxidizing ability, chemical stability, high reactivity, ease of preparation, abundance, cheap, non-toxic, and long-term photostability. Many photocatalysts, especially TiO₂-based, are reported in the literature that can be used in water disinfection. However, their photocatalytic efficiencies are limited under visible light, which reduces their practical applications. Many approaches have been documented to narrow the bandgap, including doping with metal or non-metals, composite formation, coupling with different bandgap materials like carbon nanotubes, or small band-gap semiconductors like CdS nanoparticles, or sensitization, with organic dyes. In addition, nanomaterials can inspire the future development of antimicrobial semiconductor photocatalysts due to their high surface area that increases the contact area available for the reaction between the microorganism and the photocatalyst. Therefore, doping with noble metals nanoparticles is reported to increase the absorption under visible light due to their unique optical properties. As well, metal-free nano-photocatalysts, such as graphite carbon nitride (g-C₃N₄) based photocatalysts, showed antiviral and antibacterial activities under visible light. While the inactivation of bacteria by photocatalysts has been extensively studied in the literature, viral inactivation by photocatalysts has received less attention. Thus, viral photocatalytic disinfection is required to be explored more. Furthermore, future work should focus on understanding the mechanisms of microorganisms' inactivation by photocatalytic materials using computer simulation.

Generally, designing and synthesizing reliable nano-photocatalysts for solar water disinfection need further improvements, especially those based on metal oxides, sulfides, semiconductors, metal-free, graphene, and natural mineral photocatalysts. All the above directions can offer both challenges and future opportunities for more research in photocatalysis and water disinfection.

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