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REVIEW PAPER

Developments in photocatalytic antibacterial activity of nano TiO_2: A review

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Abstract−TiO_2, which is one of the most explored materials, has emerged as an excellent photocatalyst material for environmental and energy fields, including air and water purification, self-cleaning surfaces, antibacterial and water splitting. This review summarizes recent research developments of TiO_2-based photocatalyst used for photocatalytic antibacterial applications. Several strategies to enhance the efficiency of TiO_2 photocatalyst are discussed, including doping with metal ions, noble metals, non-metals, and coupling with other materials. The mechanism of photocatalytic antibacterial activity in the presence of nano-sized TiO_2 is also discussed. The modified TiO_2 photocatalyst significantly inhibits the growth of bacterial cells in response to visible light illumination. TiO_2 photocatalysis appears to be promising as a route of advanced oxidation process for environmental remediation.

Keywords: Antibacterial, TiO_2, Photocatalysis, Bacteria, Photocatalytic Disinfection

INTRODUCTION

Bacterial contamination has become a crucial problem due to causing many infections in food storage, medical implants, hospital settings, biosensors and public health events [1]. There is an increasing awareness of human health and diseases and techniques in which we control microbes from affecting the safety and compromising the health of individuals [2]. Traditional techniques of manual cleaning with wiping are not effective in the longer term, cannot be standardized, and are time-consuming and staff intensive. Moreover, there are several problems associated with the use of aggressive compounds [3]. However, wiping every surface with these antibacterial agents develops an environment where the resistant bacteria survive [4].

Antibacterial agents are used extensively in hospitals and other public areas. A variety of biocide organic or metallic biocides has been used for mold inhibition are only operative for short-term and can themselves be toxic [5]. Some antimicrobial agents are very irritating and harmful, and recent investigations are targeted toward formulating new types of safe and inexpensive biocidal materials [6]. The development of simple, low-cost and more effective antibacterial methods is very important, because, in recent years, damage caused by harmful microorganisms has become a serious social problem, as demonstrated repeatedly by the occurrence of *Legionella* infections in full-time baths, food poisoning caused by *Staphylococcus aureus* (*S. aureus*), and hospital infections caused by medicine-resistant bacteria such as *Methicillin-Resistant S. aureus* (MRSA) are more common in hospital environments. Surfaces act as reservoirs of microorganisms which could, in turn, lead to the spread of microbial infections [7]. Particularly in areas of intensive medical use, regular and thorough disinfection of surface is required in order to reduce the number of bacteria and to prevent bacterial transmission [3].

The applications of the nano-sized TiO_2 photocatalytic process is a conceptually simple and promising technology to inhibit bacterial contamination. Titanium dioxide exists in three crystalline phases, anatase, rutile, and brookite [8]. The most common are anatase and rutile as brookite is less stable. In the crystal structure of TiO_2, each Ti^{4+} ion is surrounded by an octahedron of six oxygen (O^{2-}) ions, while each oxygen atom by three titanium atoms. The octahedron in rutile is irregular, showing a slight orthorhombic distortion. The octahedron in anatase is significantly distorted so that its symmetry is lower than orthorhombic. The structures of anatase and rutile crystals have been demonstrated generally in terms of chains of TiO_6 octahedra having common edges. In the rutile structure, each octahedron is in contact with ten neighbor octahedrons (two sharing edge oxygen pairs and eight sharing corner oxygen atoms); while in the anatase structure, each octahedron is in contact with eight neighbors (four sharing an edge and four sharing a corner) and in brookite both edges and corners are shared to give an orthorhombic structure [8]. In view of the three major polymorphs of TiO_2, the rutile TiO_2 is the most comprehensively explored in fundamental studies, and anatase is the most widely investigated phase in the applied studies, which plays a central role in many industrial applications [9]. Anatase type TiO_2 is considered as the most photoactive phase and extensively applied semiconducting material for environmental applications [10].

Since the discovery of the "Honda-Fujishima effect" [11] TiO_2 has proved to be one of the most efficient material for environmental remediation because of its various desirable properties. Disinfection of a surface by photochemical transformations on TiO_2 is a suitable possible alternative to using chemical disinfectants such as chlorine bleach, because it avoids the use of chemicals for which there are currently concerns about possible toxicity and mutagene-

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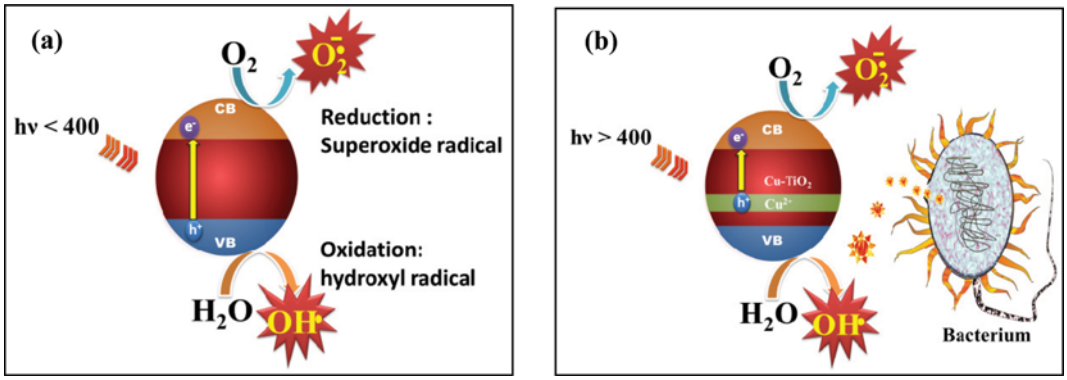

Fig. 1. Schematic diagram of (a) The ultraviolet (UV)-responsive TiO_2 photocatalytic reaction, (b) the visible light responsive Cu-TiO_2 photo-killing mechanism [19].

sis [12-14]. Subsequently, scientists and engineers are involved in developing alternative antibacterial techniques. In recent years, immobilized TiO_2 has been utilized as a self-cleaning and disinfectant material for coating many clinical tools including sanitary ware, food packaging, tableware, building materials and medical devices. In 1985, Matsunaga et al. first demonstrated the photocatalytically killing mechanism for the microbial cells of *Saccharomyces cerevisiae* (yeast), *Lactobacillus acidophilus* and *Escherichia coli* (bacteria), and *Chlorella vulgaris* (green algae) in water using a Pt-TiO_2 photocatalyst [15]. Since then, much research has been performed on the photocatalytic antimicrobial performance of nano-sized TiO_2. With energy provided larger than the band gap of TiO_2, the electron (e^-)/hole (h^+) pairs are generated and react with O_2 and H_2O to form superoxide anion radicals (O_2^-) and hydroxyl radicals (·OH). These oxidative species (h^+, ·OH, and O_2^-) are all extremely reactive, which are considered to be the dominant oxidative species contributing to the destruction of microorganism cells [10]. However, the bare TiO_2 photocatalyst can be activated by ultraviolet light irradiation due to its wide band gap energy of 3.2 eV. Recent research has identified the chemically modified TiO_2-based photocatalysts, which work under visible and UV light illumination, offering the potential to extend their application in photocatalytic disinfection.

Several reviews have been published on the photocatalytic performance of TiO_2 over the past years that mainly discuss properties of TiO_2 [16], photocatalytic water splitting technology [17], and photodegradation of organic compounds [18]. However, hardly any attention has been paid to photocatalytic antibacterial properties of modified TiO_2-based photocatalysts.

The present review considers the recent progress of the photocatalytic efficiency of modified TiO_2 and demonstrates their potential applications in the biomedical and environmental field. This review emphasizes the photocatalytic antibacterial performance of modified TiO_2, doping TiO_2 with metal ions and non-metals, and coupling TiO_2 with other materials. We believe that this comprehensive review on TiO_2-based photocatalytic antibacterial materials would help to promote TiO_2-based photocatalysts research for the development of alternative disinfection technology. TiO_2-based photocatalyst technology is a very promising as it is, highly stable, low cost, and environmentally benign.

MECHANISM OF PHOTOCATALYSIS

In photocatalysis, a semiconductor material interacts with light of sufficient energy to generate reactive oxygen species (ROS), which are responsible for photochemical transformations. Traditional TiO_2 photocatalyst shows activity under UV light only. In photocatalysis, the light of energy greater than the bandgap of the semiconductor excites an electron from the valence band to the conduction band, creating a pair of a negatively charged free electrons and a positively charged electron hole. The electrons are then free to migrate within the conduction band and the holes may be filled by an electron from an adjacent molecule. This process can be repeated. Thus, holes are also mobile. The electrons and holes generated by the reactions have strong reducing and oxidizing power. Electrons and holes may recombine (bulk recombination) a non-productive reaction, or, when they reach the surface, react to give reactive oxygen species (ROS) such as O_2^- and ·OH (Fig. 1(a)). These in solution can react to give H_2O_2, further hydroxyl, and hydroperoxyl radicals. The reaction of these ROS with organic compounds results in the mineralization.

$$TiO_2+h\nu \rightarrow TiO_2\ (e_{cb}^- + h_{vb}^+) \quad (1)$$

$$O_2+e_{cb}^- \rightarrow O_2^{\cdot-} \quad (2)$$

$$H_2O+h_{vb}^+ \rightarrow \bullet OH+H^+ \quad (3)$$

$$\bullet OH+\bullet OH \rightarrow H_2O_2 \quad (4)$$

$$O_2^{\cdot-}+H_2O_2 \rightarrow \bullet OH+OH^-+O_2 \quad (5)$$

$$\bullet OH+Organic+O_2 \rightarrow CO_2+H_2O \quad (6)$$

The preponderance of evidence on photocatalytic chemistry in aqueous solution suggests that the hydroxyl radical generated by hole transfer does not diffuse from the surface of the TiO_2 into bulk aqueous phase [20]. ROS are extremely reactive when in contact with microbes; therefore, microorganisms in air and water can be destroyed when they come into contact with the surfaces of a photocatalyst. This also provides a promising strategy for the degradation of environmental pollutants [10]. Photocatalysis has been shown to be capable of killing a wide range of organisms, including Gram-negative and Gram-positive bacteria, including endospores,

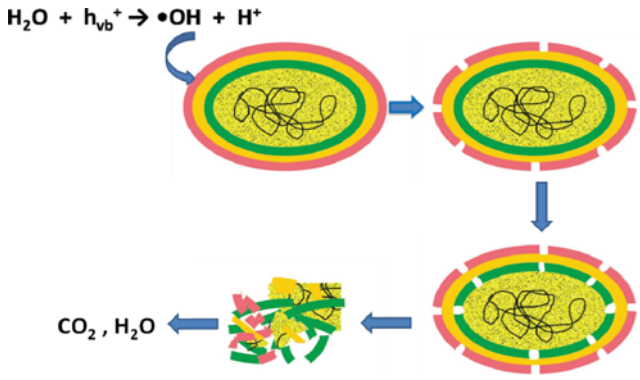

Fig. 2. Proposed bactericidal mechanism in the presence of TiO_2 photocatalyst.

fungi, algae protozoa and viruses [21]. The hydroxyl radical is an extremely aggressive oxidant, and as such, it can attack various biological molecules and impair their proper functioning (Fig. 1(b)).

Different mechanisms of killing have been proposed, including (a) the killing mechanism implies an oxidation of the intracellular coenzyme A (CoA), which inhibits cell respiration and subsequently causes cell death as a result of a direct contact between TiO_2 and target cell, leading to cell death [22]; and (b) bacterial death is caused by a significant disorder in the cell permeability and decomposition of the cell walls [23]. It is suggested that cell wall damage might take place prior to cytoplasmic membrane damage. Fig. 2 shows a proposed mechanism for the photocatalytic bactericidal effects. During the photooxidation process, the UV light irradiation also causes cell damage. Oguma et al. [23] reported that long wavelength UV light (i.e., 320-400 nm) mainly damages microorganisms by exciting photosensitive molecules within the cell, and the generated ROS adversely affect the genome and other intracellular molecules sub-lethally or lethally causing cell mutations, growth delay. Sunada et al. [24] reported cell membrane damage due to the photocatalytic degradation of endotoxin from *Escherichia coli* (*E. coli*) with TiO_2 thin films. Another study by Maness et al. [25] showed the photo-oxidation of bacterial cell components responsible for cell death. Damage to the cell membrane directly leads to leakage of minerals, proteins, and genetic materials, causing cell death. Keller et al. [26] disputed that many parameters were acting significantly at the biological level and not taken into account for chemicals. Gogniat et al. [27] showed that the rate of adsorption of cells onto TiO_2 is positively correlated with its bactericidal effect. The adsorption was consistently associated with a reduction bacterial membrane integrity, as revealed by flow cytometry. They suggested that adsorption of cells onto aggregated TiO_2, followed by loss of membrane integrity, was key to the bactericidal effect of photocatalysis.

STRATEGIES FOR IMPROVING TiO_2 PHOTOACTIVITY

Different approaches have been adopted for improving TiO_2 photocatalytic efficiency, all of them consisting of either morphological modifications, such as increasing surface area and porosity, or the incorporation of additional components, such as metals or a second semiconductor phase. However, contradictory reports are available in the literature devoted to TiO_2 improvement, very likely because changing composition or morphology unavoidably modifies other parameters which also affects efficiency. The major drawback in the semiconductor photocatalysis is the recombination of photogenerated charge carriers as it lowers the activity [28]. To increase photocatalytic activity, various strategies have been adopted, including doping with metals, non-metals and heterojunction coupling, which can narrow the electronic properties and, thus, alter the optical properties of TiO_2. For making visible light driven photocatalyst and retard possible electron-hole recombination, doping of TiO_2 with transition metal ions is one of the most successful strategies. Potential applicability of TiO_2 photocatalyst is prevented by its wide band gap, which lies in the UV light region.

1. Metal Doping

Transition metal ions can provide additional energy levels within the band gap of a semiconductor. Electron transfer from one of these levels to the conduction band requires lower photon energy than in the situation of an unmodified semiconductor [29]. TiO_2 has been doped with many different transition metals for visible light photocatalytic activity, but very few reports are available on visible light antibacterial activity (Table 2). Metal-doping of TiO_2 has been extensively explored as a way to improve photoactivity under visible light [30]. Nevertheless, foreign cations frequently act as recombination centers and, therefore, significant improvements are only possible at low concentration of dopants, and using careful synthesis methods to limit lattice distortion. Optimum composition metal ion dopant in TiO_2 extends visible light absorption due to decrease in the band gap values (Table 1). The development of copper-modified photocatalysts with antibacterial capacities in the dark and enhanced photocatalytic activities under light conditions has been reported in a number of studies, and may present a low-cost alternative to noble metal based biocidal photocatalysts. As part of a study to investigate the effect of metal ion doping in TiO_2 nanoparticles, our group has recently reported superior visible-light-induced photocatalytic activities of copper, nickel and iron-doped TiO_2 nanoparticles towards *E. coli* and *S. aureus* bacterium [19,31,32]. Sayilkan et al. evaluated the antibacterial activity of hydrothermally synthesized Sn^{4+} ion doped TiO_2 thin films against *E. coli* and *S. aureus* in the presence of weak UV light [33].

To enhance photoactivity, TiO_2 doped with metal ions can im-

Table 1. Metal ion dopant concentration and band gap values

Dopant concentration	Band gap value (eV)	Ref.
Bare TiO_2	3.23	[36]
V (3.0-13.0)	2.84-2.56	[37]
Fe (0.5-1.0 mol%)	3.03-3.02	[38]
Fe (1.0-3.0 mol%)	3.02-2.72	[32]
Co (5.0 wt%)	--	[39]
Ni (1.0-3.0 mol%)	2.95-2.36	[31]
Cu (2.0 wt%)	2.83	[40]
Cu (1.0-3.0 mol%)	2.89-2.60	[19]
Sn (10-50 wt%)	3.32-2.28	[33]

prove the trapping-to-recombination rate ratio. However, when metal ions are incorporated into TiO_2 host lattice, the impurity energy levels formed in the band gap of TiO_2 can also lead to decrease the rate of recombination between photogenerated charge carriers. When the trapped electron and hole are transferred to the surface of the photocatalyst, then photocatalytic reactions occur and for this, metal ions should be doped near the surface of the photocatalyst to allow efficient charge transfer. Not all metal-doped TiO_2 photocatalyst will exhibit positive effects. The dopant content directly influences the rate of e^-/h^+ recombination [34]; there is an optimum concentration of dopant ions where the thickness of the space-charge layer is similar to the depth of light penetration. Xin et al. [35] reported enhanced photocatalytic activity of TiO_2 at low doping content of Fe^{3+} (Fe/Ti≤0.03 mol%) and decreased photocatalytic activity at higher content.

2. Noble Metal Loading

The addition of noble metals is another approach for the modifying photocatalysts. Active antimicrobial noble metals (silver, gold, platinum) were incorporated in TiO_2 photocatalyst to enhance the bactericidal activity (Table 2). Because the Fermi levels of these noble metals are lower than that of TiO_2, photo-excited electrons can be transferred from the conduction band of TiO_2 to metal particles deposited on the surface of TiO_2, while photogenerated holes in the valence band remain on TiO_2. This greatly reduces the possibility of electron-hole recombination, resulting in efficient separation and higher photocatalytic activity [29].

Caballero et al. reported antibacterial activity of TiO_2 commercial powders doped with Pt against *E. coli* under fluorescent light irradiation. Platinum doped TiO_2 photocatalyst showed excellent bactericidal activity due to the effective distribution of the TiO_2 nanoparticles and the better charge separation in the doped semiconductor photocatalyst [41].

Silver-modified TiO_2 photocatalyst materials have been extensively studied in the past decades [42-44]. Silver is a well-known antibacterial agent in the absence of light. The mode of bactericidal action has been proposed to be due to the sorption of silver ions onto the negatively charged bacterial cell wall, causing deactivation of cellular enzymes, disruption of the permeability of the membrane, and causing eventual cell lysis and death [45-47]. In the case of noble metal modified TiO_2 photocatalyst, the role of interfacial charge transfer between noble metal and TiO_2 is emphasized as a photocatalysis-enhancing mechanism, which may contribute to photocatalytic inactivation in addition to the antibacterial and oligodynamic effects of the incorporated noble metals.

Armelao et al. prepared TiO_2 and Au/TiO_2 nanosystems using a hybrid RF-sputtering/sol-gel approach and tested photocatalytic antibacterial activity against *B. subtilis*. They claimed that an increase in the annealing temperature enhances the antibacterial properties of both TiO_2 and Au/TiO_2 systems [48]. In another study, Li et al. reported that the gold nanoparticles modified TiO_2 nanotubes can potently destroy *S. aureus* and *E. coli* in darkness. The authors proposed an antibacterial mechanism from the perspective of localized surface plasmon resonance of Au nanoparticles, respiratory electrons of bacterial membrane transfer to Au nanoparticles and then to TiO_2, which makes bacteria steadily lose electrons until death [49].

3. Non-metal Doping

Among the many chemical modifications adopted for shifting the TiO_2 band gap to lower energy, currently the most promising route seems to be the partial substitution of oxygen with non-metals (N, C, and S). Extensive research on a non-metal doping technique for enhancement of bactericidal activity of TiO_2 has been reported (Table 2). In particular, most of the studies have focused on non-metal doped TiO_2, which shows remarkable photoactivity under visible light illumination. Doping of non-metal ions (N, C, S etc.) in TiO_2 host lattice could shift its photoresponse in the visible region [50-53]. Asahi et al. reported theoretical calculations for the narrowing band structure of nitrogen-doped TiO_2 [54]. It was found that N atoms substituted the lattice oxygen sites responsible for narrowing the band gap by mixing the N2p and O2p states. Mei et al. studied the effect of material microstructure, the nature of paramagnetic radicals and the role of the calcination temperatures on the effective incorporation of nitrogen in the TiO_2 lattice [55]. The photocatalytic proprieties of N-TiO_2 under the visible light show a promising extension for environmental application because doping nitrogen into TiO_2 changes the refraction index, hardness, electrical conductivity, elastic modulus, and the photocatalytic activity of visible light absorption [56].

Pathakoti et al. [57] demonstrated the mechanisms of toxicity of sulfur-doped TiO_2, nitrogen-fluorine-codoped TiO_2 in a model organism *E. coli* after exposure to simulated solar light and visible light irradiation. They found that the sulfur-doped TiO_2 did not show enhancement in photocatalytic activity towards *E. coli* inactivation under visible light. On the other hand, Lee et al. found an excellent antibacterial activity for nanoporous C-TiO_2 and S-TiO_2 towards *E. coli* and *S. aureus* under visible light irradiation [58].

He et al. reported efficient photocatalytic activity under visible light against *E. coli* by N-doped TiO_2 prepared by sol-gel method [50]. Raut et al. [59] reported the synthesis of nanodot chains as well as self-aligned nano-platelets of N-doped TiO_2 thin film, by ultrasonic spray pyrolysis and their antimicrobial properties were studied at near UV, normal room light, and sunlight against *Pseudomonas aeruginosa*. A similar enhancement due to the presence of nitrogen in TiO_2 for the degradation of methylene blue and Gram-positive bacteria (*Bacillus amyloliquifacience*) was reported by Soni et al. [60,61]. Kajitvichyanukul et al. studied the antibacterial effects of Ni-doped and N-doped TiO_2 nanoparticles and found that the N-doped TiO_2 nanoparticles have more antibacterial activity than the Ni-doped TiO_2 [62]. Yu et al. tested visible light induced photocatalytic inactivation of *E. coli* in presence of N-TiO_2 nanopowders as well as nanofilms [63].

Similarly, carbon doping also shifts the band gap energy in the visible light region. Cheng et al. [64] reported the visible light activity of carbon containing TiO_2 against several human pathogens including *Staphylococcus aureus*, *Shigella flexneri*, and *Acinetobacter baumannii*. They also studied the interaction of photocatalyst with pathogens using scanning electron microscopy and confocal Raman spectroscopy techniques. A low temperature non-hydrothermal low power microwave synthesized carbon-doped anatase-brookite titania nano-heterojunction photocatalysts for *S. aureus* under visible light tested by Etacheri et al. [51]. They found that the interband C2p states were responsible for the band gap narrowing

of the carbon doped heterojunctions. They also proposed that the efficient electron-hole separation at the anatase-brookite interface is responsible for superior visible-light-induced photocatalytic and antibacterial activity of carbon-doped anatase-brookite nano-heterojunctions. More recently, Shim et al. [65] investigated microbial inactivation kinetics and mechanism of carbon-doped TiO_2 under visible light irradiation and found that the antibacterial activity was attributed to the release of ROS on the surface of the C-TiO_2.

4. Hybrid Nanocomposites

It is possible to create coupled colloidal structures, in which illumination of one semiconductor produces a response in the other semiconductor at the interface between them, and the semiconductor nanocomposite exhibits very high photocatalytic activity [66]. The geometry of particles, surface texture, and particle size play a significant role in interparticle electron transfer [29]. A ternary hybrid CdS/Pt-TiO_2 nanotube photoelectrode developed by dipping and deposition technique and ionic layer adsorption and reaction (SILAR) showed higher bactericidal activity for *E. coli* [67]. Hamal et al. [68] demonstrated that TiO_2 codoped with silver, carbon, and sulfur can serve as a multifunctional generic biocide as well as a visible light activated photocatalyst. It shows strong antimicrobial properties without light activation against both *E. coli* and *B. subtilis* spores. Several other nanocomposites of TiO_2 exhibited bactericidal activity in the dark (Table 2), indicating that undetermined mechanisms additional to photocatalytic ROS production were responsible for toxicity.

Since their discovery, carbon nanotubes (CNTs) have attracted great attention for their extraordinary mechanical, electrical, and optical properties. Akhavan et al. reported [69,70] sol-gel synthesis of CNT-doped TiO_2 thin films for visible light photoinactivation. For this, *E. coli* bacteria were irradiated by a 110 $mWcm^{-2}$ mercury lamp at room temperature. N-doped TiO_2 photocatalyst added polytetrafluoroethylene composite material was developed to remedy these shortcomings. This paper reports the surface characteristics, and the bactericidal and self-cleaning performance of the newly developed composite material [71]. Also, Chen et al. observed the excellent antibacterial activity of sol-gel synthesized MWCNT/TiO_2 composites with sunlight against *E. coli* [72].

Bacterial infection has been a major threat to ornamental fish in aquariums. Reducing the bacterial pathogen loading in water is an ecofriendly alternative to control fish disease. Yeh et al. [73] demonstrated a fish pathogen reduction procedure using TiO_2 sol-gel coating Fe_3O_4@TiO_2 powder on a glass substrate. After 3 h of visible light irradiation, the immobilized Fe_3O_4@TiO_2 inhibition efficiencies for fish bacterial pathogen were, respectively, 50% for *Edwardsiella tarda* (BCRC 10670) and 23% for *Aeromonas hydrophila* (BCRC 13018). Moreover, the authors reported the bactericidal effect of TiO_2/Fe_3O_4 towards marine fish pathogen under LED light irradiation [74].

Janpetch et al. demonstrated efficient antibacterial activity against *E. coli* and *S. aureus* bacterium under fluorescent light using the hybrid nanocomposite material of bacterial cellulose nanofibers and N-F-codoped TiO_2 nanoparticles [75].

The antimicrobial properties of apatite-coated TiO_2 cotton textiles were investigated by Kangwansupamonkon et al. [76]. The antibacterial performance was observed under black light, visible light, and dark conditions. Apatite-coated TiO_2 suspensions after black-light exposure demonstrated strong antimicrobial activity against four types of bacteria (*S. aureus*, *E. coli*, *S. aureus* (MRSA), and *M. luteus*) and at a higher extent as compared with visible light and dark conditions.

In another study, Chen et al. [77] tested the antibacterial performance of Cu/TiO_2/chitosan three-component nanoparticles. They reported that this hybrid material exhibits excellent antibacterial ability against *E. coli* and *S. aureus* due to the synergistic antibacterial effect of the Cu, TiO_2 and chitosan components in the nanoparticles.

Rana et al. [78] showed that the introduction Nd^{3+} dopant into the TiO_2 photocatalytic shell of TiO_2-coated nickel ferrite composite nanoparticles significantly enhances the photocatalytic antimicrobial performance. The increased performance was correlated to the inhibition of electron-hole recombination and a decrease in the band gap energy of TiO_2.

PHOTOCATALYTIC ACTION ON BACTERIA

Various studies involving the photo-killing effect on Gram-positive and Gram-negative bacterium by modified TiO_2 have been conducted (Table 2). The photocatalytic antibacterial performance of TiO_2 is mainly dependent on the structure of the bacterial cell wall. Many studies have been performed on various species, nevertheless; the results are too some extent contradictory. Some authors reported that Gram-positive bacteria were more sensitive to photocatalysts than Gram-negative [79-81]. Although, there is a large amount of research that demonstrated Gram-negative bacteria were more resistant to photocatalytic bactericidal activity than Gram-positive bacteria [32,82]. Gram-negative bacteria are relatively more resistant because of the nature of their cell wall, which restricts absorption of many molecules to movements through the cell membrane [19,82]. *Lactobacillus* was found to be more sensitive than *E. coli* on a Pt-doped TiO_2 photocatalyst [15].

The variance in photocatalytic inactivation of bacteria is typically attributed to the difference in cell wall structure between Gram-negative and Gram-positive bacteria (Fig. 3). Gram-negative bacteria have a triple-layer cell wall with an inner membrane, a thin peptidoglycan layer, and an outer membrane, whereas Gram-positive bacteria have a thicker peptidoglycan without an outer membrane. Also, this may relate to different affinities for photocatalyst and cell wall of bacteria. To achieve better photocatalytic inactivation, direct contact between bacteria and surface of TiO_2 is crucial, which will increase the probability of attack by ROS. From this, it can be concluded that the rate of photocatalytic antibacterial activity is governed not only by cell wall thickness but also by the morphology of cell envelope and resistance of the outer membrane to the ROS produced on the surface of photocatalyst [81].

Some fungi can persist in severely stressful conditions where bacteria cannot due to their stronger cell wall structure; fungi can survive at high osmotic pressures. Although, fungal diseases are not as widespread as those caused by bacteria [83]. However, some fungi, algae, and protozoa have been shown to be susceptible towards TiO_2 photocatalyst. The photocatalytic fungicidal activity on *Can-*

Table 2. Antibacterial activity with modified TiO_2 photocatalyst

Bacteria	Metal	Non-metal	Nobel	Composite	Activity in dark	Activity in light	Ref.
Gram-negative							
Aeromonas hydrophila (BCRC 13018)				Fe_3O_4/TiO_2	--	Yes	[73]
Edwardsiella tarda (BCRC 10670				Fe_3O_4/TiO_2	--	Yes	[73]
Escherichia coli (ATCC8739)			Pt-TiO_2		--	Yes	[41]
Escherichia coli	Fe-TiO_2				No	Yes	[32]
Escherichia coli			Ag-TiO_2		Yes	--	[49]
Escherichia coli				CNT-TiO_2	Yes	Yes	[70]
Escherichia coli				Apatite/TiO_2	Yes	Yes	[76]
Escherichia coli	Cu-TiO_2				Yes	Yes	[40]
Escherichia coli		N-TiO_2			No	Yes	[63]
Escherichia coli		S-TiO_2			--	Yes	[58]
Escherichia coli		S-TiO_2			Yes	Yes	[57]
Escherichia coli	Fe-TiO_2				--	Yes	[38]
Escherichia coli		N-TiO_2			No	Yes	[50]
Escherichia coli				MWCNT/TiO_2	Yes	Yes	[72]
Escherichia coli (8099)				Cu/TiO_2/C	Yes	--	[77]
Escherichia coli (ATCC 23282)	Sn-TiO_2				--	Yes	[33]
Escherichia coli (ATCC 25922)			Ag-TiO_2		--	Yes	[42]
Escherichia coli (DH 5R)	V-TiO_2			Au-TiO_2	No	Yes	[37]
Escherichia coli (DH5α)			Au-TiO_2		No	Yes	[43]
Escherichia coli (DH5α)			Ag-TiO_2		No	Yes	[43]
Escherichia coli (IFO 3301)				Cu/TiO_2	Yes	Yes	[24]
Escherichia coli (NBRC 3972)				N-TiO_2 : PTFE	No	Yes	[71]
Escherichia coli (NCIM 2066)	Cu-TiO_2				No	Yes	[19]
Escherichia colik-12 (ATCC 29181)				Nd^{3+}-$TiO_2/NiFe_2O_4$	--	Yes	[78]
Photobacterium damselae subsp. piscicida				TiO_2/Fe_3O_4	No	Yes	[74]
Salmonella typhimurium (KCCM 11862)	Co-TiO_2				Yes	--	[39]
Gram-positive							
Micrococcus luteus				Apatite/TiO_2	Yes	Yes	[76]
Micrococcus lylae		S-TiO_2			No	Yes	[53]
Staphylococcus aureus				Apatite/TiO_2	Yes	Yes	[76]
Staphylococcus aureus			Ag-TiO_2		Yes	--	[49]
Staphylococcus aureus		S-TiO_2			--	Yes	[58]
Staphylococcus aureus (MRSA)				N-TiO_2 : PTFE	No	Yes	[71]
Staphylococcus aureus (ATCC 6538)				Cu/TiO_2/C	Yes	--	[77]
Staphylococcus aureus (ATCC No 35696)	Sn-TiO_2				--	Yes	[33]
Staphylococcus aureus (MRSA)				Apatite/TiO_2	Yes	Yes	[76]
Staphylococcus aureus (NCIM 2654)	Cu-TiO_2				No	Yes	[19]
Staplylococcus aureus (KCCM 11256)	Co-TiO_2				Yes	--	[39]
Staphylococcus aureus			Ag-TiO_2		Yes	Yes	[44]
Bacillus subtilis				Au-TiO_2	No	Yes	[48]
Bacillus megaterium (QM B1551)	V-TiO_2			Au-TiO_2	No	Yes	[37]
Bacillus amyloliquifacience		N-TiO_2			No	Yes	[61]
Listeria monocytogenes		C-TiO_2			No	Yes	[65]

dida albicans (MTCC-1637), *Candida glabrata* (MTCC-3019), *Candida tropicalis* (MTCC-184), and *Candida parapsilosis* (MTCC-2509) has shown good resistance to pure TiO_2 as well as TiO_2 : Fe thin films, whereas *Candida glabrata* (MTCC-3019), showed less resistance [83,84].

Ochiai et al. [85] investigated the role of TiO_2-coated materials in the inactivation and removal of algae. They assessed the inhibition ability of the TiO_2-coated materials using *Anabaena flosaquae* and found that the fabric-supported Pd/TiO_2 showed high inhibition activity for algal growth. Some researchers studied photocata-

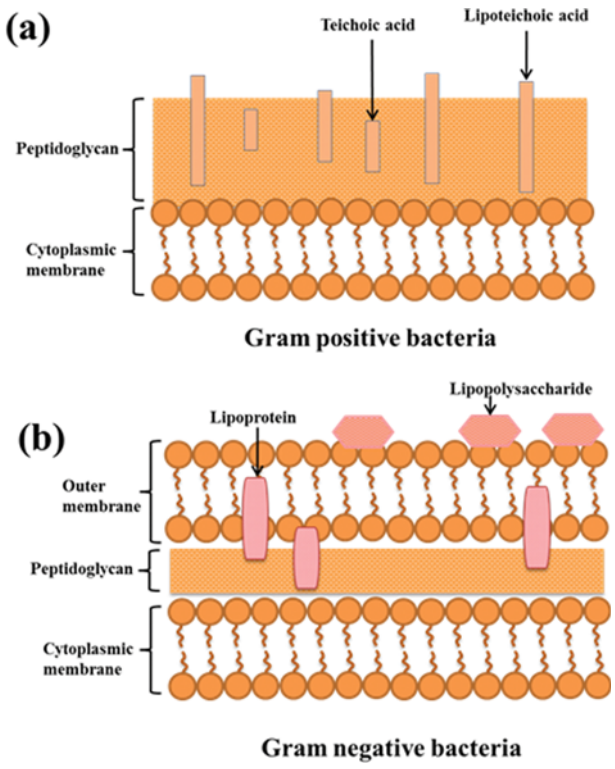

Fig. 3. Structures of the cell walls of different classes of microbial cells. (a) Gram-positive bacteria cell wall is composed of a thick, complex peptidoglycan sheath outside of the cytoplasmic membrane and composed of peptidoglycan, teichuronic acids, and lipoteichoic acids. (b) Gram-negative bacteria have a thin single layer of peptidoglycan and lipid bilayer containing lipopolysaccharide and providing a permeability barrier of small hydrophilic molecules across the membrane.

lytic inactivation of three species of algae including *Anabaena*, *Microcystis*, and *Melosira* using TiO_2 coated glass beads and UV-light irradiation. Complete photocatalytic inactivation of *Anabaena*, *Microcystis*, and *Melosirawas* was obtained in about 30 minutes, while the inactivation efficiency for *Melosira* was somewhat lower due to the inorganic siliceous wall surrounding the cells [86].

Gram-positive bacteria, Gram-negative bacteria, and green algae have cell walls of different composition. Matsunaga et al. [15] showed the *Chlorella vulgaris* has a thick cell wall mainly composed of polysaccharides and pectin, and 55% of *Chlorella vulgaris* retained viability when the organism was incubated for 120 min with TiO_2/Pt particles under metal halide lamp irradiation.

UV light-assisted photocatalytic disinfection is progressively used for drinking water treatment due to its effectiveness against cyst-forming protozoa such as *Giardia* and *Cryptosporidium* [87]. Still, some pathogenic viruses such as adenoviruses are highly resistant to UV disinfection system. An arrangement of photocatalyst and light source that offers additional inhibition mechanisms may be able to overcome this critical obstacle.

It was found that few naturally adapted bacteria species are tolerant to specific toxins or nanoparticles that exist in the environment. Cu-doped TiO_2 nanoparticles were able to inhibit the growth of *Mycobacterium smegmatis*, but had no effect against *Shewanella oneidensis* MR-1 [88]. This type of bacterium can be considered as a promising candidate for cleaning of metal oxide nanoparticles from the environment.

Several mechanisms have been reported for the photocatalytic antibacterial activity of modified TiO_2 nanoparticles, which generally depends on various parameters, such as particle size, surface area, crystal structure, pH of solution, catalyst concentration, composition, surface modification, light intensity, intrinsic properties and the bacterial species [32]. These reports specify that the mechanism of photocatalytic antibacterial activity of modified TiO_2 nanoparticles is very complex and depends on several parameters and is still only partially understood. However, modified TiO_2 nanoparticles are able to reduce the rate of photogenerated charge carriers and produce ROS under light irradiation, resulting in damage to bacterial cells. Thus, to achieve an appropriate photocatalytic antibacterial efficiency, it is very important to control the composition ratio in the modified TiO_2.

PHOTOCATALYTIC BACTERICIDAL APPLICATIONS OF TiO_2

TiO_2 is a semiconducting material; the electron-hole pairs can be generated upon irradiation with light may separate charge carriers and migrate to the surface where they react with water and oxygen to produce reactive oxygen species. These come in contact with organic molecules and can ultimately lead to complete mineralization [89,90]. The application of this process has a wide range: the purification of air, waste water, disinfection based on bactericidal properties for coating various materials such as wood, plastic, fabrics, papers, ceramics, sanitary wares, use of self-cleaning on a car windshield.

Supplying clean and inexpensive water to meet human needs is the grand challenge of the 21st century [91]. The extraordinary properties of TiO_2 are an ideal platform for constructing multifunctional materials which can be utilized to remove heavy metals and organic pollutants from contaminated water [92]. Upon light irradiation, modified TiO_2 photocatalysts can degrade organic contaminants and inactivate microorganisms. This helps reduce organic and biological fouling as well as remove contaminants. Photocatalytic water disinfection is a green technology and same materials can be used repeatedly. A variety of UV and visible-light-driven water disinfection systems have proven their effectiveness for treating polluted water [13,88,92-97].

The development of facile and reliable antibacterial materials and methods is very important because infection caused by harmful microorganisms has become a serious social problem. TiO_2 films many applications, particularly as photocatalytic coatings. Thus, TiO_2 coated materials such as wood [98,99], fabrics [5,100,101], medical devices [102], dental implants [103], building materials [99, 104], food packaging coating [105,106] plastic coating [106] are effective for controlling pathogenic infections.

FUTURE PROSPECTS OF NANO TiO_2 IN ANTIBACTERIAL

Visible light photocatalytic antibacterial activity appears to be a

promising and innovative approach for environmental and biomedical research and an alternative technique to inhibition bacterial growth. Since 1985, photocatalytic disinfection technology using TiO_2 has retained its importance in research because of the extraordinary physiochemical aspects of nano TiO_2, and its capability to mineralize pollutants as well as microorganisms. Nano TiO_2 possesses large surface area and small particle size and is useful in photocatalytic disinfection. Photogenerated ROS on the surface of TiO_2 is responsible for killing a wide range of organisms in water, in the air and on surfaces. Different modified TiO_2 based photocatalysts have been synthesized and found to be effective for the photocatalytic disinfection. The surface coating is another option for developing real systems, which is auspicious for the commercialization of the technology. The urge is to develop a standard protocol for the testing of the photocatalytic antimicrobial efficiency of a photocatalyst. Future advances in nanotechnology will present great opportunities for designing more effective photocatalytic disinfection systems, particularly the visible light driven ones. Photocatalytic systems that use a low-cost visible light lamp and solar light to achieve adequately high output are of great interest. Photocatalytic bactericidal technology has great potential applications in biomedical and environment remediation but further research is necessary.

REFERENCES

1. S. Ferraris and S. Spriano, *Mater. Sci. Eng. C*, **61**, 965 (2016).
2. F. Regan, T. Sullivan and J. Chapman, *Nanoparticles in Anti-Microbial Materials: Use and Characterisation*, The Royal Society of Chemistry, Cambridge CB4 0WF, UK (2012).
3. K. P. Kühn, I. F. Chaberny, K. Massholder, M. Stickler, V. W. Benz, H.-G. Sonntag and L. Erdinger, *Chemosphere*, **53**, 71 (2003).
4. G. J. Tortora, B. R. Funke and C. L. Case, *Microbiology: An Introduction*, Pearson (2013).
5. F. Chen, X. Yang and Q. Wu, *Build. Environ.*, **44**, 1088 (2009).
6. J. L. Endrino, R. G. S. V. Prasad, D. Basavaraju, K. N. Rao, A. Mosquera, C. S. Naveen and A. R. Phani, *Nanosci. Nanotechnol. Lett.*, **3**, 629 (2011).
7. M. Machida, K. Norimoto and T. Kimura, *J. Am. Ceram. Soc.*, **88**, 95 (2004).
8. A. L. Linsebigler, G. Lu and J. T. Yates, *Chem. Rev.*, **95**, 735 (1995).
9. W. Q. Fang, X. Gong and H. G. Yang, *J. Phys. Chem. Lett.*, **2**, 725 (2011).
10. M. R. Hoffmann, S. T. Martin, W. Choi and D. W. Bahnemannt, *Chem. Rev.*, **95**, 69 (1995).
11. A. Fujishima and K. Honda, *Nature*, **238**, 37 (1972).
12. K. Page, M. Wilson and I. P. Parkin, *J. Mater. Chem.*, **19**, 3819 (2009).
13. R. J. Watts, S. Kong, M. P. Orr, G. C. Miller and B. E. Henry, *Water Res.*, **29**, 95 (1995).
14. A. Vohra, D. Y. Goswami, D. A. Deshpande and S. S. Block, *J. Ind. Microbiol. Biotechnol.*, **32**, 364 (2005).
15. T. Matsunaga, R. Tomoda, T. Nakajima and H. Wake, *FEMS Microbiol. Lett.*, **29**, 211 (1985).
16. K. Nakata and A. Fujishima, *J. Photochem. Photobiol. C.*, **13**, 169 (2012).
17. M. Ni, M. K. H. Leung, D. Y. C. Leung and K. Sumathy, *Renew. Sustain. Energy Rev.*, **11**, 401 (2007).
18. M. Pelaez, N. T. Nolan, S. C. Pillai, M. K. Seery, P. Falaras, A. G. Kontos, P. S. M. Dunlop, J. W. J. Hamilton, J. A. Byrne, K. O'Shea, M. H. Entezari and D. D. Dionysiou, *Appl. Catal. B Environ.*, **125**, 331 (2012).
19. H. M. Yadav, S. V. Otari, V. B. Koli, S. S. Mali, C. K. Hong, S. H. Pawar and S. D. Delekar, *J. Photochem. Photobiol. A Chem.*, **280**, 32 (2014).
20. H. A. Foster, I. B. Ditta, S. Varghese and A. Steele, *Appl. Microbiol. Biotechnol.*, **90**, 1847 (2011).
21. T. Matsunaga, R. Tomoda, T. Nakajima, N. Nakamura and T. Komine, *Appl. Environ. Microbiol.*, **54**, 1330 (1988).
22. T. Saito, T. Iwase, J. Horie and T. Morioka, *J. Photochem. Photobiol. B.*, **14**, 369 (1992).
23. K. Oguma, H. Katayama and S. Ohgaki, *Appl. Environ. Microbiol.*, **68**, 6029 (2002).
24. K. Sunada, T. Watanabe and K. Hashimoto, *Environ. Sci. Technol.*, **37**, 4785 (2003).
25. P. C. Maness, S. Smolinski, D. M. Blake, Z. Huang, E. J. Wolfrum and W. A. Jacoby, *Appl. Environ. Microbiol.*, **65**, 4094 (1999).
26. S. Josset, N. Keller, M.-C. Lett, M. J. Ledoux and V. Keller, *Chem. Soc. Rev.*, **37**, 744 (2008).
27. G. Gogniat, M. Thyssen, M. Denis, C. Pulgarin and S. Dukan, *FEMS Microbiol. Lett.*, **258**, 18 (2006).
28. W. Choi, A. Termin and M. R. Hoffmann, *J. Phys. Chem.*, **98**, 13669 (1994).
29. S. M. Gupta and M. Tripathi, *Chinese Sci. Bull.*, **56**, 1639 (2011).
30. X. Chen and S. S. Mao, *Chem. Rev.*, **107**, 2891 (2007).
31. H. M. Yadav, S. V. Otari, R. A. Bohara, S. S. Mali, S. H. Pawar and S. D. Delekar, *J. Photochem. Photobiol. A Chem.*, **294**, 130 (2014).
32. H. M. Yadav, T. V. Kolekar, S. H. Pawar and J.-S. Kim, *J. Mater. Sci. Mater. Med.*, **27**, 57 (2016).
33. F. Sayilkan, M. Asiltürk, N. Kiraz, E. Burunkaya, E. Arpaç and H. Sayilkan, *J. Hazard. Mater.*, **162**, 1309 (2009).
34. J. M. Herrmann, *Catal. Today*, **53**, 115 (1999).
35. B. Xin, Z. Ren, P. Wang, J. Liu, L. Jing and H. Fu, *Appl. Surf. Sci.*, **253**, 4390 (2007).
36. S. D. Delekar, H. M. Yadav, S. N. Achary, S. S. Meena and S. H. Pawar, *Appl. Surf. Sci.*, **263**, 536 (2012).
37. G. Fu, P. S. Vary and C.-T. Lin, *J. Phys. Chem. B*, **109**, 8889 (2005).
38. C. C. Trapalis, P. Keivanidis, G. Kordas, M. Zaharescu, M. Crisan, A. Szatvanyi and M. Gartner, *Thin Solid Films*, **433**, 186 (2003).
39. T. Amna, M. Shamshi Hassan, M. Pandurangan, M.-S. Khil, H.-K. Lee and I. H. Hwang, *Ceram. Int.*, **39**, 3189 (2013).
40. C. Karunakaran, G. Abiramasundari, P. Gomathisankar, G. Manikandan and V. Anandi, *J. Colloid Interface Sci.*, **352**, 68 (2010).
41. L. Caballero, K. a. Whitehead, N. S. Allen and J. Verran, *J. Photochem. Photobiol. A Chem.*, **276**, 50 (2013).
42. A. A. Ashkarran, *J. Theor. Appl. Phys.*, **4**, 1 (2011).
43. J. Š. Ogorevc, E. Tratar-Pirc, L. Matoh and B. Peter, *Acta Chim. Slov.*, **59**, 264 (2012).
44. Q. Zhang, C. Sun, Y. Zhao, S. Zhou, X. Hu and P. Chen, *Environ. Sci. Technol.*, **44**, 8270 (2010).
45. J. Gamage McEvoy and Z. Zhang, *J. Photochem. Photobiol. C.*, **19**, 62 (2014).
46. H. T. Patte, *Environ. Toxicol. Chem.*, **18**, 89 (1999).

47. V. Sambhy, M. M. MacBride, B. R. Peterson and A. Sen, *J. Am. Chem. Soc.*, **128**, 9798 (2006).
48. L. Armelao, D. Barreca, G. Bottaro, A. Gasparotto, C. Maccato, C. Maragno, E. Tondello, U. L. Štangar, M. Bergant and D. Mahne, *Nanotechnology*, **18**, 375709 (2007).
49. J. Li, H. Zhou, S. Qian, Z. Liu, J. Feng, P. Jin and X. Liu, *Appl. Phys. Lett.*, **104**, 261110 (2014).
50. P. He, J. Tao, X. Huang and J. Xue, *J. Sol-Gel Sci. Technol.*, **68**, 213 (2013).
51. V. Etacheri, G. Michlits, M. K. Seery, S. J. Hinder and S. C. Pillai, *ACS Appl. Mater. Interfaces*, **5**, 1663 (2013).
52. W. Wang, Y. Yu, T. An, G. Li, H. Y. Yip, J. C. Yu and P. K. Wong, *Environ. Sci. Technol.*, **46**, 4599 (2012).
53. J. C. Yu, W. Ho, J. Yu, H. Yip, P. K. Wong and J. Zhao, *Environ. Sci. Technol.*, **39**, 1175 (2005).
54. R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki and Y. Taga, *Science*, **293**, 269 (2001).
55. P. Mei, M. Henderson, A. Kassiba and A. Gibaud, *J. Phys. Chem. Solids*, **71**, 1 (2010).
56. R. Daghrir, P. Drogui and D. Robert, *Ind. Eng. Chem. Res.*, **52**, 130226090752004 (2013).
57. K. Pathakoti, S. Morrow, C. Han, M. Pelaez, X. He, D. D. Dionysiou and H.-M. Hwang, *Environ. Sci. Technol.*, **47**, 9988 (2013).
58. H. U. Lee, S. C. Lee, S. H. Choi, B. Son, S. J. Lee, H. J. Kim and J. Lee, *Appl. Catal. B Environ.*, **129**, 106 (2013).
59. N. C. Raut, T. Mathews, P. K. Ajikumar, R. P. George, S. Dash and A. K. Tyagi, *RSC Adv.*, **2**, 10639 (2012).
60. S. S. Soni, M. J. Henderson, J.-F. Bardeau and A. Gibaud, *Adv. Mater.*, **20**, 1493 (2008).
61. S. S. Soni, G. S. Dave, M. J. Henderson and a. Gibaud, *Thin Solid Films*, **531**, 559 (2013).
62. J. Ananpattarachai, Y. Boonto and P. Kajitvichyanukul, *Environ. Sci. Pollut. R.*, **23**, 4111 (2015).
63. B. Yu, W. M. Lau and J. Yang, *Nanotechnology*, **24**, 335705 (2013).
64. C.-L. Cheng, D.-S. Sun, W.-C. Chu, Y.-H. Tseng, H.-C. Ho, J.-B. Wang, P.-H. Chung, J.-H. Chen, P.-J. Tsai, N.-T. Lin, M.-S. Yu and H.-H. Chang, *J. Biomed. Sci.*, **16**, 7 (2009).
65. J. Shim, Y.-S. Seo, B.-T. Oh and M. Cho, *J. Hazard. Mater.*, **306**, 133 (2016).
66. A. Mills and S. Le Hunte, *J. Photochem. Photobiol. A Chem.*, **108**, 1 (1997).
67. Q. Kang, Q. Z. Lu, S. H. Liu, L. X. Yang, L. F. Wen, S. L. Luo and Q. Y. Cai, *Biomaterials*, **31**, 3317 (2010).
68. D. B. Hamal, J. a Haggstrom, G. L. Marchin, M. a Ikenberry, K. Hohn and K. J. Klabunde, *Langmuir*, **26**, 2805 (2010).
69. O. Akhavan, M. Abdolahad, Y. Abdi and S. Mohajerzadeh, *Carbon*, **47**, 3280 (2009).
70. O. Akhavan, R. Azimirad, S. Safa and M. M. Larijani, *J. Mater. Chem.*, **20**, 7386 (2010).
71. K. Yamauchi, Y. Yao, T. Ochiai, M. Sakai, Y. Kubota and G. Yamauchi, *J. Nanotechnol.*, **2011**, 1 (2011).
72. M. Chen, F. Zhang and W. Oh, *Bull. Mater. Sci.*, **34**, 835 (2011).
73. N. Yeh, Y. C. Lee, C. Y. Chang and T. C. Cheng, *Thin Solid Films*, **549**, 93 (2013).
74. T. C. Cheng, K. S. Yao, N. Yeh, C. I. Chang, H. C. Hsu, F. Gonzalez and C. Y. Chang, *Thin Solid Films*, **519**, 5002 (2011).
75. N. Janpetch, C. Vanichvattanadecha and R. Rujiravanit, *Cellulose*, **22**, 3321 (2015).
76. W. Kangwansupamonkon, V. Lauruengtana, S. Surassmo and U. Ruktanonchai, *Nanomed-Nanotechnol.*, **5**, 240 (2009).
77. S. Chen, Y. Guo, S. Chen, H. Yu, Z. Ge, X. Zhang, P. Zhang and J. Tang, *J. Mater. Chem.*, **22**, 9092 (2012).
78. S. Rana, J. Rawat, M. M. Sorensson and R. D. K. Misra, *Acta Biomater.*, **2**, 421 (2006).
79. S. Swetha, M. K. Singh, K. U. Minchitha and R. G. Balakrishna, *Photochem. Photobiol.*, **88**, 414 (2012).
80. A. Pal, S. O. Pehkonen, L. E. Yu and M. B. Ray, *J. Photochem. Photobiol. A Chem.*, **186**, 335 (2007).
81. E. V. Skorb, L. I. Antonouskaya, N. a. Belyasova, D. G. Shchukin, H. Möhwald and D. V. Sviridov, *Appl. Catal. B Environ.*, **84**, 94 (2008).
82. L. Caballero, K. a. Whitehead, N. S. Allen and J. Verran, *J. Photochem. Photobiol. A Chem.*, **202**, 92 (2009).
83. D. M. Blake, P. C. Maness, Z. Huang, E. J. Wolfrum, J. Huang and W. A. Jacoby, *Sep. Purif. Rev.*, **28**, 1 (1999).
84. S. J. Cavalieri, *Manual of Antimicrobial Susceptibility Testing*, American Society for Microbiology (2005).
85. T. Ochiai, T. Fukuda, K. Nakata, T. Murakami, D. a. Tryk, Y. Koide and A. Fujishima, *J. Appl. Electrochem.*, **40**, 1737 (2010).
86. A. J. Feitz, T. D. Waite, G. J. Jones, B. H. Boyden and P. T. Orr, *Environ. Sci. Technol.*, **33**, 243 (1999).
87. Q. Li, S. Mahendra, D. Y. Lyon, L. Brunet, M. V. Liga, D. Li and P. J. J. Alvarez, *Water Res.*, **42**, 4591 (2008).
88. B. Wu, R. Huang, M. Sahu, X. Feng, P. Biswas and Y. J. Tang, *Sci. Total Environ.*, **408**, 1755 (2010).
89. L. Zheng, W. Zhang and X. Xiao, *Korean J. Chem. Eng.*, **33**, 107 (2015).
90. M. E. Olya and A. Pirkarami, *Korean J. Chem. Eng.*, **32**, 1586 (2015).
91. I. J. Esfahani, J. Rashidi, P. Ifaei and C. Yoo, *Korean J. Chem. Eng.*, **33**, 351 (2016).
92. X. Qu, P. J. J. Alvarez and Q. Li, *Water Res.*, **47**, 3931 (2013).
93. Z. Xiong, J. Ma, W. J. Ng, T. D. Waite and X. S. Zhao, *Water Res.*, **45**, 2095 (2011).
94. M. Lazar, S. Varghese and S. Nair, *Catalysts*, **2**, 572 (2012).
95. D. Zhang, X. Song, R. Zhang, M. Zhang and F. Liu, *Eur. J. Inorg. Chem.*, **2005**, 1643 (2005).
96. R. van Grieken, J. Marugán, C. Sordo, P. Martínez and C. Pablos, *Appl. Catal. B Environ.*, **93**, 112 (2009).
97. Y.-S. Chai, J.-C. Lee and B.-W. Kim, *Korean J. Chem. Eng.*, **17**, 633 (2000).
98. D. D. Sun, J. H. Tay and K. M. Tan, *Water Res.*, **37**, 3452 (2003).
99. M. Azimzadehirani, M. Elahifard, S. Haghighi and M. Gholami, *Photochem. Photobiol. Sci.*, **12**, 1787 (2013).
100. T. Zuccheri, M. Colonna, I. Stefanini, C. Santini and D. Gioia, *Materials (Basel)*, **6**, 3270 (2013).
101. K. Qi and J. H. Xin, *ACS Appl. Mater. Interfaces*, **2**, 3479 (2010).
102. D. Hua, K. Cheuk, Z. Wei-ning, W. Chen and X. Chang-fa, *Trans. Nonferrous Met. Soc. China*, **17**, s700-3 (2007).
103. F. Martinez-Gutierrez, P. L. Olive, A. Banuelos, E. Orrantia, N. Nino, E. M. Sanchez, F. Ruiz, H. Bach and Y. Av-Gay, *Nanomed-Nanotechnol*, **6**, 681 (2010).

104. H. Hu, W. Zhang, Y. Qiao, X. Jiang, X. Liu and C. Ding, *Acta Biomater.*, **8**, 904 (2012).
105. H. Bodaghi, Y. Mostofi, A. Oromiehie, Z. Zamani, B. Ghanbarzadeh, C. Costa, A. Conte and M. A. Del Nobile, *Food Sci. Technol-LEB*, **50**, 702 (2013).
106. C. Chawengkijwanich and Y. Hayata, *Int. J. Food Microbiol.*, **123**, 288 (2008).