Research progress of photocatalytic sterilization over semiconductors

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Considering the situation that environmental issues become more serious day by day, research on practical applications of semiconductor photocatalysis for environmental purification has attracted broad attention, including the remediation of water pollution, air contaminant treatment, photocatalytic sterilization etc., among which the application of semiconductor photocatalytic properties for the disinfection of soil surfaces, air and water, such as TiO₂, is of great interest. In this paper, we give an overview of the photocatalytic antibacterial ability of TiO₂ and other novel carbon material semiconductors. We have introduced the background information of photocatalytic disinfection and the disinfection mechanism of pure TiO₂. Furthermore, other modified TiO₂ sterilization materials are listed, such as those with doping modification. In addition, some novel carbon based nanomaterials are discussed as well in this review, for instance, g-C₃N₄, carbon nanotubes and graphene nanosheets. Finally, we present an outlook over two dimensional (2D) materials and coupling techniques based on the combination of photocatalysis and other sterilization technologies.

1 Introduction

With the increasing need of human material life, people pay more attention to the hygiene situation of work and living environments than ever, thus a variety of antibacterial materials have come into being. Commonly, antibacterial agents can be classified into two types: organic antibacterial agents and inorganic antibacterial agents. Moreover, inorganic antimicrobial agents mainly depend on silver ions, which merely kill bacteria, but cannot break down endotoxins. TiO₂ photocatalytic sterilization can be used to overcome the shortcomings of the traditional silver inorganic antibacterial agents. The active hydroxyl radicals generated by TiO₂ photocatalytic reactions possess a reaction energy of 120 kcal mol⁻¹, which is higher than that of various chemical bonds in organic compounds, such as C-C (83 kcal mol⁻¹), C-H (99 kcal mol⁻¹), C-O (84 kcal mol⁻¹), and H-O (111 kcal mol⁻¹) bonds. Therefore, hydroxyl radicals can quickly and efficiently decompose organic compounds, such as the main component of the bacterium. Additionally, the synergy of hydroxyl radicals and other reactive radicals generated from the photocatalysis, for instance "OOH and O₂⁻", makes the attacks on bacteria more frequent and causes reactions with biological macromolecules such as lipids, enzymes and nucleic acid macromolecules, which causes extensive damage to biological cell structures either directly or through a series of oxidative chain destructions. Moreover, some other nanomaterials, such as ZnO, CdS, CeO₂ and BiVO₄ etc., show excellent performance in photocatalytic sterilization. TiO₂ has always been considered as the most promising catalyst in the photocatalytic disinfection of bacteria; however, due to the wide band gap of anatase TiO₂ (3.2 vs. 3.0 eV of rutile), it is limited to UV light at wavelengths less than 385 nm, which accounts for less than 5% of solar energy. Thus, it is indeed of great necessity to expand its adsorption region from UV light to the visible light region. Some modifications have been well done on TiO₂, for instance non-metal and metal doping or construction of heterojunction semiconductors. Another effective strategy is to develop novel candidate nanomaterials for photocatalytic disinfection. Carbon materials, represented by g-C₃N₄, carbon nanotubes (CNTs) and graphene oxide (GO) have been deeply investigated in photocatalysis. Hence, in this review, we have not only reviewed the representative TiO₂ nanomaterials, but also emphasized the brand new carbon nanomaterials of g-C₃N₄, carbon nanotubes (CNTs) and graphene oxide (GO) for disinfection applications. To this end, we propose the future research direction in photocatalytic sterilization over semiconductors.

2 Photocatalytic disinfection of TiO₂

2.1 Photocatalytic disinfection of pure TiO₂

Heterogeneous photocatalytic oxidation technology has always been a hot spot at home and abroad. Since 1972, Fujishima
and Honda\textsuperscript{15} reported that the redox reaction of light-emitting TiO\textsubscript{2} could sustainably take place in photovoltaic cells. After that, in 1976, Carey \textit{et al.}\textsuperscript{16} successfully applied the TiO\textsubscript{2} photocatalytic oxidation method to dechlorination and detoxification of PCB compounds in water. In 1985, Tadashi Matsunaga \textit{et al.}\textsuperscript{17} firstly found that TiO\textsubscript{2} had a bactericidal effect under ultraviolet light. The experimental results showed that with the loading of TiO\textsubscript{2} nanoparticles, co-cultured Lactobacillus acidophilus, yeast, and Escherichia coli could be completely killed under the irradiation of a halide lamp for 60–120 min. Their findings opened a new era in the field of sterilization, thus resulting in attempts to use this novel photocatalytic technology for disinfecting drinking water and removing bioaerosols from indoor air environments. In 1993, Ireland \textit{et al.}\textsuperscript{18} found that titanium dioxide in the anatase phase could be used as a photocatalyst to generate hydroxyl radicals in a Flow-Through water reactor as shown in Fig. 1.

In 1994, Wei \textit{et al.}\textsuperscript{19} found that the irradiation of suspensions containing \textit{Escherichia coli} (~106 cells per mL) and TiO\textsubscript{2} (anatase) under UV-visible light with a wavelength longer than 380 nm resulted in the killing of the bacteria within minutes. Apart from \textit{Escherichia coli}, \textit{Giardia lamblia} is another target in photocatalytic sterilization. In 2004, Lee \textit{et al.}\textsuperscript{20} utilized a TiO\textsubscript{2} colloidal solution to sterilize the \textit{Giardia lamblia}. To be more specific, the TiO\textsubscript{2} solution was made into films using a modified hydrothermal method, and directly coated on a UV-lamp. As a result, the TiO\textsubscript{2} films were transparent until 5-times coating. In 2015, Wang \textit{et al.}\textsuperscript{21} reported visible-light-sensitive sub-5 nm TiO\textsubscript{2} nanoparticles, which were applied in the degradation of organic pollutants in water and air, and the bacterial disinfection field. Those sub-5 nm TiO\textsubscript{2} nanoparticles were fabricated without any doping or calcination treatments, maintaining abundant hydroxyls on the surfaces and subsurface, which indicated a high ratio of surface to bulk defects. Fig. 2(a) shows a lattice space of ~0.36 nm, which is indexed to the {101} facets of anatase TiO\textsubscript{2}. The gel (1.0 wt%) shows a high efficiency for visible-light-driven photocatalytic dye degradation (Fig. 2(c)). Significantly, the TiO\textsubscript{2} gel also shows impressive durability, with almost no loss of visible-light activity after 5 runs. Finally, qualitative (Fig. 2[b]) antibacterial evaluations are considered for TiO\textsubscript{2} gel. It can effectively sterilize bacteria SA under visible light.

![Schematic diagram of the experimental TiO\textsubscript{2} photoreactor showing the flow configuration (this figure has been reproduced from ref. 18 with permission from Elsevier).](image)

2.2 The mechanism of the antibacterial properties of TiO\textsubscript{2}

Advanced Oxidation Processes (AOPs) involving TiO\textsubscript{2}-mediated photocatalysis technology have attracted considerable attention from scientists. Among them, the photocatalytic oxidation process is mainly started by photogenerated electrons and holes through the irradiation of a semiconductor (e.g., such as TiO\textsubscript{2}) via sunlight. When irradiated by light, the electrons (e\textsuperscript{−}) are excited into the conduction band (CB), thus leaving a hole (h\textsuperscript{+}) in the valence band (VB) of the photocatalyst. Then, these charge carriers (e\textsuperscript{−}/h\textsuperscript{+} pair) migrate to the surface/interface of the photocatalyst and participate in the redox reactions. The whole mechanism is illustrated in eqn (1)-(8) as follows, involving reactive oxygen species (ROS) species such as HO\textsuperscript{•}, O\textsubscript{2}•\textsuperscript{−}, HO\textsubscript{2}•, etc. It is recognized that hydroxyl radicals are primarily responsible for this disinfection property, especially against bacteria.\textsuperscript{22}

\[
\begin{align*}
\text{TiO}_2 + h\nu & \rightarrow \text{TiO}_2 (e_{CB}^- + h_{VB}^+) \quad (1) \\
\text{TiO}_2 (h_{VB}^-) + \text{H}_2\text{O}_{ad} & \rightarrow \text{TiO}_2 + \cdot\text{OH}_{ad} + \text{H} \quad (2) \\
\text{TiO}_2 (h_{VB}^-) + \cdot\text{OH}_{ad} & \rightarrow \text{TiO}_2 + \cdot\text{OH} \quad (3) \\
\text{TiO}_2 (e_{CB}^-) + \text{O}_2 & \rightarrow \text{TiO}_2 + \text{O}_2^- \quad (4) \\
\text{O}_2^- + \text{H}^+ & \rightarrow \text{HO}_2^- \quad (5) \\
\text{O}_2^- + \text{H}_2\text{O}_2 & \rightarrow \cdot\text{OH} + \text{O}_2 + \text{H}_2\text{O}_2 \quad (6) \\
2\text{HO}_2^- & \rightarrow \text{O}_2 + \text{H}_2\text{O}_2 \quad (7) \\
\text{TiO}_2 (e_{CB}^-) + \text{H}_2\text{O}_2 & \rightarrow \text{TiO}_2 + \cdot\text{OH} + \cdot\text{OH} \quad (8)
\end{align*}
\]

Furthermore, other ROS species (such as singlet oxygen and hydrogen peroxide) also play a pivotal role in the sterilization, as they can actively participate in the oxidation of cellular components, membrane leakage of the microbial cell wall, and other processes.\textsuperscript{23} As shown in Fig. 3, the full mechanism was
clearly exhibited. Other various types of metal oxide and metal modified TiO$_2$ were also displayed, such as the following example consisting of Ag$^+$ as the M$^{II}$ species.$^{23}$ Firstly, TiO$_2$ based photocatalysts were mixed with bacteria, and then could be adsorbed onto the surface of cell membranes. After irradiation by sunlight, the ROS/M$^{II}$ would start to attack cells, the cell membranes were destroyed and were finally deactivated.$^{23}$

### 2.3 Photocatalytic disinfection of modified TiO$_2$ materials

In addition to the application of pure TiO$_2$ nanoparticles in sterilization, other modified TiO$_2$ materials and TiO$_2$ nanocomposites have been extensively investigated. Trapalis et al.$^{24}$ studied the bactericidal activity against *Escherichia coli* of Fe$^{III}$ doped TiO$_2$ thin films on glass substrate. Saylkan et al.$^{25}$ prepared Sn$^{IV}$ doped TiO$_2$ (TiO$_2$-Sn$^{IV}$) particulates by a hydrothermal process. TiO$_2$-Sn$^{IV}$ was coated onto glass surfaces to investigate the photocatalytic antibacterial effect of Sn$^{IV}$ doping to TiO$_2$ against Gram negative *Escherichia coli* (E. coli) and Gram positive *Staphylococcus aureus* (S. aureus). Fig. 4(a) elaborately shows the preparation steps of TiO$_2$-Sn$^{IV}$ particulates. Prior to preparing the coating solution, TiO$_2$-Sn$^{IV}$ sols composed of a large number of TiO$_2$-Sn$^{IV}$ particulates were prepared by dispersing the particles into deionized water in the absence of dispersant. Then the mixture was merely treated in an ultrasonic bath for a few minutes, thus the transparent TiO$_2$-Sn$^{IV}$ sols were obtained. The bacterial test results for *Escherichia coli* are shown in Fig. 4(b). It could be clearly seen that 50% (w/w) TiO$_2$-Sn$^{IV}$ exhibited the optimal antibacterial effect.

Furthermore, Wu et al.$^{26}$ synthesized a photocatalyst called PdO/TiON composed of palladium oxide and nitrogen-doped titanium oxide using a sol-gel process. Moreover, the photocatalytic activity of the PdO/TiON catalyst was investigated by using different bacterial indicators, including Gram-negative cells of *Escherichia coli* and *Pseudomonas aeruginosa*, and Gram-positive cells of *Staphylococcus aureus*. In 2010, Karunakaran et al.$^{27}$ reported the highly efficient photocatalytic disinfection of bacteria using Cu-doped TiO$_2$ under visible light for the first time. Additionally, a TiO$_2$-NiFe$_2$O$_4$ photocatalyst was synthesized by Misra.$^{28}$ In this work, the reverse micelle and chemical hydrolysis techniques had been successfully combined to synthesize composite nanoparticles consisting of a photocatalytic shell of titania and a magnetic core of nickel ferrite. Fig. 5(a) shows the TEM and HRTEM images of anatase and brookite titania-coated NiFe$_2$O$_4$ nanoparticles. Fig. 5(b) presents the degradation efficiency of methyl orange under UV light.

Misra and his co-workers$^{29}$ introduced Nd$^{3+}$ dopant into the TiO$_2$ shell of titania-coated nickel ferrite composite nanoparticles. As a result, the as-prepared catalyst could significantly enhance the photocatalytic degradation of methyl orange and the anti-microbial performance, which was attributed to the restriction of electron–hole recombination and the decrease of the titania band gap energy. Moreover, the retention of magnetic strength ensured that the movement of the composite nanoparticles could be controlled by a magnetic field, facilitating their application as removable anti-microbial photocatalyst nanoparticles. Fig. 6(a) shows the HRTEM image of the TiO$_2$–NiFe$_2$O$_4$ composite. The NiFe$_2$O$_4$ magnetic core is 4–6 nm and the TiO$_2$ shell is 2–3 nm, whereas the HRTEM image of Nd$^{3+}$-doped TiO$_2$-coated NiFe$_2$O$_4$ nanoparticles is shown in Fig. 6(c). The NiFe$_2$O$_4$ magnetic core is 8–10 nm and the TiO$_2$ shell is 2–3 nm. The specific degradation performance of methyl
orange and *E. coli* bacterial inactivation activity are exhibited in Fig. 6(b) and (d).

Similarly, Nardi *et al.* investigated functionally graded epoxy composites with various concentration profiles of Fe$_3$O$_4$@TiO$_2$ core–shell nanoparticles (NPs), and focused on their antibacterial properties. It was revealed that the composite surfaces showed effective antibacterial performance but were inactivated in a few hours, which was attributed to the suitable amount of NPs and their anisotropic distribution in the subsurface layers facing the bacteria.

In the above section, we have reviewed the disinfection ability of pure TiO$_2$ and modified TiO$_2$ nanomaterials, accompanied by the disinfection mechanism. It is well known that hydroxyl radicals are primarily responsible for this disinfection property. Besides, other reactive oxygen species (ROS, such as singlet oxygen and hydrogen peroxide) also play a pivotal role in sterilization. What's more, on one hand, one of the obstacles in employing TiO$_2$ nanomaterials for industrial use is the recycling problem due to the small particle size. On the other hand, the light utilization efficiency of TiO$_2$ was mainly restricted to the UV region, which restrains the application in practical photocatalytic disinfection of contaminated water. Thus, to some extent, the modification of TiO$_2$ nanomaterials, such as non-metal and metal doping, compounded with other semiconductors, is beneficial for fully utilizing solar light.

### 3 Photocatalytic sterilization of carbon materials

Apart from the conventional photocatalysts of metal oxide semiconductors, carbon based semiconductors, such as g-C$_3$N$_4$, have been well considered to be highly efficient visible-light-driven photocatalysts in recent years. g-C$_3$N$_4$ is a semiconductor material with a narrow band gap and is equipped with visible light response, which can increase the separation efficiency of photogenerated electron–hole pairs. Thus, g-C$_3$N$_4$ has been used to modify TiO$_2$ for improving its photocatalytic performance. For instance, Tian *et al.* prepared g-C$_3$N$_4$/TiO$_2$ composite photocatalysts, which were applied to enhance the sterilization performance of fluorocarbon resin (PEVE) coatings. The g-C$_3$N$_4$ was prepared using melamine thermolysis as shown in Fig. 7. The antibacterial activity of coatings under UV and visible light were also investigated. The sterilization performance of the PEVE composite coatings was enhanced by the addition of TiO$_2$ and g-C$_3$N$_4$/TiO$_2$ under UV and visible-light irradiation.

What's more, in 2016, Bi$_2$MoO$_6$/g-C$_3$N$_4$ heterojunctions were fabricated using an *in situ* solvothermal method via using g-C$_3$N$_4$ nanosheets as precursors by Li *et al.* The photocatalytic activities were tested with hydrogen evolution from water splitting and disinfection of bacteria under visible light irradiation. The results indicated that exfoliating bulk g-C$_3$N$_4$ to g-C$_3$N$_4$ nanosheets greatly enlarged the specific surface area and shortened the diffusion distance for photogenerated charges, which could not only promote the photocatalytic performance but also benefit the efficient interaction between Bi$_2$MoO$_6$ and g-C$_3$N$_4$ nanosheets.

Zhu's group prepared a porous g-C$_3$N$_4$ nanosheet (PCNS) photocatalyst with a thickness of 2.0 nm using a simple two-step template-free approach without the addition of extra reagents. In comparison with the bulk g-C$_3$N$_4$ (BCN), PCNSs possess more surface reactive sites, which obviously improve the charge transfer efficiency, and thereby accelerates the separation of photogenerated electron–hole pairs. As a result, the visible-light-driven photocatalytic disinfection performance of the PCNSs was significantly enhanced. *Escherichia coli* (E. coli) cells were inactivated within 30 min under visible light irradiation.
could be killed completely by PCNSs within 4 h, whereas only 77.1% of them could be killed by BCN. Fig. 9 clearly illustrates the disinfection of porous g-C3N4 nanosheets (PCNS) and the TEM images of *E. coli* cells after disinfection for 4 h by using PCNS.

Besides g-C3N4, other carbon based antibacterial nanomaterials, including carbon nanotubes (CNTs) and graphene oxide (GO), are always renewable, easier to obtain and cheaper than silver materials and metal oxides.55 CNTs are the type of carbon nanomaterials with a hollow structure and large surface area. However, CNTs have been found to be cytotoxic recently.36,37 Fortunately, graphene, another type of carbon nanomaterial, and its derivatives have high antibacterial activity due to physical damage that occurs upon direct contact of bacterial membranes with sharp edges of the graphene sheets; however, the improved oxidative stress induced by graphene-based materials can lead to the apoptosis of mammalian cells.38 Bao et al.39 successfully fabricated GO nanosheets, which were impregnated with silver nanoparticles (Ag NPs) via the *in situ* reduction of adsorbed Ag⁺ by hydroquinone (HQ) in a citrate buffer solution. The Ag NP/GO composites performed efficiently in decreasing the count of *E. coli* from 10⁶ CFU mL⁻¹ to 0 with 45 mg L⁻¹ GO in water.

A possible mechanism proposed for the GO nanosheet mediated Ag deposition process is schematically illustrated in Fig. 10(a). The Ag NPs are homogeneously assembled on the micron scale GO (Fig. 10(b)). To check the antibacterial effect in aquatic media, GO and composite suspensions were added into bacteria-containing water, respectively. In Fig. 10(c and d), as to the GO samples, no obvious antibacterial effect was observed, whereas the bacteria cells of *E. coli* or *S. aureus* were reduced greatly in the presence of the composites.

More importantly, as a common medical reagent, H₂O₂ is widely used in wound disinfection to avoid bacterial infection. Nevertheless, the disinfection ability of H₂O₂ is lower than that of hydroxyl radicals, so a high concentration of H₂O₂ is needed to solve this problem.40 Graphene quantum dots (GQDs) are defined as a kind of 0D material, and possess characteristics derived from both graphene and carbon dots (CDs).41 Simultaneously, GQDs display a higher peroxidase-like activity than graphene due to their excellent electron transportation properties.42,43 Sun et al.44 reported an antibacterial system combining the “safe” carbon based nanomaterials of GQDs with a low level of H₂O₂. All the experimental data in vitro showed that this intrinsic activity realized a high enhancement of the antibacterial activity of H₂O₂, and the particular system
TiO2 materials were modified for photocatalytic sterilization. Commonly, the most used TiO2 are commonly operated under visible light or UV light. E. coli and G. lamblia were sterilized by TiO2 in less time to achieve high efficiency under UV light. A review is made of a variety of catalysts will be the focus of research.

Table 1 Comparison of various photocatalysts for disinfection

| Bacteria          | Concentration | Photocatalyst     | Duration | Light source | Ref. |
|-------------------|---------------|-------------------|----------|--------------|------|
| E. coli           | ~10^6 CFU mL^-1 | TiO2 (anatase)    | 120 min  | UV light     | 19   |
| G. lamblia        | 8.55 x 10^4 CFU mL^-1 | TiO2 film (anatase) | 60 min  | UV light     | 20   |
| S. aureus         | 8.55 x 10^4 CFU mL^-1 | TiO2 (anatase)    | 20 min   | Visible light | 21   |
| E. coli           | 10^6 CFU mL^-1   | Fe^{3+}-doped TiO2 | 4 h      | UV light     | 24   |
| E. coli, S. aureus| 10^6 CFU mL^-1   | Sn^{2+}-doped TiO2 | 10 h     | UV light     | 25   |
| E. coli           | 10^6 CFU mL^-1   | Nd^{3+}-doped TiO2 | 150 min  | UV light     | 29   |
| E. coli           | 2.5 x 10^7 CFU mL^-1 | Bi_2MoO_6/g-C_3N_4 | 5 h      | Visible light | 33   |
| E. coli           | 5.0 x 10^6 CFU mL^-1 | g-C_3N_4 nanosheets | 4 h      | Visible light | 34   |
| E. coli           | 10^6 CFU mL^-1   | Ag NP/GO sheets   | 24 h     | Visible light | 39   |
| E. coli           | 10^6 CFU mL^-1   | Graphene quantum dots | 48 h   | Dark         | 44   |

In this section, we have reviewed novel carbon materials, such as g-C_3N_4, carbon materials and graphene. These materials can act as independent materials or excellent supporting materials in disinfection. In combination with the present trend, 2D transition metal materials may possess similar or more excellent ability in photocatalytic sterilization, owing to the large surface area and excellent utilization of light. Although photocatalytic sterilization has made great progress in recent years, one of the main obstacles to bringing photocatalytic water disinfection into practical application is photocatalyst recycling and photocatalytic reactor design. This is because most of the synthesized photocatalysts are in powder form, which is difficult to be reused and recycled in industry. Additionally, the light utilization of semiconductor photocatalysts in water is very limited, leading to low efficiency of disinfection rate. All of these problems greatly limit the possibility of practical application of photocatalytic sterilization in the future. Regarding this, future research direction may focus on the synthesis of photocatalytic membranes, magnetic photocatalysts and three-dimensional catalysts that can be easily recycled. Moreover, it is imperative to develop other coupling techniques with the photocatalytic method, such as Advanced Oxidation Processes (AOPs), including Fenton, Fenton-like and photo-Fenton processes and peroxydisulfate (PMS) activation etc. Therefore, improving the dispersion of the semiconductor photocatalysts in water and the utilization of light, and the development of the coupling techniques based on the combination of photocatalysis and other sterilization technologies such as adsorption or AOPs are major research areas that need to be further investigated.

4 Conclusions and outlook

In summary, since the discovery of the application of TiO2 in photocatalytic sterilization, scientists around the world have made many efforts to develop huge amounts of nanomaterials, which are commonly operated under visible light or UV light irradiation for photocatalytic sterilization. Commonly, the most widely used photocatalyst is still TiO2. In addition, after several years of development, some novel carbon based photocatalytic nanomaterials emerged, such as g-C_3N_4, carbon materials and graphene. These materials can act as independent materials or excellent supporting materials in disinfection. In combination with the present trend, 2D transition metal materials may possess similar or more excellent ability in photocatalytic sterilization, owing to the large surface area and excellent utilization of light. Although photocatalytic sterilization has made great progress in recent years, one of the main obstacles to bringing photocatalytic water disinfection into practical application is photocatalyst recycling and photocatalytic reactor design. This is because most of the synthesized photocatalysts are in powder form, which is difficult to be reused and recycled in industry. Additionally, the light utilization of semiconductor photocatalysts in water is very limited, leading to low efficiency of disinfection rate. All of these problems greatly limit the possibility of practical application of photocatalytic sterilization in the future. Regarding this, future research direction may focus on the synthesis of photocatalytic membranes, magnetic photocatalysts and three-dimensional catalysts that can be easily recycled. Moreover, it is imperative to develop other coupling techniques with the photocatalytic method, such as Advanced Oxidation Processes (AOPs), including Fenton, Fenton-like and photo-Fenton processes and peroxydisulfate (PMS) activation etc. Therefore, improving the dispersion of the semiconductor photocatalysts in water and the utilization of light, and the development of the coupling techniques based on the combination of photocatalysis and other sterilization technologies such as adsorption or AOPs are major research areas that need to be further investigated.

Conflicts of interest

There are no conflicts to declare.

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