



A review on recent developments in structural modification of TiO₂ for food packaging applications

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ARTICLE INFO

Keywords:

Titanium dioxide nanoparticles
Visible light photocatalysis
Doping
2-D nanomaterials
Graphene
Antimicrobial activity
Food packaging

ABSTRACT

Structural modification of titanium dioxide has offered a novel template to develop advanced functional materials which demonstrate visible light photocatalytic activity. There had been many attempts to modify the band gap of TiO₂ in order to realize its potential as an antimicrobial material in food coatings and packaging. This review gathers most recent advancements of developing TiO₂ based functional nanohybrids which include doping with metals, non-metals, co-doping, and development of hybrids with 2-D nanomaterials. In particular, nanohybrids prepared with of TiO₂ with graphene incorporation has opened up a novel platform to reduce the band gap while minimizing the inherent drawback of electron pair recombination in TiO₂. In this review, critical analysis of the recent literature on the mechanisms involved in structural modifications are discussed broadly and the electronic and functional properties of resulting materials are presented with a greater scientific depth. In addition, the available structural modification techniques have been compared with a particular emphasis on food preservation and post-harvest loss mitigation applications. More importantly, an outlook on the industrial applications, future directions and challenges have been suggested and discussed.

1. Introduction and background

Food spoilage caused by microbial contamination is one of the leading contributors that challenges global food security [1]. Approximately, 3.7 billion tons of fruits and vegetables are produced each year, with an estimated annual loss of 1.3 billion tons due to spoilage due to physiological deterioration, mechanical damage and microbial contamination [1–3]. Microbial spoilage is the major cause that leads to both chemical and biological deterioration [4–8]. Globally, conventional strategies such as cold storage, hot water treatment, gamma irradiation [9], silver treatment, controlled temperature high humidity

processes and chemical treatments such as application of chloride-based liquids, peroxy acetic acid, hydrogen peroxide (H₂O₂) are practiced during the transportations and storage of post-harvest crops [9–21]. High investment, loss of nutrients, safety risk, undesirable residues, and lack of facilities to undertake some of these treatments on a commercial scale are major drawbacks of these methods [13,16,21,22]. Therefore, the potential advanced technologies such as nanotechnology have been explored as a scalable solution in a variety of fields.

In particular, current advances in nanoscience and nanotechnology have offered a novel template for addressing the issues in the field of food sciences [23–29]. Nanomaterials are expected to provide

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<https://doi.org/10.1016/j.progsolidstchem.2022.100369>

extraordinary benefits in improving barrier properties, biodegradability, biocompatibility, enhancing antimicrobial properties even at low concentrations due to smaller size, high surface area to volume ratio, ease of surface modification, and quantum confinement [24,30,31]. They have, in particular, demonstrated improved antimicrobial potency towards a variety of pathogens that causes food spoilage, resulting in reduced shelf life [32–37]. The size reduction to the nanosize leads to a wide range of catalytic and antimicrobial effects against different fungi, bacteria and viruses [37,38]. Throughout the last decade, many attempts have been focused on the development of multifunctional nanomaterial-polymer nanocomposites [28,39]. These nanocomposites have been used in a variety of applications including extending shelf life of fruits and vegetables without diminishing their qualities [24,35,40–44]. Recently, metal and metal oxide nanomaterials have received increased attention as promising antibacterial and antifungal agents due to their high efficacy [4,32,45–48]. Commonly used metal and metal oxide nanoparticles are Ag, Cu, ZnO, WO₃, Fe₂O₃, Fe₃O₄, CdS, BiVO₄, CuO and TiO₂ [49–57]. The basic antimicrobial mechanism of these nanoparticles occurs by releasing metal ions or reactive oxidative species to attack the micro-organism cells. The shape, surface area, size, chemical reaction time as well as chemical functionalization of nanoparticles are some of the main factors that directly influence antimicrobial activity [58,59]. For example, silver ions, silver nanoclusters and silver nanoparticle based compounds are well known and frequently reported as strong antimicrobial agents against food-borne pathogens [32,60,61]. According to literature, the positively charged Ag⁺ ions adhere to the negatively charged microbe cell surfaces via electrostatic attraction, and damage the cell wall. Subsequently, the Ag⁺ ions enter the cell and bind with ATP and DNA. Finally, bacteria die when their ATP synthesis and DNA replication are slowed [32,62]. In contrast, Sondi and coworkers found that the antimicrobial activity of silver nanoparticles was linked to the formation of “pits” in the cell wall of bacteria. The concentration of silver determines the antimicrobial effect, that the accumulated nanoparticles in the bacterial membrane cause the permeability resulting in cell death [63]. The electron spin resonance investigation of Ag nanoparticles by Danilczuk et al. revealed the process of free radical production in Ag nanoparticles as the cause of its antimicrobial activity [64]. Kim and co-workers reported that the antimicrobial effect of Ag nanoparticles is related to the formation of radicals and subsequent radical induced membrane damage in microorganisms [65]. However, these metal and metal oxide nanoparticles are most commonly used in food preservation applications due to their significant antimicrobial properties [58,59].

On the otherhand, TiO₂ nanoparticles have received increased scientific focus in material science, physics, chemistry and biotechnology among a variety of metal and metal oxides [66–72]. The low toxicity [73–75], low cost, commercial availability and eco-friendly nature have further qualified it as a candidate in food preservation [47,76–78]. It shows photocatalytic and antimicrobial performances by releasing free oxygen radicals under ultraviolet radiation [68]. TiO₂ exhibits long term antimicrobial activity against a wide spectrum of pathogenic microorganisms [47,49,79–81]. However, due to the higher wavelength light absorption, TiO₂ can merely be excited under UV light which is only 5% of the solar spectrum compared to the 45% for visible light [82]. At the same time, the rapid electron-hole recombination has become a hindrance to its significant catalytic antimicrobial activity. It lowers the quantum efficiency of the overall photocatalytic reaction [83].

To overcome these limitations, TiO₂ has been doped with various elements such as metals, and non-metals as well as hybridized with 2-D nano matrices such as graphene and graphitic nitrides (g-C₃N₄) and their derivatives [84–91]. These modifications have led to a reduction of photogenerated electron-hole recombination and have enhanced the electronic band structure of TiO₂ resulting in a shift of band gap to absorb light in the visible region of the solar spectrum [74,92–104]. Generally, TiO₂ has a valence band consisting of hybridized Ti-3d, O-2p orbitals, while the conduction band consists of primary Ti-3d orbitals.

The optical and electronic properties of TiO₂ are modified via doping, which involves replacing oxygen and titanium orbital positions with either metal ions or non-metal ions. It successfully suppresses the recombination process during the photocatalytic activity. The efficiency of metal doping is determined by the factors such as type and concentration of metal dopant, d-electron configuration, and energy band level. However currently, there are a number of flaws in doping techniques which has motivated scientists to look for alternative methods [105, 106]. As a result, throughout the last few years, there has been a steady focus on alternative approaches for modification of TiO₂.

Hybridization of TiO₂ with 2-D layer materials such as graphene, graphdiyne [94,107,108], graphitic carbon nitride (g-C₃N₄) [93, 109–112] and 2-D layered transition metal dichalcogenide (MoS₂) has begun to gain attention as the best alternative for improving the photocatalytic activity. 2-D nanomaterials possess single sheet-like structures with single or few nanometer thick layers and large specific surface areas with massive coordinated unsaturated surface atoms provide abundant active sites for the absorption of a higher amount of energy for the photocatalytic reaction [107,113–117]. Moreover, high charge mobility, flexible preparation methods, and structural stability of these materials have gained remarkable attention in the modification of titania for visible light photocatalytic and antimicrobial activity [108]. When nanohybrid is prepared with TiO₂, the synergistic effect of both 2-D materials and pristine TiO₂ can significantly improve the catalytic activity. Thus, hybrids of TiO₂/2-D materials are ideal photocatalysts for a variety of applications in particular for post-harvest loss mitigation and food preservation.

Graphene is one of the most widely used 2-D nanomaterials with excellent electrical mobility ($2 \times 10^5 \text{ cm}^2 \text{ v}^{-1} \text{ s}^{-1}$), high specific surface area ($2600 \text{ m}^2 \text{ g}^{-1}$) and excellent light transparency (97%) [118–121]. These superior features of graphene enable it to serve as a matrix or template for TiO₂ nanoparticle band gap modification. The electrical mobility of graphene provides a route to remove electrons by reducing the recombination of photo generated electrons and holes in TiO₂, while high specific surface areas of graphene retain more adsorbed pollutants and microorganisms. Although, doping provides better photocatalytic activity, 2-D nanomaterials including graphene show extraordinary benefits such as comparable photostability, the highest surface-area-to-volume-ratio, superior electrical conductivity and excellent adsorption of pollutants [49,74,78,85,92,114,122–133]. Herein, this article provides a comparative review on heterogeneous photocatalytic disinfection performance of doped TiO₂, and 2-D material incorporated TiO₂ nanohybrids with particular emphasis on the mechanism of the decomposition of microorganisms using TiO₂ nanohybrids and its potential applications and challenges in the agro-food industry.

2. Basic principles and mechanism of TiO₂ photocatalytic activity

2.1. Structural and electronic properties

Ti is the ninth most abundant element in the earth crust [134–137]. It is present as TiO₂, which shows three naturally forming crystalline polymorphs, namely anatase, rutile, and brookite [83]. Rutile is the most common thermodynamically stable and naturally occurring primary source of Ti. All these three polymorphs can be easily produced in the laboratory, and metastable brookite and anatase can be transformed irreversibly into rutile with calcination at temperatures higher than 600 °C [138,139]. In TiO₂ crystalline structure, octahedral TiO₆ is formed by the coordination of six oxygen (O²⁻) with Ti⁴⁺ [140]. The chains of distorted TiO₆, are linked through edge and corner-sharing in different ways to form these polymorphs. Octahedral sharing of corners, edges at (001) planes gives rise to the anatase and rutile structures, respectively while both edges and corner sharing lead to the brookite structure. Anatase has a body-centered tetragonal structure with lattice

parameters of $a = 3.7845$, $c = 9.5143$ Å, orthorhombic brookite has lattice parameters $a = 9.1819$, $b = 5.4558$, $c = 5.1429$ Å while tetragonal rutile has lattice parameters of $a = 4.5937$, $c = 2.9587$ Å as shown in Fig. 1 [141–144].

TiO₂ is an n-type semiconductor. The electronic bandgaps of anatase, rutile and brookite are ~ 3.2 eV, ~ 3.0 eV and ~ 3.4 eV, respectively [145,146]. Photocatalytic activity is merely dependent on the synthesis method, polymorph ratio, surface area, particle size, crystal structure as well as defect concentrations of TiO₂ [141,147]. Anatase is the most photoactive polymorph due to the high surface absorptivity capacity and, high mobility of charge carriers, while the photocatalytic activity of rutile TiO₂ is not promising due to the high recombination rate of photogenerated electrons and holes [138,148,149]. However, different studies have shown that different ratios of these polymorphs are more photoactive than the anatase TiO₂ [150]. The commercially available standard TiO₂ powder used for photocatalysis, called P-25 (Degussa) is a mixture of these polymorphs [151].

2.2. Mechanism of TiO₂ photocatalytic activities

“Photocatalysis” is a catalytic chemical reaction that triggers or speeds up specific reduction and oxidation (redox) reactions with an irradiated wavelength that can absorb a specific amount of light related to its bandgap energy [136,137,152,153]. The photocatalytic reaction occurs with the reduction of an electron acceptor on the TiO₂ surface while oxidation of the adsorbed water by photogenerated holes. Thus, this heterogeneous reaction produces reactive oxygen species to efficient degradation of pollutants, including microorganisms. Therefore, photocatalysis implies the production of radical species with the photon

rather than the aid of light as a catalyst in reaction.

TiO₂ consists of the occupied valence band (VB) and unoccupied conduction band (CB), as shown in Fig. 2. The energy differences between these two bands are called the bandgap energy (E_g), where the magnitude determines whether the TiO₂ is an insulator, conductor or semiconductor [154]. TiO₂ contains many defects on its surface. These are oxygen vacancies and can be considered as unpaired electrons which are present in the valence band. These unpaired electrons can migrate into the conduction band [154,155]. Therefore, when TiO₂ is exposed to the light of energy equal or greater than the band gap of TiO₂, it promotes the unpaired electrons to the conduction band by leaving positive holes in the valence band [154]. The excitation process happens continuously with the formation of a large number of holes (h_{vb}^+) and electrons (e_{cb}^-) (equation (1)).



These generated electrons can be trapped as Ti^{3+} and O^- in the lattice structure of TiO₂ or recombination can happen. The photoexcited electrons are captured by the electron acceptors on the titania surface and initiate the redox reaction by reducing the O₂ (electron acceptors) to form superoxide radicals (O_2^-) (equation (3)). Formed positive h_{vb}^+ in the valence band react with water (H_2O) or HO^- to form hydroxyl radicals ($\text{OH}^\cdot$), hydrogen peroxide (H_2O_2) and protonated superoxide radicals ($\text{HOO}^\cdot$) (equation (2) and (5)) [156,157]. Collectively these reactive oxidizing species ($\text{HO}^\cdot$, HO_2 , O_2) and h_{vb}^+/e_{cb}^- react with the impurities including organic materials (bacteria, virus and other biological materials) leading to complete oxidation into carbon dioxide and water (equation (6) and (7)) [149]. The photocatalytic activity of TiO₂ mainly

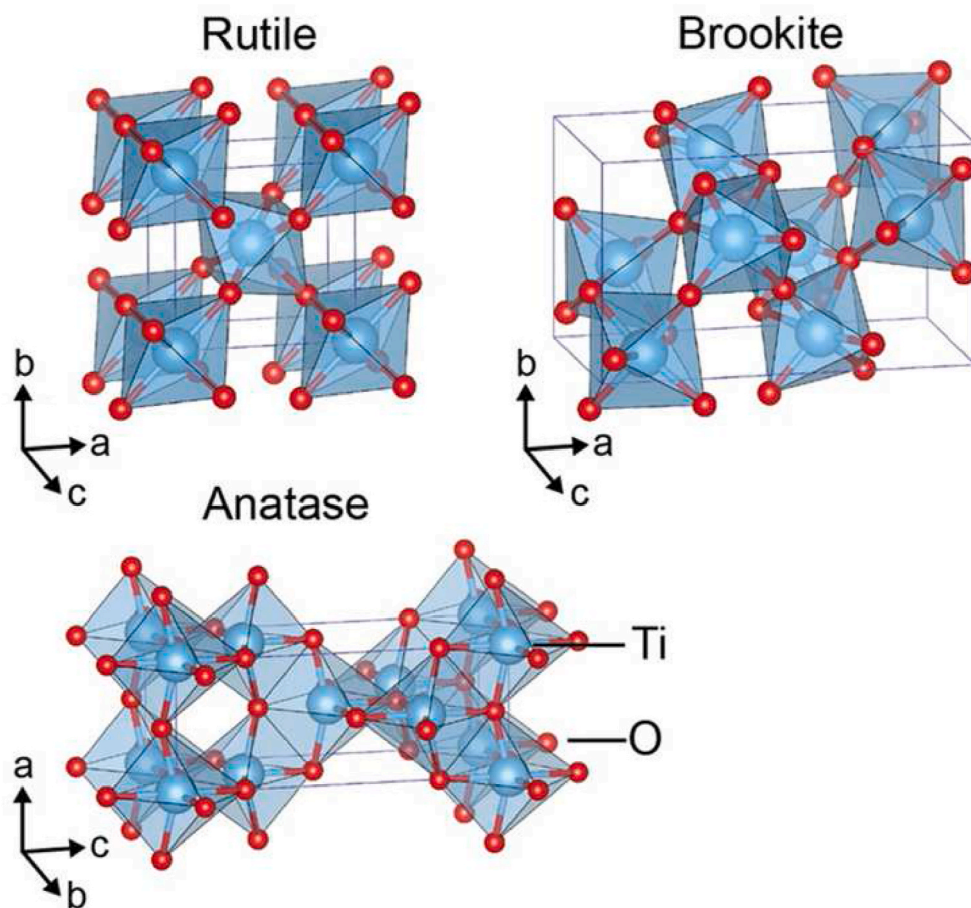


Fig. 1. The crystal structures of rutile, anatase and brookite. Oxygen atoms are red, and titanium atoms are blue (Reproduced with the permission from Haggerty et al. [141]).

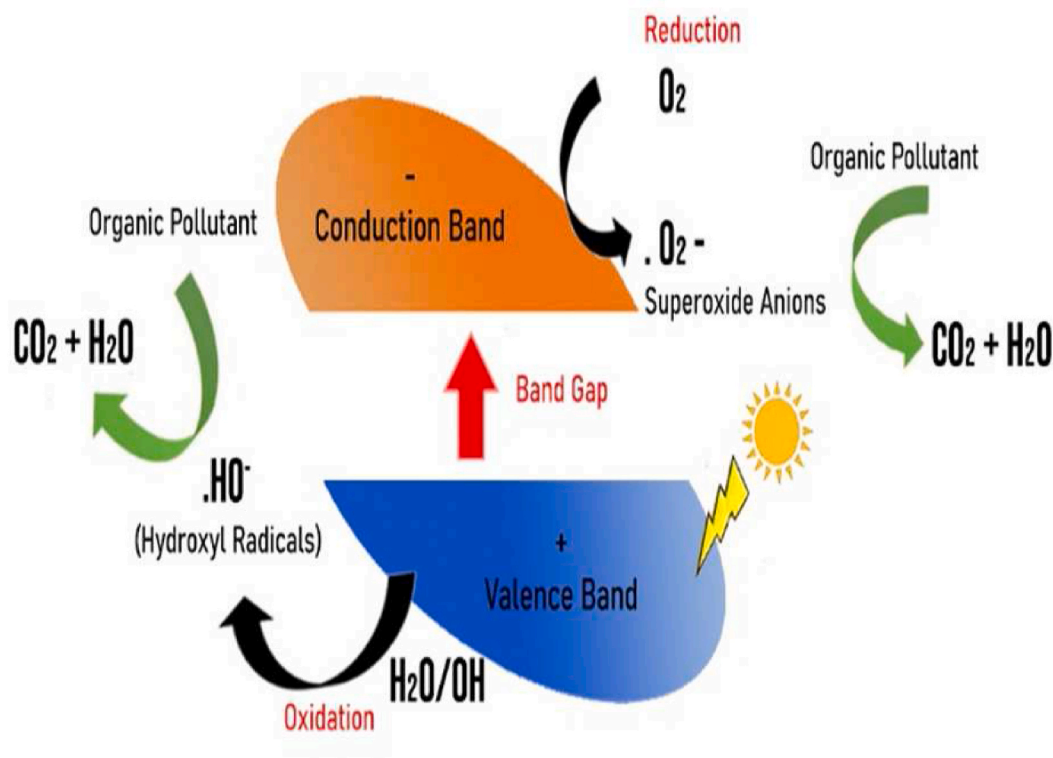


Fig. 2. Schematic diagram showing photocatalytic mechanism of TiO_2 .

depends on the surface area, particle size, crystal structure, defect concentration, and phase purity [158]. Low band gap (E_g) energy makes this process run faster and creates reducing and oxidizing agents very quickly.



As shown in Scheme 1, two sets of competing activities may occur during the photocatalytic activity. Competition between trapping and recombination that may occur within a picosecond and a nanosecond time intervals vs the competition between outer membrane charge transferring and trapped electron-hole recombination, which may occur within a millisecond to a microsecond. Finally, the dominating effect would determine the effectiveness of the photocatalytic process [154]. Some studies have reported that hydroxyl radicals as the primary oxidizing agents in TiO_2 photocatalytic mechanism. In brief, TiO_2 photocatalysis can be summarized as the formation of electrons and holes with the absorption of photons, trapping of photogenerated electrons, and redox reaction on the surface of TiO_2 results in the decomposition of pollutants. Generally, it is a sustainable technique with zero-waste generation, including lower cost and eco-friendly nature. Therefore, TiO_2 is applied in different platforms under both ultraviolet light and visible light depending on its structure and the bandgap [159].

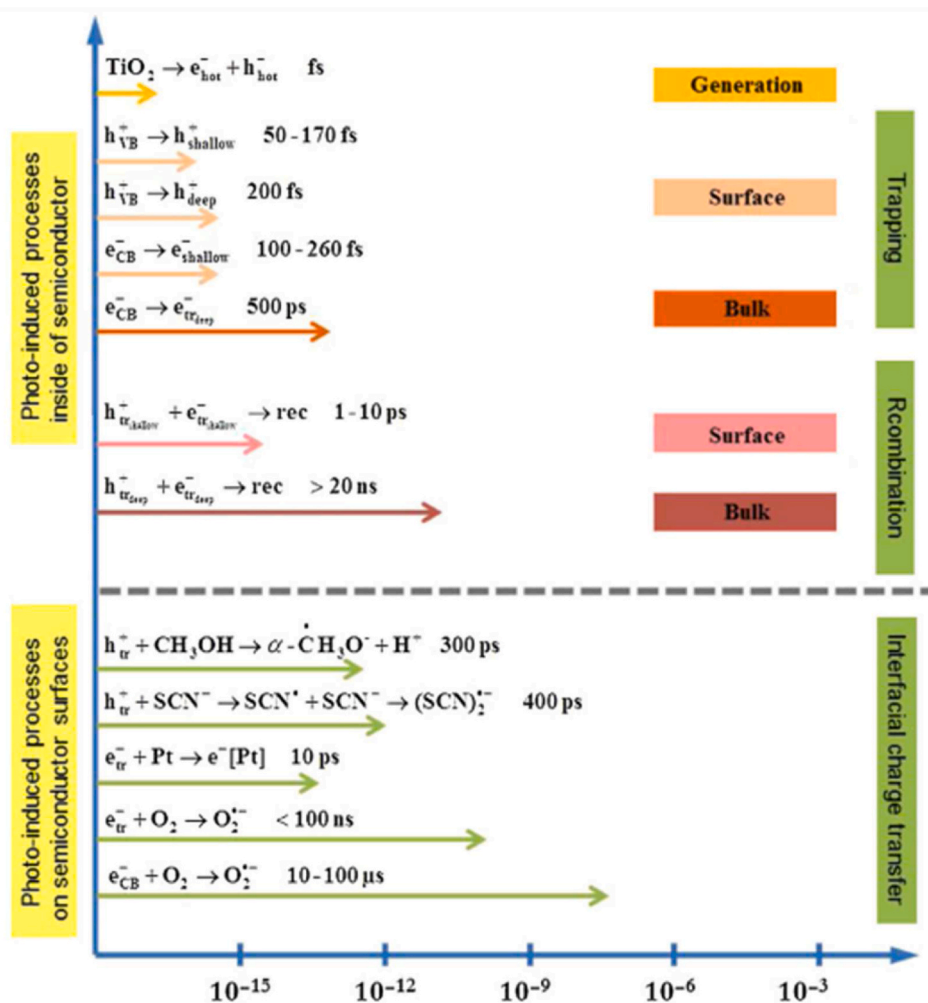
2.3. Antimicrobial mechanism

Photocatalysis is one of the most economically viable, simple and promising technologies to address antimicrobial contamination [160,

161]. Several authors have reported titania nanoparticles as one of the most studied metal oxide [4,68,137,154,162,163]. However, the first report on antimicrobial activity of TiO_2 was done by the Matsunaga et al., in 1985 and reported the antimicrobial activity of TiO_2 by using *Saccharomyces cerevisiae*, *Escherichia coli* and *Lactobacillus acidophilus* as model organisms [164].

Since then, the antimicrobial activity of TiO_2 has been intensively studied on a broad spectrum of microorganisms such as bacteria, viruses, algae, fungi and pathogenic cells. The decomposition of microorganisms (bacteria, virus, fungi) occurs due to the presence of reactive oxygen species and energy-rich electron and hole pairs [165]. They can react directly with the microbial cells by disrupting cell membrane, oxidizing cell components or interrupting the intermembrane electron transfer process as shown in Fig. 3 (see Fig. 4).

Upon exposure of TiO_2 to ultraviolet light or photons of sufficient energy, electrons in the valence band are excited to the conduction band by leaving holes on the valence band. As elucidated in the first part of the review, several reactive radical species such as $\text{HO}^\cdot$, $\text{HO}_2^\cdot$, O_2^- are produced through redox reactions [166]. These superoxide and hydroxyl radicals are highly reactive due to the presence of unpaired valence shell electrons, leading to the destruction of the biomolecules such as lipids, proteins, nucleic acids (DNA, RNA). Mainly, radicals attack the phospholipids on the cell membrane and cell structure resulting in the leakage of the internal component, lipid peroxidation or interrupting intermembrane electron transfer causing the death of microorganisms as shown in Fig. 4. Thereby, the process suppresses the growth of microorganisms [166,167]. Hashimoto et al. have reported that the cell cover of *Escherichia coli* consists of the outer membrane, peptidoglycan layer and cytoplasmic membrane. The outermost membrane of bacteria cells is with phospholipids, amino acids and lipopolysaccharide that determine the direct damage to the cell wall. Therefore, effectiveness of the TiO_2 catalytic antimicrobial activity is affected by the presence or absence of a cell wall [168]. Microorganisms with cell walls have some restrictions to the reactive radical species that result in a lower rate of photo killing activity compared to the



Scheme 1. Schematic representation of photocatalytic mechanism in TiO_2 . (Reproduced with the permission from Schneider et al. [155]).

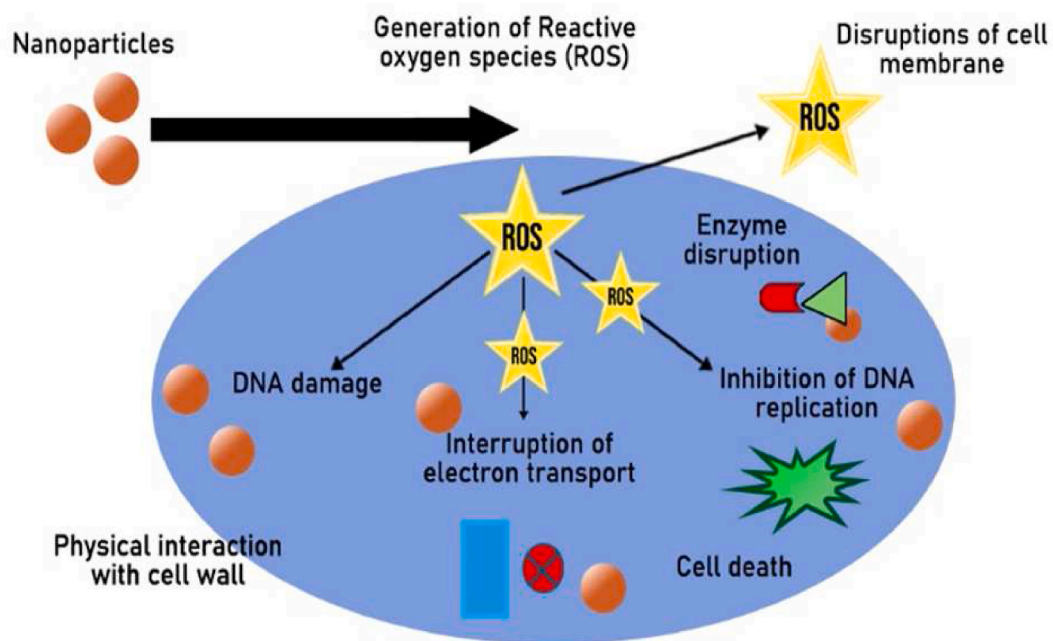


Fig. 3. Antimicrobial mechanism of TiO_2 .

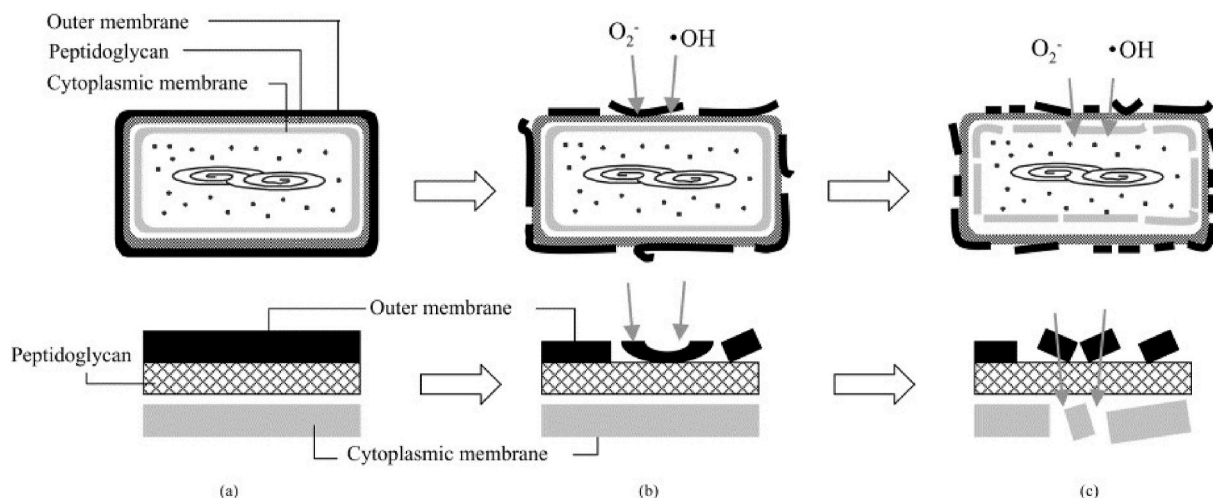


Fig. 4. Schematic representation of the photokilling of *Escherichia coli* by the TiO_2 (Reproduced with the permission from Sunada et al. [168]).

microorganisms without a cell wall. This is because of the direct contact of photogenerated radical species with the cytoplasmic membrane of microorganisms without cell walls.

Podporska-Carroll et al. have reported the antimicrobial activity of titania nanotubes against *Escherichia coli* and *Staphylococcus aureus*. It has shown superior antimicrobial activity of 97.53% and 99.94% with *Escherichia coli* and *Staphylococcus aureus*, respectively under UV irradiation within 24 h time duration. Their results suggested that the antimicrobial activity of TiO_2 depends on several factors such as surface properties, morphology, physicochemical properties of TiO_2 and the biological analysis conditions [79]. In addition, they mentioned the availability of a higher amount of surface-active hydroxyls for the absorption of microbes on the TiO_2 as a major factor that enhances the antimicrobial activity [79]. Compared to the superoxide anion, hydroxyl radicals are much more effective for the decomposition of organic compounds. Li et al. study showed the hydroxyl radicals as a nonselective and strong oxidant that can attack a variety of biomolecules such as proteins, lipids, nucleic acids (DNA, RNA), and amino acids which are the main components of microorganisms [169]. Meanwhile, Cho et al. also reported hydroxyl radicals as major responsible reactive oxygen species against microorganisms. Zhang et al. showed the antimicrobial activity of TiO_2 for the inactivation of *Bacillus subtilis* spores under ultra violet radiation and proposed the lipid peroxidation as a stem of the microbial inactivation process [170]. In brief, the contact of TiO_2 surface with bacteria cell wall results in the damage of bacteria cell wall due to the attack of reactive oxidative species continuing to the cytoplasmic membrane leading to penetrating to the cell causing cell content leakage, lipid peroxidation, cytoplasmic leakage, enzyme function alteration and finally the death of cells. Thus, there is a significant effect of the antimicrobial activity of TiO_2 in many fields, including food preservation.

2.4. Limitations of TiO_2 photocatalysis

When TiO_2 absorbs enough energy to excite electrons from the valence band to the conduction band, electrons end up with two major fates which determine the effectiveness of the photocatalytic process. One is the trapping of charge carriers (valence electrons) by electron acceptors to occur interfacial reactions. Other one is the recombination of electrons and holes that generate energy radiatively or non-radiatively as heat or light. This recombination may occur either in bulk or on the surface of TiO_2 [45,130,171,172]. Generally, recombination is engineered by the impurities, defects and other surface or bulk imperfections. Serpone et al. reported that more than 90% of photo-generated electrons and holes recombine while the remaining charge

carriers support the interfacial reactions with the acceptance of Ti^{3+} species within 30 ps [155]. However, in order to achieve higher photocatalytic activity, the rate of interfacial charge transfer should be greater than the rate of electron-hole pair recombination.

However, apart from that, another reported limitation is TiO_2 's poor thermal stability. As mentioned under the section of the structure of titania, anatase is the most photoactive polymorph of titania compared to other TiO_2 polymorphs (rutile, brookite). The band gap of rutile (3.0 eV) is smaller than that of the anatase (3.2 eV). So, anatase exhibits a lower recombination rate compared to rutile. The rate of recombination is inversely proportional to the bandgap. Under normal conditions, non-irreversible conversion of anatase to rutile can occur under high temperatures (above 600 °C) [173]. The movement of Ti^{4+} ions and O^{2-} involves breaking the edge shared anatase crystals to the corner shared rutile structure as shown in Fig. 5. The temperature at which anatase is converted to rutile is determined by the TiO_2 particle size, impurity content, reaction atmosphere, and synthesis method. This thermal instability limits its applications in high temperature process. Thus, TiO_2 cannot show its photocatalytic activity in processes such as ceramics and glass. Generally, nanocrystalline TiO_2 is used as coatings on ceramics that are used to create more hygienic environments in hospitals and toilets. The thermal instability of anatase is the main problem in this application [174]. Therefore, different studies have introduced metal dopants to obtain the thermal stable TiO_2 to be used in such applications [175].

In addition to the aforementioned weakness, the wide bandgap of anatase makes it active only in the presence of ultraviolet light, which is only a minor percentage of the solar spectrum. In summary, superior performance of TiO_2 is restricted by quick recombination of photo-generated electron-holes, poor photocatalytic efficiency and wide bandgap. Many strategies such as doping TiO_2 with metals, non-metals and fabricating with 2-D nanomaterials have been widely focused to deal with the aforementioned challenges.

3. Development of visible light active TiO_2 photocatalyst with doping

The optical behavior of any material merely depends on its structure. The structural features of the materials are related to the chemical bonding between the ions or atoms, physical dimensions and the atomic arrangement of the materials. Therefore, the visible light absorption of photocatalysts can be modified by engineering them through doping [176–179]. TiO_2 consists of metallic (Ti) and non-metallic (O) components, and substitution with suitable elements can be used as a tool to alter the optical properties in a flexible manner. Thus, doping minimizes

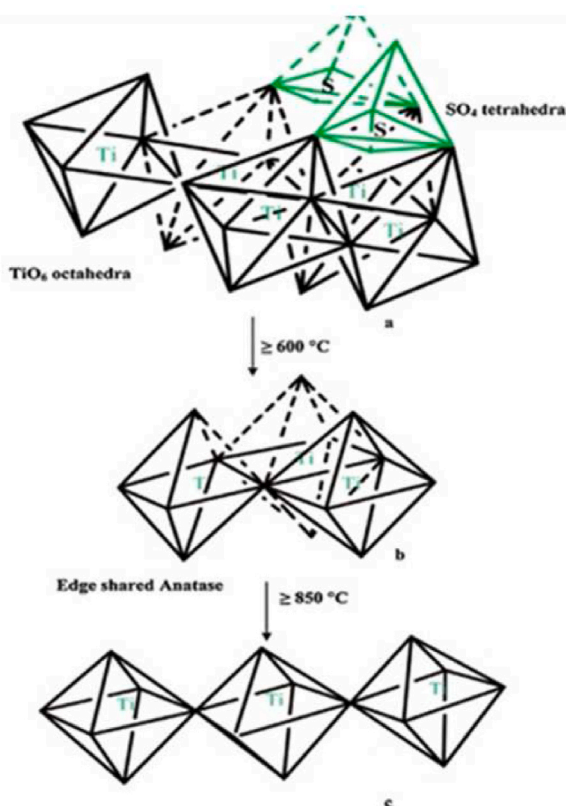


Fig. 5. Schematic representation of the formation corner shared rutile from the edge shared anatase (Reproduced with permission from Periyat et al. [174]).

the high recombination of photo generated electrons-holes, enhances the absorption of visible light and also extends the anatase phase stability to high temperatures. Asahi et al. reported that three requirements should be fulfilled in doping of TiO₂. (i) visible light absorbing state should be introduced in the TiO₂ band gap (ii) the new impurity state should be present higher as that of TiO₂ or the H₂/H₂O level (iii) newly introduced gap should overlap with the TiO₂ band states [180]. Several studies have reported the doping of TiO₂ as one attractive option to utilize abundant solar radiation by minimizing above mentioned drawbacks for the catalytic decomposition and antimicrobial activity [181]. Therefore, the next section will be elucidate with a brief overview of doping.

3.1. Metal ion doping, photocatalytic and antimicrobial activity

3.1.1. Transitional metal doping

Transition metals such as vanadium (V), chromium (Cr), copper (Cu), iron (Fe), manganese (Mn), and nickel (Ni) are widely used in modification of TiO₂ [183–185]. These transition metal substitution to the Ti⁴⁺ ions in the TiO₂ lattice leads to narrowing down the bandgap of the transition metal-doped TiO₂ and suppress the recombination of photogenerated electrons and holes by acting as an electron acceptor, hole acceptor or both electron and hole acceptor. Generally, it is easy to introduce dopants to titania that have a similar ionic radius to that of Ti⁴⁺ (0.75 Å) in TiO₂ lattice. When we take the transition metal, electron or hole acceptance process happens as below (equation (8) and (9)).



Where the new energy levels $X^{n+}/X^{(n-1)+}$ present below the conduction band while $X^{n+}/X^{(n+1)+}$ present above the valence band [49,186–188]. The mechanism of transition metal doping can be explained with the

Fe-doped titania. Zhu et al. has reported the doping effect of Fe²⁺ and Fe³⁺ on the photocatalytic activity of TiO₂ by explaining the decomposition of active yellow XRG dye. Results obtained for the doped TiO₂ showed the Fe³⁺ in doped TiO₂ as a both electron and hole trapper while Fe²⁺ acts as a hole trapper [189]. Ambrus et al. also reported the photocatalytic activity of Fe³⁺ doped TiO₂ [190]. Tong et al. reported the optimal Fe³⁺ doping concentration as 0.1% and 0.2% for the effective degradation of methylene blue under ultraviolet radiation and visible light respectively [191]. Therefore, the mechanism of Fe³⁺ in TiO₂ can be explained using equations 10–14. The Fe³⁺ doped TiO₂ consists of Fe²⁺/Fe³⁺ energy level closer to the conduction band (Ti³⁺/Ti⁴⁺) while Fe³⁺/Fe⁴⁺ level above the valence band as shown in Fig. 6. When Fe³⁺ doped TiO₂ is exposed to irradiation of light, Fe³⁺ ions received photogenerated electrons from the valence band of titania resulting in the conversion of Fe³⁺ to Fe²⁺ (equation (10)). According to the crystal field theory, Fe²⁺ ions are unstable due to the loss of half filled spin (d5) and quickly convert to Fe³⁺ by transferring electrons to O₂ on the surface of TiO₂ (equation (11)). This electron transferring process leads to the formation of reactive radicals for the interfacial redox reactions. In this way, Fe³⁺ act as an electron acceptor. The hole trapping ability of Fe³⁺ can be explained with equation (13) and (14). Fe³⁺/Fe⁴⁺ energy levels present above the valence band of TiO₂ leads to conversion of Fe³⁺ to Fe⁴⁺ subsequently formation of hydroxyl radicals for degradation of organic pollutants [182,190,191].



Fe³⁺ doped titania has been utilized in a variety of applications including the photodecomposition of pollutants in the gas phase as well as liquid phase [192–195]. However, there are few studies on Fe²⁺ doped titania. Fe²⁺ acts as only a hole tapping site (equation (15)) which enhances the recombination compared to the interfacial charge transfer process. Therefore, Fe³⁺ doped titania is a more effective photocatalyst compared to the Fe²⁺ doped titania.



Choi and coworkers have investigated the synthesis of visible light active TiO₂ by doping with different 21 metals. The low photocatalytic effect was observed for the TiO₂ doped with Ga (III), Nb (V), Ta (V), Zr (IV) which are closed-shell configurations containing metals [83,196]. Irie et al. have done experiments on Cu (II) doped TiO₂ and observed a better photocatalytic activity for Cu (II)/TiO₂ nanohybrid under visible light. In the Irie et al. study Cu (II) ions in the Cu doped TiO₂ has acted as the photogenerated electron acceptors and inhibited the electron – hole recombination result in enhancement of 2-propanol decomposition under visible light with 8.8% quantum efficiency [95,197]. Yu et al. has reported 22% quantum efficiency (400–530 nm) for the Fe (III) doped TiO₂ and light absorption wavelength has shifted up to 580 nm with the 10% quantum efficiency [95]. The study of Morikawa et al. investigated that Cu, Fe and Pt doped TiO₂ as superior photocatalysts with improved oxidation towards photodecomposition of acetaldehyde with the highest oxidation rate of acetic acid and toluene with Pt and Cu doped TiO₂. Collectively, all these results mentioned that the transition metal d state in the transition metal-doped TiO₂ leads to redshift in the absorption of light with superior inhibition of charge recombination in turn enhancing its antimicrobial performance [198]. Since transition metal-doped TiO₂ exhibits improved photocatalytic activity, that can be used for efficient elimination of a wide spectrum of microorganisms. Table 1 summarizes some examples of transitional metal-doped TiO₂ for its applications as an antimicrobial agent. Interestingly, transitional metal-doped TiO₂

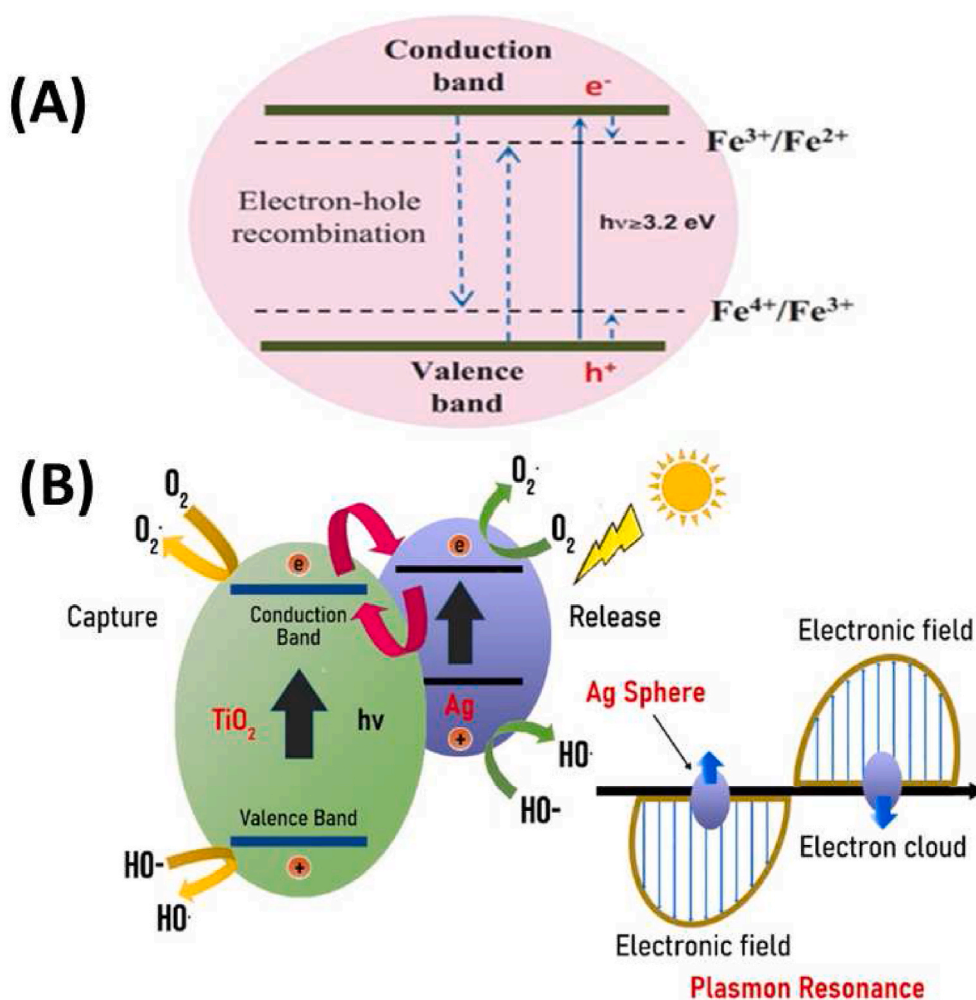


Fig. 6. (A) Fe^{3+} in Fe doped TiO_2 (Reproduced with permission from Tieng et al. [182]) (B) electron transfer mechanism in Ag-doped TiO_2 .

Table 1

Some examples of transition metal-doped TiO_2 that were tested for their anti-microbial activity.

Transition metal-doped TiO_2 nanoparticles	Bacterial strain tested	Key references
Cu-doped TiO_2 Cuprous oxide-doped TiO_2	<i>Escherichia coli</i> , <i>Staphylococcus aureus</i>	[183, 199–204]
Ni-doped TiO_2	Gram positive bacteria (<i>Staphylococcus aureus</i> , <i>Bacillus Subtilis</i>) Gram negative bacteria (<i>Escherichia coli</i> and <i>Salmonella abony</i>)	[205]
Fe-doped TiO_2 sol gel technique	Gram positive bacteria (<i>staphylococcus aureus</i>) gram negative bacteria (<i>Escherichia coli</i>)	[206]
Mn-doped TiO_2	Gram positive bacteria (<i>staphylococcus aureus</i>) gram negative bacteria (<i>klebsiella pneumonia</i>)	[207]
Cr-doped TiO_2	<i>Escherichia coli</i>	[208]
Co-doped TiO_2	<i>Staphylococcus aureus</i> , <i>Candida albicans</i>	[209]

shows higher antimicrobial activity under visible light compared to the pristine TiO_2 .

3.1.2. Noble metal doping

The fabrication of noble metals-doped TiO_2 promotes the charge transferring at the surface by acting as electron trapping sites which minimize the electron-hole recombination [177,210–213]. Ag, Pt, Rh,

Pd and Au are extensively used as noble metal dopants. They possess superior unusual optical and electronic properties due to their surface plasmon resonance effect [98,214,215]. Localized surface plasmon resonance (LSPR) enhanced photocatalysis is related to the noble metal-doped TiO_2 . LSPR is the combined oscillation of the surface electrons with the electromagnetic field of the light that leads to the collective oscillation of surface electrons in the metal dopants. Light exposure leads to the collective oscillation of surface electrons in the metal dopants. This effect enhances the absorption of both the visible region as well as the infrared region. The non-radiative decay of LSPR, after excitation, results in production of hot electrons and holes with Landau damping [216,217]. These electrons and holes are highly energetic. Thus, when these noble metals are doped to TiO_2 , noble metals act as electron donors by supplying these generated electrons to the conduction band of TiO_2 . In turn, the holes created on the noble metals due to the plasmonic effect can act as effective capturing sites of electrons emitted by the TiO_2 valence band [210,211] thereby suppressing the higher electron-hole recombination. This localized plasmon resonance effect can be observed in these noble metals and has been used to enhance the efficiency of photocatalytic activity of TiO_2 . Therefore, collectively the superior features of noble metal plasmonic nanoparticles together with TiO_2 provides excellent photocatalytic and antimicrobial activity [212,218].

The localized plasmon resonance effect of Ag and Au nanoparticles has been reported by many researchers [214]. As a result, the plasmonic photocatalysis effect of Ag and Au doped TiO_2 has received considerable

interest among the scientific community for enhancing the efficiency of decomposition of organic pollutants, activity of photovoltaic devices, and for water splitting [218,219]. A number of methods such as hydrothermal method, sol-gel process, impregnation, and photo deposition have been used to fabricate noble metal-doped TiO₂ for visible light activation. Bamwenda et al. reported the enhancement of TiO₂ photocatalytic activity with Pt and Au, while Seery et al. reported about the silver doped TiO₂. Li and coworkers reported the Au nanoparticle modified TiO₂ nanotubes with their enhanced catalytic antimicrobial activity [220,221]. Furube et al., as well as Nishijima et al., have reported the Au loaded TiO₂ for the efficient utilization of visible light irradiation. They have synthesized titania nanotubes by electrochemical anodization following the Au coated with magnetron sputtering. The resulting product has effectively destroyed *Escherichia coli* and *Staphylococcus aureus* [214,222].

Petica and coworkers synthesized silver TiO₂ nanocomposite with improved antimicrobial and antifungal activity which act as a superior photocatalyst. They have electrochemically deposited the Ag nanoparticle on TiO₂ and reported the significant photodecomposition of orange II dye compared to the pristine TiO₂ [223]. Gunawan et al. reported the reversible photoswitching of nanosilver on titania with the controlled oxidation state changes. Initially, the valence band electrons in titania excited to the conduction band and subsequently migrated to the silver nanoparticles by reducing Ag₂O to metallic silver ($\text{Ag}^+ + e^- \rightarrow \text{Ag}^0$). The formed metallic silver ions are responsive to the visible light through LSPR, as mentioned above. Therefore, Ag^+ is oxidized by supplying electrons from silver to TiO₂. Thus, this study explains the effect of reversible photoswitching in nanosilver for the improvement of TiO₂ photocatalytic activity [224]. The work function of the noble metals affects photocatalytic activity. Sakthivel et al. synthesized the Pt, Pd and Au doped TiO₂ for the photodecomposition of acid green-16 and the highest photocatalytic effect was observed for the doped TiO₂ with lower than 1 wt % metal percentage. The highest photonic efficiency was observed for both Pt and Au-doped TiO₂ compared to the Pd-doped TiO₂ due to the highest work function and the optimum electron affinity associated with the Au and Pt. They suggested that the photonic activity of metal-doped TiO₂ depends on the electron affinity and the work function to form a favorable contact between noble metals and TiO₂ to charge transfer effectively. The potential barrier between metals and semiconductors at their interface is known as Schottky barrier, effectively suppresses the charge recombination in semiconductors. In Ag-doped TiO₂ nanocomposites, the Fermi level of TiO₂ is higher than the Ag nanoparticles. The excited electrons in TiO₂ eject from TiO₂ to Ag metal across the barrier at the Ag and TiO₂ junction. Briefly, under the visible light, Ag-doped TiO₂ utilizes the LSPR effect to transfer electrons from Ag to the TiO₂ while lower fermi level of Ag with Schottky barrier electrons move from TiO₂ to Ag under the ultraviolet irradiation or without plasmonic effect. Optimum noble metal content is also significant for exhibiting effective photocatalytic activity. This is because the excess noble metal acts as electron-hole recombine site centers or has the ability to reduce the light absorption of TiO₂ by covering the active sites on TiO₂. Thus, the synergistic effect of Ag and TiO₂ is favorable for the catalysis of organic materials as well as a variety of microorganisms [218,225–227]. Table 2 summarizes some examples of noble metal-doped TiO₂ for its applications as an antimicrobial agent. Interestingly, noble metal-doped TiO₂ shows higher antimicrobial activity under visible light compared to the pristine TiO₂.

3.1.3. Rare earth metal doping

Several studies have reported the rare earth metal doping of TiO₂ to enhance the shelf life. Lanthanide (La), cerium (Ce), ytterbium (Yb), and erbium (Er) are some of the commonly used doping rare-earth metals [234]. There are 4f, 5d and 6s orbitals in these metals and they introduce new energy levels between the conduction band and valence band in TiO₂(see Fig. 7(A)). This impurity energy level acts as a trapping site of photogenerated electron-holes and shift of band gap leading to the

Table 2

Some examples of noble metal-doped TiO₂ that were tested for their antimicrobial activity.

Noble metal-doped TiO ₂ nanoparticles	Bacteria strain tested	Key references
Au-doped TiO ₂	<i>Staphylococcus aureus</i> , <i>Escherichia coli</i> , <i>Aspergillus niger</i> , <i>Aspergillus melleus</i> , <i>Penicillium chrysogenum</i> , <i>Candida albicans</i>	[98,214,228, 229]
Ag-doped TiO ₂	<i>Escherichia coli</i> , <i>Aspergillus niger</i> , <i>Aspergillus melleus</i> , <i>Penicillium chrysogenum</i> , <i>Candida albicans</i> , <i>Pseudomonas aeruginosa</i> , <i>Staphylococcus aureus</i> , <i>Salmonella Albany</i>	[98,177,178, 223,230–233]

strong decomposition of microorganisms via formation of radicals under visible light [234–236]. The charge and ionic difference between dopant and Ti result in the generation of defects in doped TiO₂. Kasinathan et al. synthesized Ce doped TiO₂, which has shown better photocatalytic and antimicrobial action against *Escherichia coli* under visible light due to the narrow down of titania bandgap and suppression of electron-hole recombination by Ce doping [237]. Other than the Ce doping [238], La-doped TiO₂ also has been extensively studied [234–236,239]. Yan et al. reported the synthesis of Ce doped TiO₂ with sol-gel method and suggested that the Ce dopants introduce a new energy level between conduction band and valence band of titania. This additional electronic state acts as a photogenerated electron acceptor and minimizes the electron-hole recombination and directly promotes the electrons in the energy level to conduction band of TiO₂ for the superior visible light absorption to degrade methylene blue compared to the pristine TiO₂. Li and coworkers reported the synthesis of rare earth metal doped TiO₂ such as (Ce, Pr, La, Sm) by using sol-hydrothermal method. Their results suggested that the rare earth metals substitute the Ti^{4+} in TiO₂.

3.1.4. Non-metal doping

Non-metal doping of TiO₂ is another TiO₂ modification method [240]. Although metal ion doping enhances the visible light activity of TiO₂, it showed several weaknesses such as enhancing the thermal instability of anatase TiO₂, introducing extra recombination sites with increased metal ion (cation) dopants concentration, higher modification cost and the formation of secondary phases. Such drawbacks have promoted the doping of TiO₂ with non-metals leading to a great promise in achieving visible light photocatalytic and antimicrobial activity. Thus, non -metals such as B, C, N, F have been widely utilized for narrowing the band gap, increasing the lifetime of photogenerated electron-holes by suppressing recombination and upgrading light response to visible light [240]. Kuo and coworkers have reported the excellent photocatalytic efficiency of the non-metal doped TiO₂ under visible light. Non-metals I, N, P and B doped TiO₂ have shown 100%, 94%, 93% and 88% of photocatalytic degradation of aqueous bisphenol An under solar light [240].

Among these non-metal dopants, nitrogen is the most suitable anionic dopant to substitute the O in TiO₂ lattice structure due to several reasons. The smaller size of N atoms compared to the O atoms, high stability, and the small ionization energy leads to efficient doping activity. Such doping results in significant changes in the structural, electronic and optical properties of titania. The first experiment of non-metal doping was done by Asahi and his coworkers in 2001. Asahi et al. prepared crystalline TiO_{2-x}N_x by sputtering a TiO₂ in a N₂/Ar gas mixture followed by annealing at 550 °C in an inert environment. These films absorbed light below 500 nm. During the N doping, the 2p orbital of the N is hybridized with the O 2p state in TiO₂ lattice structure. The bonding state is present below the TiO₂ valence band while antibonding state is present above the valence band. The antibonding state acts as a ladder to transfer exciting valence electrons in TiO₂ to the conduction band, Fig. 7(B). Therefore, it enhances the efficient transfer of charge carriers. Thus, N-doping extends the absorption of TiO₂ to the visible

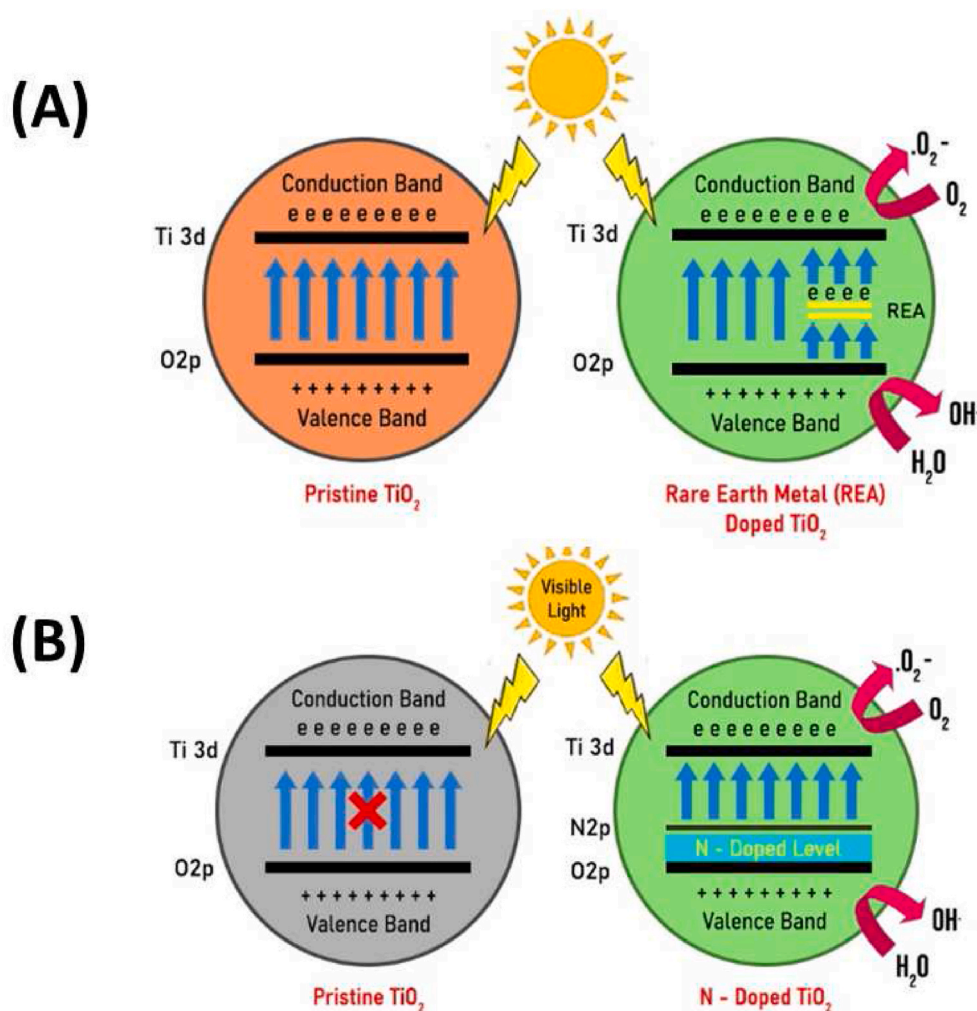


Fig. 7. (A) electron transfer mechanism of rare earth metal-doped TiO₂ and (B) band structure of N-doped TiO₂.

region by narrowing the band gap and also suppressing the recombination to enhance the photocatalytic efficiency. When we go through the research studies on non-metal doping of TiO₂, doping can occur in two ways, either substitutional or interstitial doping. However, there are some conflicts in reported studies about the better photocatalyst producing approach. In the substitutional N-doping method, O in TiO₂ is substituted by the N forming an N-2p energy state just above the valence band of TiO₂. This slightly reduces the band gap of TiO₂ from 3.2 eV to ~3.06 eV. Interstitial N-doping occurs by inserting N into the TiO₂ titania lattice structure. The newly formed energy level is present in the middle of the valence band and conduction band. Thus, compared to the substitutional doping, interstitial doping significantly reduces the band gap of anatase to 2.46 eV [176]. The nitrogen source used for the doping affects the photocatalytic activity of doped TiO₂. Thiourea, hydrazine hydrate, triethylamine, urea are the other major nitrogen sources used in TiO₂ doping. Cong and coworkers have prepared N-doped TiO₂ using these nitrogen sources and reported the triethylamine as the best nitrogen source that showed highest photocatalytic activity in degradation of 2, 4-dichlorophenol. Furthermore, N-doping stabilizes the oxygen vacancies for the visible light absorption. Different chemical and physical methods have been extensively used in synthesis of N-doped TiO₂ [241]. Sato et al. synthesized N-doped TiO₂ with 50% absorption of light in the visible region by using a wet chemical method. They have synthesized doped TiO₂ by the introduction of NH₄OH in a TiO₂ sol, followed by calcination of the resulting powder. Livraghi et al. has employed hydrothermal, pyrolysis and sol-gel methods to synthesize

N-doped TiO₂ and investigated the different properties of the prepared nanoparticles. All the samples have shown superior photocatalytic activity under the visible light irradiation exposure [241]. Nolan et al. has synthesized N-doped TiO₂ with sol-gel technique by using 3-diaminopropane as a precursor. The prepared sample calcined at 500 °C has shown better photocatalytic activity against 4-chlorophenol with the irradiation of visible light. The undoped TiO₂, which was prepared by using the same method, hasn't shown photocatalytic degradation under visible light [99].

Fluorine doping showed exceptions from other nonmetal doping due to its highest electronegativity. It has a filled 2p orbital. When lattice oxygen of TiO₂ is replaced with the F, it improves the surface acidity by converting Ti⁴⁺ into Ti³⁺. This occurs due to the charge compensation between Ti⁴⁺ and F⁻ [148,242]. The formed Ti³⁺ suppress the recombination of photogenerated carriers. Also, Li et al. showed the formation of additional energy levels below the conduction band of TiO₂ due to the creation of O vacancies. Although, F doping does not involve a band gap shift of TiO₂, it stabilizes the anatase by elevating anatase to rutile phase transformation temperature more than 600 °C. Czoska and coworkers synthesized F-doped TiO₂ via sol gel methods and investigated two types of fluorine in F-doped TiO₂. One F⁻ ions species substituted the O²⁻ ions in the TiO₂ crystal structure by forming Ti-F-Ti bond, and the other species present at both internal and external surfaces replaced hydroxyl groups without forming reduced centers. They suggested that insertion of F leads to the formation of Ti³⁺ reduced centers without generating oxygen vacancies. This author has explained the possible effect of F in

surface and bulk as explained by Yu et al.

P, C and S are also other potential dopants that can modify the TiO₂ to extend the light absorptivity to the solar or visible light [243–246]. Nagaveni et al. synthesized a C-doped TiO₂ photocatalyst that showed better photodecomposition of methylene blue and phenol under visible and ultraviolet light compared to TiO₂ and Degussa. Normally, in TiO₂, the charge transition occurs from O 2p to Ti d orbitals. Nagaveni and coworkers suggested the substitution of carbide ion (C⁴⁻) for and O²⁻ leads to the narrow down of band gap in C-doped TiO₂ due to the lower binding energy of carbide ion compared to the O²⁻ 2p band. Furthermore, it facilitates the optical transition from carbon 2p to TiO₂ Ti valence band. Huang et al. reported the visible light degradation ability of C-doped TiO₂ for the decomposition of NO like common indoor pollutants. XPS results confirmed the successful substitution of oxygen sites in TiO₂ by carbon atoms by forming a C–Ti–O–C bond. Yu et al. also has synthesized, C self-doped TiO₂ sheets with exposed facets using hydrothermal methods. They reported that the prepared sample consists of C in two forms as interstitial carbon and carbon substituting O atoms in TiO₂. It has shown better photocatalytic decomposition of methylene blue with the narrow downing of the band gap and redshift of absorption of the C-doped TiO₂. Finally, this experimental work suggested that this C-doped TiO₂ has a potential to be used in sensors, optoelectronic devices, solar cells and catalysts. The aforementioned studies indicate carbon doping as a promising approach for the effective extension of titania photocatalytic activity to the visible irradiation. The large ionic radius of S makes it difficult to insert into the TiO₂ compared to N. It is more favorable to dope S⁶⁺ cation than the anionic S²⁻. Both S and F doping have the ability to stabilize anatase titania to elevated temperatures. This enables the use of doped TiO₂ for the photocatalytic applications that need higher temperatures for their activity. Table 3 summarizes some examples of non-metal-doped TiO₂ for its applications as an antimicrobial agent. Interestingly, non-metal-doped TiO₂ shows higher antimicrobial activity under visible light compared to the pristine TiO₂.

3.1.5. Drawbacks of doping

Although metal doping approaches showed improvement in photocatalytic activity under visible light, these elements have a higher possibility to act as recombination sites which decrease the quantum efficiency [258]. Dopant concentration highly affects the enhancement of trapping sites in metal-doped TiO₂. The recombination process in metal-doped TiO₂ can be explained by using the Fe-doped TiO₂. The following reactions (equations 16–19) take place in both Fe³⁺/Fe²⁺ doped TiO₂ when they act as recombination sites. Therefore, the competition among recombination processes and interfacial charge transferring processes determine the quantum efficiency of the titania photocatalytic activity.

Table 3

Some examples of non-metal-doped TiO₂ that were tested for their antimicrobial activity.

Non-metal-doped TiO ₂ nanoparticles	Bacteria strains	Key references
N-doped TiO ₂	<i>Shigella flexneri</i> , <i>Listeria monocytogenes</i> , <i>Vibrio fischeri</i> , <i>Staphylococcus aureus</i> , <i>Streptococcus pyogenes</i> , <i>Bacillus subtilis</i> , <i>Bacillus subtilis</i> spores, <i>Bacillus thuringiensis</i> spores, <i>Bacillus anthracis</i> spores, <i>Escherichia coli</i> , <i>Streptococcus mutans</i>	[247–253]
S-doped TiO ₂	<i>Escherichia coli</i>	[179,254]
C-doped TiO ₂	<i>Escherichia coli</i> , <i>Staphylococcus aureus</i> , <i>Shigella flexneri</i> , <i>Acinetobacter baumannii</i> , <i>Aspergillus niger</i>	[255]
B-doped TiO ₂	<i>Escherichia coli</i>	[256,257]



As mentioned above, thermal instability, expensive implantation facilities, formation of secondary byproducts are the highlighted drawbacks of doping [259]. Secondary by-product formation could be explained with the Rempel et al. study. The proposed sandwich structure of TiO₂–CdS has shown the partial conversion of calcium sulfide to cadmium sulfate under visible light that resulted in a decrease of photocatalytic activity [157]. Furthermore, there is a potential to react with these metals with pollutants in the environment, leading to lowering the photocatalytic efficiency. Thus, the release of Cd can be a serious environmental problem and the generation of secondary impurities [157].

In order to get rid of the aforementioned drawbacks with doping, recent research studies have been focused on the modification of TiO₂ with 2-D nanomaterials which are better-supporting material to enhance the photoinduced catalysis such as photo-electro-catalysis, photocatalysis, and CO₂ photoreduction due to their unique planar structure, ability to provide high surface area as well as the stabilization of charge separation via trapping electrons transferred from TiO₂ [34,93,113,114]. Therefore, 2-D materials fabricated TiO₂ nanohybrids have been studied extensively in the past few years [130,260–264]. The next section provides a brief overview of the 2-D nanomaterials, especially about the graphene family and its performance to enhance the photocatalytic activity of TiO₂.

4. Development of visible light active TiO₂ by fabrication with 2-D nanomaterials

4.1. Introduction to 2-D nanomaterials

2-D nanomaterials are a new category of nanostructures with sheet-like structures and their thickness is less than 5 nm with a single or few atomic layers [267]. They are with a unique shape that endows nanomaterials with unexpected physical, chemical and biological properties. As the thinnest material, these 2D materials consist of a large specific surface area. Therefore, they possess large reservoirs and anchoring sites to accept electrons and to enhance the catalytic reactions. These nanohybrids are used in applications such as supercapacitors, batteries, photovoltaics, optoelectronics, antimicrobial agents and catalysis.

The most studied 2-D materials include graphene and graphene oxides, graphdiyne [113,265,268–270], graphitic carbon nitride (g-C₃N₄), transitional metal chalcogenides (MoS₂), hexagonal boron nitride, and layered double hydroxides, Fig. 8(A). The 2-D nanomaterials have been explored as matrices to prepare hybrids with TiO₂ in order to enhance the photocatalysis action under visible light. 2-D material modification of titania leads to remarkable performances with their large surface area which provides more sites for the catalytic reaction. Thus, the synergistic effects of the 2-D nanomaterials and TiO₂ provide remarkable catalytic behavior.

4.2. Graphdiyne modified TiO₂

Graphdiyne is a two dimensional carbon allotrope that contains both sp and sp² hybridized carbon atoms arranged in a crystal lattice [91,268]. The 2-D structure is formed with the conjugation of benzene rings by 1,3-diyne bonds [268]. It has been promising in versatile applications such as capacitors, batteries and catalysis due to its high [π]-conjugation, a natural band gap, rigid carbon mesh, uniformly distributed pores and unique tunable chemical, electrical and mechanical properties [91,268,270–272]. Li et al. synthesized graphdiyne successfully on the surface of the copper using hexa methyl benzene precursor with a cross coupling

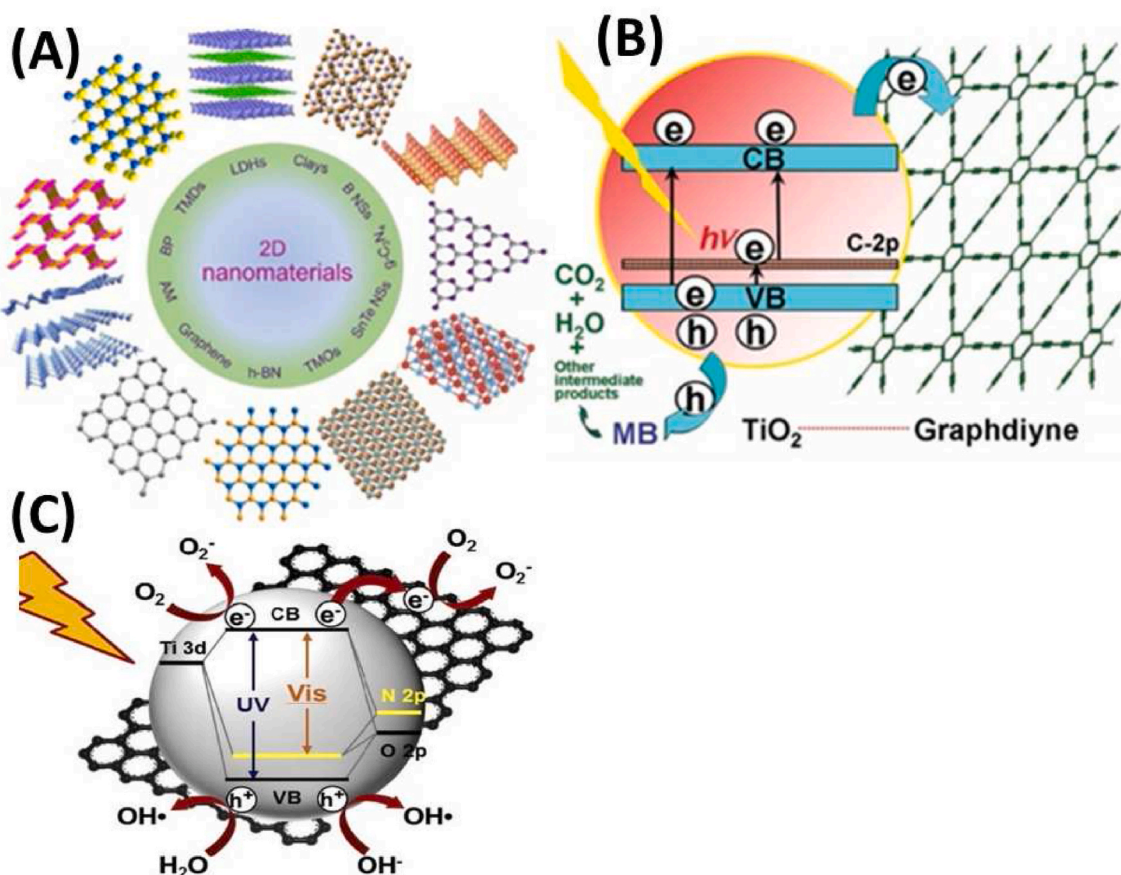


Fig. 8. (A) 2-D nanomaterials (Reproduced with permission from Hu et al. [265]), (B) Graphdiyne modified TiO₂ (Reproduced with permission from Wang et al. [94]), (C) Photocatalytic mechanism of N-doped TiO₂ coating on reduced graphene oxide (Reproduced with permission from Zhang et al. [266]).

reaction. The resultant material showed a conductivity of $2.516 \times 10^{-4} \text{ S m}^{-1}$ with more active sites for the catalysis. Jin et al. has reported graphdiyne as a novel large carbon transporting material. According to Long et al., the calculated intrinsic charge mobility for graphdiyne is $105 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at room temperature. They have analyzed electronic structures and the charge mobility for both the sheet and nano ribbon type of graphdiyne. Such an excellent electron transport property is highly beneficial in graphdiyne modified photocatalytic nanocomposite to provide a longer life time to the photogenerated electron-hole pairs. Furthermore, the large surface area provides more active sites for the catalysis process [273]. Potential photocatalysis and other applications of graphdiyne, including the graphdiyne modified TiO₂ have been extensively investigated in recent research studies due to the aforementioned advantages [91]. Studies conducted by Xue et al., Yang et al., Wang et al., and Jia et al. have suggested that graphdiyne is an ideal material to incorporate with TiO₂ [107,113]. Dong et al. have synthesized graphdiyne assembled nitrogen doped TiO₂ via a hydrothermal method for the degradation of rhodamine B under visible light. This showed enhanced photocatalytic activity of TiO₂ due to the synergistic effect of graphdiyne and nitrogen doping [108]. Yang and coworkers have reported the chemical structure and electronic properties of graphdiyne incorporated TiO₂ and reported the superior charge separation, oxidation ability compared to the pristine TiO₂. Their results suggested graphdiyne as a superior futuristic material in the field of photovoltaics and photocatalysis [107]. Graphdiyne weight percentage in TiO₂ nanohybrid has a direct effect on its performance.

Wang et al. synthesized P25-graphdiyne nanohybrid with different graphdiyne ratios via facile hydrothermal methods and proposed the 0.5% wt of graphdiyne as an optimal content to get higher photocatalytic activity, Fig. 8(B) [94]. The mechanism of the enhanced

photocatalysis by graphdiyne modified TiO₂ is still not fully understood. However, according to the studies, graphdiyne acts as a sink of electrons and accepts charge carriers excited from TiO₂ to prevent the electron hole recombination. Also, it introduced a new energy band to extend the visible light absorption [274,275]. Graphdiyne also has been incorporated into the nanowires, nanotubes, nanowalls, and nanosheets like different morphologies of titania to enhance their properties [107,108]. Wang and coworkers have synthesized graphdiyne incorporated TiO₂ nanofibers that produced abundant reactive oxidative species to show superior effect against methicillin-resistant *Staphylococcus aureus*. The resulting graphdiyne assembled TiO₂ nanofibers have shown superior biocompatibility and antimicrobial properties by oxidation of the structural components of microorganisms which leads to bacterial death [276].

4.3. Graphitic carbon nitride modified TiO₂

Graphitic carbon nitride (g-C₃N₄), is also a 2-D nanomaterial that has attracted significant attention among the scientific community for the visible light induced photocatalysis due to its 2.75 eV narrow bandgap [110,277,278]. It is composed of triazine (C₃N₃) or tri-s-triazine (C₆N₇) allotropes units with a strong covalent bond between carbon and nitrogen atoms, making it a stable carbon nitride. It can be synthesized by polymerization of dicyandiamide, melamine or cyanamide. It has a graphene-like structure with better electronic structures, chemical stability and thermal stability that can be applied in many fields. Wang et al. reported on the application of g-C₃N₄, for water decomposition that results in more and more attention on photocatalysts. They have modified TiO₂ nanorod arrays with g-C₃N₄ and showed efficient separation of photogenerated electron-holes for the efficient decomposition

of rhodamine under visible light. The moderate bandgap (~ 2.7 eV) of g-C₃N₄ in TiO₂ composite enables it to be used under visible light photocatalytic activity compared to the pristine TiO₂. TiO₂ modified with g-C₃N₄ has been widely studied by Wang et al., Lu et al., Ji et al. and Elbanna et al. have synthesized g-C₃N₄/TiO₂ mesocrystals metal free composite, which showed twenty times H₂ evolution rate compared to the pure g-C₃N₄ [86,116,279]. They have reported that the g-C₃N₄/P25 showed seven times lower photocatalytic activity compared to the g-C₃N₄/TiO₂ mesocrystals metal free composite. This observation is due to the superior interaction and synergetic effect between the plate shaped TiO₂ mesocrystals and the 2-D nanosheet shape g-C₃N₄ [279].

Guo et al. also synthesized composite of mesoporous TiO₂/g-C₃N₄ hollow core/shell photocatalyst that effectively decomposed organic pollutants such as rhodamine B, ciprofloxacin, congo red and phenol with 100%, 74%, 97% and 73% efficiency, respectively. They proposed that such an improved photocatalytic activity occurred due to the larger surface area, higher barrier for conduction bending, and close contact that lead to the efficient charge separation during the photocatalysis [280]. All these investigations show the importance of a high charge transfer rate across the interfaces for the improved photocatalytic activity [281–283]. Most of the studies suggested that g-C₃N₄ is analogous to the activity of graphene, carbon nanotube like carbonaceous materials. The antimicrobial activity of g-C₃N₄-TiO₂ nanohybrid has been reported in a few studies. Liu and coworkers have synthesized g-C₃N₄-TiO₂ nanohybrid with a vertical Z-scheme heterojunction via a facile hydrothermal method. It has shown higher antimicrobial properties by killing more than 96.8% of *Escherichia coli* within 30 min, whereas g-C₃N₄ nano TiO₂ showed 93.6% and 80% by itself, respectively [284]. Faraji and coworkers also have reported the antimicrobial activity of g-C₃N₄-TiO₂ nanohybrid. They have synthesized g-C₃N₄-SnO₂/TiO₂ nanotubes/Ti plates that showed antibacterial effects against *Escherichia coli* under both UV and visible illumination [285]. Thus, the semiconductor coupling has exhibited superior photocatalytic improvement in TiO₂ that can be a potential approach as a food coating.

4.4. Graphene modified TiO₂

Graphene is a two dimensional carbon allotrope with a honeycomb lattice structure. It is a thin single sheet of graphite and the basic structural unit of other graphitic materials, including charcoal, carbon nanotubes, and fullerenes [286]. The graphene family includes intermediate graphene oxide in its reduced form, reduced graphene oxide and pristine graphene. It exhibits many benefits, such as superior electron conductivity, chemical stability, large surface area and excellent flexibility [287–290]. Currently, Hummer's method, and its modified versions are used to synthesize graphene [266,291–293]. Of these methods, Tour's method is considered the greener approach that can be used for the large-scale production of graphene oxide with a simple protocol for various material applications. More recently Jayawardena et al. developed an even more simple method for synthesizing graphene oxide using only two components namely, KMnO₄ and H₂SO₄, thus significantly enhancing scalability of the process, which at present it commercially exploited [294]. Furthermore, both these processes do not generate toxic gasses and the temperature used in the synthesis process could be easily controlled [292,295,296].

Highly oxidized graphene acts as an electrical insulator while partially oxidized graphene acts as a semiconductor [295]. The structure, high interfacial contact, higher charge carrier mobility, large specific surface area, and electrical and thermal conductivity properties facilitate its applications in the preparation of nanohybrids. Furthermore, it is a superior candidate for the preparation of inexpensive metal free nanohybrids including graphene/TiO₂ nanohybrids with superior photocatalytic activity [130,291,295,297–299]. To date, several studies have explored the methods and benefits of the graphene and graphene oxide assembled TiO₂ for different catalysis applications [78,128,156,260,263,300]. The 2-D structure of graphene has enabled it to act as a

superior scaffold to anchor TiO₂ nanoparticles, Fig. 8(C). The ejection of photogenerated electrons from the titania to the graphene surface occurs easily because of the higher positive Fermi level of the graphene compared to the TiO₂. Briefly, the work function of TiO₂ and graphene are 4.2 eV and 4.6 eV respectively. The Fermi level of the pristine TiO₂ is much more negative compared to the graphene. Therefore, in order to maintain a constant fermi level in graphene/TiO₂ nanohybrid, at thermal equilibrium, photo generated electrons move to the graphene [301]. The π -d conjugation between the titania and graphene acts as a ladder to transferring of the electrons. Hu and coworkers have synthesized graphene/TiO₂ nanohybrid by ultrasonicate mixing and reported that the electron transferring process mainly occurs through quantum tunneling. Their findings suggested that generally 10¹¹ electrons transfer between graphene/TiO₂ nanohybrid per second under 1.5-G one solar intensity and enable better catalytic performances. Huang et al. synthesized graphene/TiO₂ nanocomposite via the solvothermal method and has discussed the effective charge transferring via Ti-C chemical bond. They described that mechanical mixing is not involved in the creation of effective interfacial contact between graphene and TiO₂ while chemical bonding enhances the better interaction between them. This chemical interaction leads to intimate special conditions for better charge transfer. This effectively reduces the recombination of photogenerated electrons and holes compared to the mechanical mixing method [172]. Furthermore, as we know, graphene is a superior futuristic material with a high electron conductivity. When an electron ejects to the graphene surface as above mentioned path, it acts as an electron sink and transfers the electrons throughout the graphene network. Thus the delocalized π electrons suppress the recombination of photogenerated electron-holes and enhance the life time for the improvement of photocatalytic activity [5,172,302–305]. Several studies have proposed that Ti-O-C bond formation in graphene/TiO₂ nanohybrid is important to extend the light absorption range in the spectrum. Therefore, the chemical bonding of graphene oxide with TiO₂ has narrowed down the E_g resulting in nanohybrid response to the visible light range [306–310]. Furthermore, graphene's high surface area enhances the absorption of reactants, allowing for the most efficient photocatalytic degradation of microbes [311,312]. However, some studies show that adding more graphene to TiO₂ nanohybrids reduces photocatalytic activity by preventing TiO₂ from coming into direct contact with pollutants [313]. Stengal et al. suggested that increasing graphene reduces the photocatalytic degradation of butane. Therefore, the synthesis of graphene/TiO₂ nanohybrid with an optimal ratio of graphene oxide or graphene and TiO₂ is important to obtain higher photocatalytic activity [125]. Studies such as Zang et al., Cao et al. [129], Stengal et al. [125] also proposed that some specific amount of graphene is enough to synthesize graphene/TiO₂ nanohybrid with high performance under visible light and excessive amount of graphene resulted to decreasing the surface area due to the agglomeration graphene oxide.

In-situ crystallization and ex-situ hybridization are extensively used in the synthesis of graphene oxide/TiO₂ nanohybrids. In ex-situ hybridization, pre-synthesized TiO₂ nanoparticles are dispersed in graphene or graphene oxide dispersion using mechanical mixing and ultrasonication [314,315]. Studies of Morawski et al. [314], Yong et al. [316], and Ramesh Raliya et al. [315] have reported the use of the ex-situ hybridization method to improve the quality of the graphene oxide or graphene/TiO₂ nanohybrids. However, some of the formed nanohybrid with ex-situ hybridization showed non-uniform and low density distribution of nanoparticles on the graphene sheets [317]. Therefore, in-situ crystallization method is the most widely used method and uses graphene oxide/graphene as the initial material, which acts as a nucleation point for the distribution of TiO₂ nanoparticles. A wide range of methods such as electrochemical deposition, solvothermal, hydrothermal method, sol-gel, microwave and self-assembly have been reported in literature [266,308,318–321]. The graphene/TiO₂ nanohybrid showed a lower recombination rate, smaller band-gap energy with improved photocatalytic activity. Table 4 summarizes some

Table 4

Some examples of graphene/graphene oxide fabricated TiO₂ that were tested for their antimicrobial activity.

Composite	Microorganisms	Key references
TiO ₂ /reduced graphene oxide based nanohybrid	<i>Escherichia coli</i> , <i>Pseudomonas aeruginosa</i> , <i>Staphylococcus aureus</i> ,	[322]
TiO ₂ /reduced graphene oxide photocatalyst	<i>Escherichia coli</i>	[323]
Graphene oxide/TiO ₂ /PVA	<i>Escherichia coli</i> , <i>Pseudomonas aeruginosa</i> , <i>Staphylococcus aureus</i> , <i>Streptococcus oralis</i>	[300]
Ultrafine TiO ₂ /graphene sheets nanocomposite	<i>Escherichia coli</i>	[129]
Ag/TiO ₂ /graphene composite	<i>Campylobacter Jejuni</i>	[324]
Bi-phasic TiO ₂ nanoparticles grown on reduced graphene oxide	<i>Bacillus subtilis</i> , <i>Escherichia coli</i>	[325]
Reduced graphene oxide/TiO ₂ nanohybrid	<i>Staphylococcus aureus</i> , <i>Escherichia coli</i>	[122]
Graphene oxide - TiO ₂ nanorod composite	<i>Escherichia coli</i>	
Magnetic graphene oxide/TiO ₂ composites	<i>Escherichia coli</i>	[326]
Graphene oxide and chitosan loads TiO ₂	<i>Aspergillus niger</i> , <i>Bacillus subtilis</i>	[85]

examples of graphene/graphene oxide fabricated TiO₂ for its applications as an antimicrobial agent. Interestingly, graphene/graphene oxide/TiO₂ shows higher antimicrobial activity under visible light compared to the pristine TiO₂ (see Table 5).

5. Prospective opportunities of modified TiO₂ photocatalysis in the food industry

Contamination of foods with microorganisms may occur throughout the food chain. Fresh vegetables as well as fruits are susceptible to a variety of damages and spoilage by pathogenic microorganisms. Novel technologies have proved to be energy efficient and cost effective alternatives compared to the conventional practices. In this regard, both academia and industry have been focusing on developing novel technologies for preservation of food and they are under consideration. One such emerging technology is the use of titania photocatalysis [166]. TiO₂ photocatalysis is an emerging non-thermal technology that has shown to efficiently inactivate food-borne pathogens [322,327]. UV-assisted TiO₂ photocatalysis has been widely explored as a food preservative material due to its relatively inexpensive nature and the relatively oxidizing power under UV light. Furthermore, the United States Food and Drug Administration has approved the use of titania as an additive in human foods, cosmetics, drugs and food contact materials.

As discussed in the previous sections, TiO₂ nanoparticles have been widely studied for their applications owing to their excellent antimicrobial performance against a wide range of microorganisms including fungi, gram positive bacteria, gram negative bacteria. In addition, low cost, chemical stability, non-toxicity and eco-friendliness of TiO₂ titania provide a feasible and alternative technology to encourage its further applications in the food industry [328]. For instance, TiO₂ powder coated photocatalyst packaging films have been developed by incorporation of TiO₂ nanoparticles into different polymers such as chitosan, carrageenan, polyvinyl chloride etc matrices. Some of these matrices such as chitosan also possess antimicrobial properties [329,330]. Siripatrawan and coworkers have reported the fabrication of chitosan-TiO₂ nanocomposite film as ethylene scavenging and antimicrobial active food packaging. They have prepared active packaging with chitosan and different TiO₂ concentrations (0, 0.25, 0.5, 1 and 2% w/w). The results suggested the potential use of chitosan film containing 1% TiO₂ against Gram-negative (*Escherichia coli*, *Salmonella*, *Typhimurium* and *Pseudomonas aeruginosa*), Gram-positive (*Staphylococcus aureus*) bacteria and

Table 5

Combination of visible light active TiO₂-polymer systems to improve the properties of food packaging materials.

Material	Property changes	Food applications	References
Poly (butylene adipate-co-terephthalate)/TiO ₂ /silver composite biofilms	Films with unique antibacterial performance against <i>Escherichia coli</i> ,	Potential to use as a food packaging for cherry tomatoes under visible light	[336]
Au-TiO ₂ /Sodium Alginate nanocomposite films	Films with improved antimicrobial activity against <i>Staphylococcus aureus</i> and <i>Escherichia coli</i> under visible light and easy degradation	Great potential in food packaging industry	[337]
Carboxymethyl cellulose/Copper doped TiO ₂ films	Films with high antibacterial activity against foodborne pathogenic bacteria (<i>Listeria monocytogenes</i> , <i>Escherichia coli</i>) under visible light	Effectively delaying the banana's browning with strong antibacterial and ethylene scavenging capability under visible light, has a high potential in extending the shelf life of fruits	[338]
Cobalt-doped TiO ₂ nanoparticles for antibacterial coatings	Antibacterial coating with enhanced effect against food borne Gram negative pathogens (<i>Campylobacter jejuni</i>) and Gram positive pathogens (<i>Staphylococcus aureus</i>)		[339]
Polyvinyl alcohol based Cu ₂ O-TiO ₂ /reduced graphene Oxide polymer nanocomposite films	High antimicrobial activity against both Gram positive and Gram negative bacteria	Great potential to be used in food packaging applications under ambient light conditions.	[300]
Carrageenan-based functional films integrated with CuO-doped TiO ₂ nanotubes	Exhibited high antibacterial activity than bare titania under visible light	Banana packaged with the films retained high quality in terms of weight loss, firmness and surface color	[340]
TiO ₂ nanoparticles co-doped with Nitrogen and fluorine	Exhibited antifungal activity against <i>Fusarium oxysporum</i> fungal growth under visible light	Completely inhibit the <i>Fusarium oxysporum</i> fungal growth in tomato fruit and potential to be used for sunlight-based fungal and bacterial disinfection application.	[341]

fungi (*Aspergillus* and *Penicillium*). Their results suggested the use of chitosan-TiO₂ films as active packaging for fresh produce. Thus, the synergistic effect of such polymers and TiO₂ offered a superior food preservation capability [331,332].

Kaewklin and coworkers synthesized active packaging film by incorporating nanosized titania into chitosan to extend the shelf life of cherry tomatoes when exposed to UV light. They confirmed the efficient use of chitosan-TiO₂ nanocomposites for the preservation of climacteric fruits under UV light for commercial applications [331]. The study of Hosseinzadeh et al. also provides evidence regarding the use of TiO₂ incorporated chitosan films. The author suggested that there is a higher potential to use chitosan/Cymbopogon citratus essential oil/TiO₂ food

packaging for the enhancement of the shelf life of fruits and vegetables [333]. However, as mentioned in the above sections, TiO_2 incorporated packaging films that showed their antimicrobial activity under UV light. Thus, the above benefits are limited to UV light. According to the literature, the exposure to UV rays damage the organs, mainly eye's of the human (visual defects), reduce the functionality of the immune system and the performance of the plastic packaging material may be reduced with the prolonged exposure to the UV rays [334]. Thus, it is impractical to use UV source to excite the electron-hole pairs in the polymer- TiO_2 systems for the applications in the food industry. Therefore, the development of visible light active nanocomposite system is considered of technological interest and practical importance. Several research studies are under consideration to enhance the photocatalytic performance of TiO_2 to the visible region [335]. As explained in the above sections, doping including metal doping, non-metal doping and 2-D nanomaterial fabrication have a potential to enhance the photocatalytic activity of titania to the visible region. Thereby, ensure to get rid of above mentioned problems arising with the utilization of UV light.

Although there are plenty of records on the utilization of TiO_2 for applications such as water purification, air purification, electronics etc., there is very limited research on doped TiO_2 for the food applications under the visible light, see Table 5. Recently, Ezati and co workers have reported the food applications of Cu doped titania and CuO doped TiO_2 by using banana as the demonstrating material [338,340]. As shown in Fig. 9, Ezati et al. has synthesized Carrageenan-based films by incorporating CuO doped TiO_2 nanotubes which exhibited an excellent performance to delay the ripening process of bananas for 12 days compared to the TiO_2 nanoparticle incorporated films. These films have shown antimicrobial activity against food pathogens such as *Escherichia coli* and

Listeria monocytogenes [340]. Cu-doped TiO_2 also has shown a better photocatalytic activity and antimicrobial mechanism under visible light as explained in the above section. Ezati and coworkers have synthesized Cu-doped TiO_2 and incorporated it with the carboxymethyl cellulose to act as a potential food packaging film. According to their results, shown in Fig. 10, it has enhanced the shelf life of bananas for 14 days. This is because the band structures of Cu and TiO_2 coincide with each other [338]. Song et al. also reported the potential of $\text{BiVO}_4/\text{P25}$ composites for the enhancement of the post harvest life of fruits and vegetables [342]. Li and coworkers also prepared Poly (Lactic acid)/nano TiO_2 /nano Ag blend films by using the solvent volatilization method and it has shown antimicrobial activity against food pathogens such as *Escherichia coli* and *Listeria monocytogene*. This suggests that the nanohybrid produced by them could be used as an antimicrobial nano-blend food packaging film without food safety risks [330]. Herein, explains the ability of doped TiO_2 to act as a potential food preservation material under visible light.

2-D materials also exhibit better antimicrobial properties [343–345]. The sharp edges of the graphene can kill microorganisms by direct contact with them. Also the high surface area provide large space to isolate microorganisms from the environment, resulting in the physical disruption of microbial cells [28,39,346–348]. Zhang et al. reported the antibacterial activity of 2D graphdiyne oxide. It showed reactive oxygen species-dependent antibacterial action [344]. Therefore, the fabrication of 2-D nanomaterial with TiO_2 amplifies the antimicrobial activity compared to the antimicrobial effect of pristine TiO_2 [326,349]. Wanag et al. also reported the antimicrobial activity of graphene- TiO_2 nano-hybrid against *Escherichia coli*. Bacterial inactivation has been tested by changing the reduced graphene oxide percentage and the light exposure

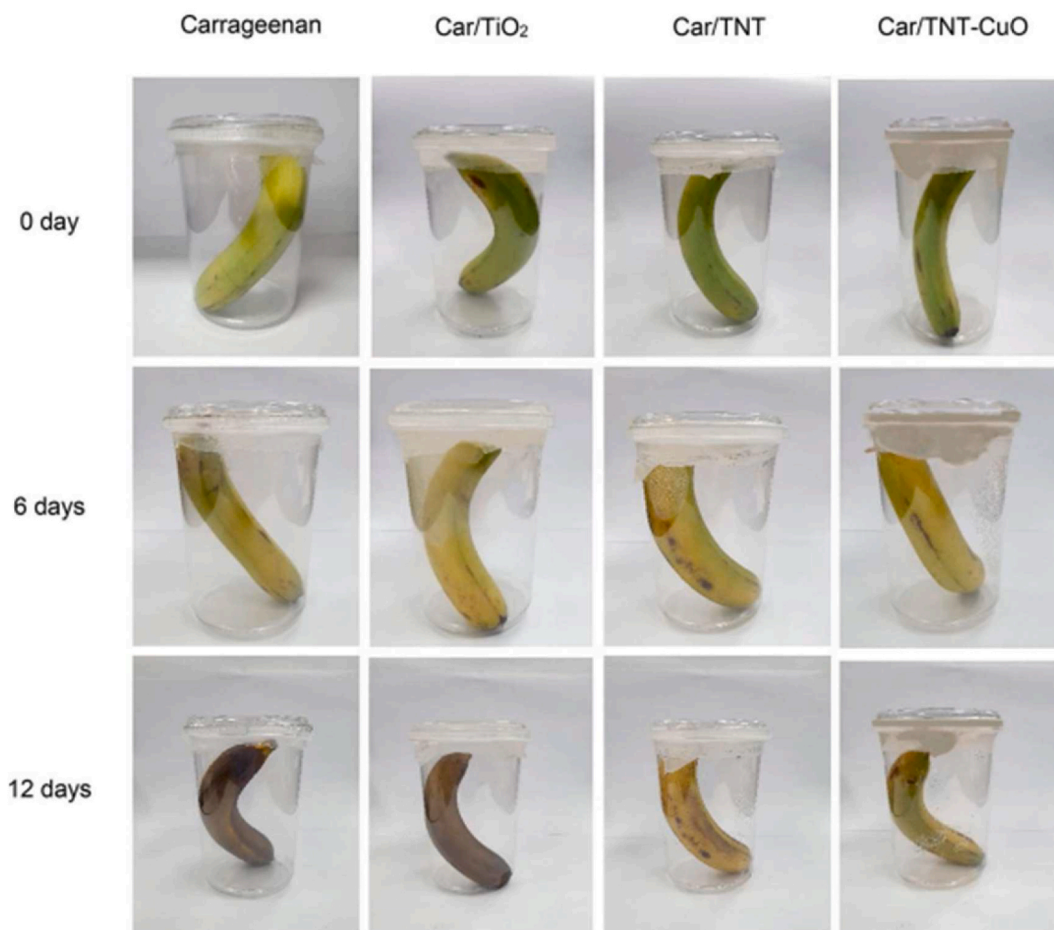


Fig. 9. CuO doped TiO_2 for visible light active food packaging application (Reproduced with the permission from Ezati et al. [340]).

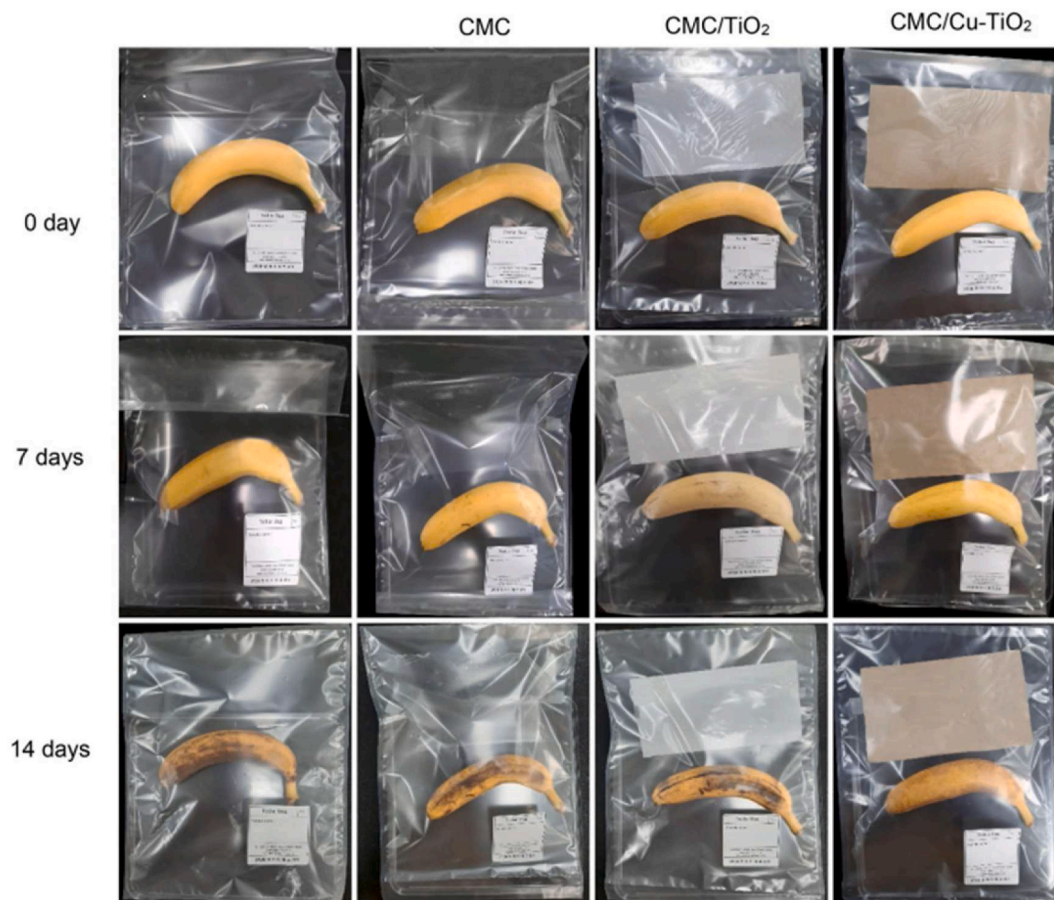


Fig. 10. Cu-doped TiO₂ for visible light active food packaging application (Reproduced with the permission from Ezati et al. [338]).

time. These results explain the different antimicrobial mechanism steps of graphene-TiO₂ including the adherence of TiO₂ to the *Escherichia coli* cell, and damage of the molecular components of the cell (DNA, lipid and proteins). The constant generation of hydroxyl radicals and superoxide radicals degrade the cellular components by making oxidative stress in cells and preventing bacterial growth. Disruption, furrowing, and crumpling of cell wall structure demonstrate the antimicrobial mechanism steps clearly [323]. The combination of several reinforcement materials with graphene-TiO₂ nanohybrids is important to obtaining higher antimicrobial activity under visible light.

El-Shafai et al. has synthesized nanocomposite with zinc oxide nanoflower, graphene oxide, silver and TiO₂ nanoparticles. It has shown antimicrobial activity against *Staphylococcus aureus*, *B. anthracis* like gram-positive bacteria and *Escherichia coli*, *P. multocida* like gram-negative bacteria. They have reported that this nanohybrid has a significant impact on the gram negative bacteria compared to the gram positive bacteria. Graphene oxide has shown higher antibacterial activity by generating reactive radical species, sharp edges that can damage cell walls while Ag nanoparticles cause bacteria cell death by damaging cell membrane, disturbing DNA replication. TiO₂ and ZnO exhibit this property by generating reactive radical species. Therefore, the total combination of above mentioned components has shown higher resistance against the growth of microbes [350]. However, there are few studies of graphene oxide-TiO₂ in packaging applications [300, 324]. Dhanasekar and co-workers have studied the polymeric Cu₂O-TiO₂/reduced graphene oxide nanohybrid and it has demonstrated higher antimicrobial activity against *Staphylococcus aureus* compared to *Escherichia coli*, *Pseudomonas aeruginosa* and *Streptococcus oralis* [300]. They have used solution casting techniques to prepare films. The resulting product has shown higher degradation of microorganisms and

it can be used as an antimicrobial agent in food packaging [300]. Thomas et al. prepared alginate-graphene oxide assembled TiO₂ nanohybrid that shows 98% efficient photocatalytic activity to degrade Congo red dye under direct sunlight. The production method used in this study could be used to synthesize films for food packaging. The dissipative convection method has been used to synthesize TiO₂ and graphene oxide incorporating strontium/alginate/carboxyl methyl cellulose nanocomposite. Initially, graphene oxide and TiO₂ were added to the mixture of Sodium alginate, carboxymethyl cellulose and strontium chloride to obtain homogenized dispersion following freeze drying to obtain a composite system [351].

Xu et al. reported the antibacterial activity of chitosan, graphene oxide and TiO₂ for the preservation of fruits and vegetables from microbial attacks. The films prepared by them have shown less permeability to the moisture and antibacterial activity against *Bacillus subtilis* and *Aspergillus niger* [85]. More recently, Noreen et al. fabricated visible light active silver-graphene/TiO₂ nanocomposite via hydrothermal process. The resulting product showed effective antimicrobial activity against food pathogens such as *Campylobacter jejuni*. This photocatalyst exhibits the best bacterial inactivation as well as the inhibition of biofilm production making its promising coating to be used to prevent the spread of *Campylobacter jejuni*. [324]. It is noteworthy to mention that modified TiO₂ nanoparticles can be used as a promising antimicrobial coating for the prevention of the spread of foodborne pathogens and for the post harvest management and extending the shelf life of foods such as fruits and vegetables.

6. Challenges and limitations

As a commonly used photocatalytic material, TiO₂ has received

significant research attention. However, the high recombination rate and the low photocatalytic activity under visible light are major drawbacks that limit its practical applications. Therefore, enhancement of its photocatalytic activity under visible light is more concern. Doping and the fabrication of titania with 2-D nanomaterial are currently explored to counter these limitations of TiO₂. Compared with bare TiO₂, these modified methods have shown efficient photocatalytic activity under visible light. Despite significant advances in the study of modified TiO₂, the use of these nanohybrids in food-related applications remains a big challenge. As discussed above, this is a non-thermal antibacterial activity that reduces the microbial contamination of food. However, to obtain better disinfection efficiency, it is necessary to present a higher surface area. If not, photocatalytic activity may not be obtained as expected. Another unavoidable problem with this modified TiO₂ photocatalyst is the difficulty in separating the catalyst from the system after the usage and reusability of the photocatalyst. As discussed earlier, it is necessary to present photo-generated radical oxygen species (ROS) to inactivate the microorganisms as well as to decompose organic substances. However, there is a higher probability of oxidizing these foods by radical oxidative species. This limits the application of photocatalyst to preserve food following unnecessary odor and other adverse effects on the sensory quality of the product. Therefore, in the future, the focus should be on developing this modified-TiO₂ nanohybrid incorporating plastic films, coatings, etc., to preserve the food without any toxic effect. Nevertheless, further works are required to advance the applications to a practical level, such as studying the biological effects of modified TiO₂ on food applications and further study of its toxic effects in food to utilize the photocatalytic activity under visible light.

7. Conclusion

TiO₂ is one of the important semiconductors, and it has been studied widely due to its photocatalytic activity and excellent chemical stability. However, TiO₂ has a wide band gap, and it can be activated only by UV light, which has only 4% of the solar spectrum. Therefore, several techniques have been used by researchers to overcome these shortcomings of TiO₂ photocatalysis and to shift and enhance the absorption at visible regions. Metal doping and fabricating with 2-D nanomaterials such as graphene and graphene oxide are novel and innovative approaches that enhance photocatalytic properties of TiO₂. Especially, 2-D nanomaterial incorporated TiO₂ led to a decrease in the bandgap energy of the prepared TiO₂ nanohybrids and reduced the recombination rate of photo-generated electrons and holes during the photocatalytic activity. In addition, it provides a large surface area to facilitate higher photocatalytic activity. This has led to a significant increase in research studies to enhance the functionality of TiO₂ nanohybrids for wide applications in different fields, including food preservation.

This review provides an overview of recent research development on the application of modified TiO₂ for food preservation due to its antimicrobial activity. Modified TiO₂ photocatalysts act as an antibacterial agent and offer an alternative approach for reducing the risk of microbial contamination on different foods. Furthermore, better disinfection efficiency can be obtained under visible light. However, most of the applications of this modified TiO₂ have been investigated for water purification and air purification, while a limited number have targeted food preservation. Therefore, there is greater scope in this area as food production sustainability is becoming a global issue as we head into the future. Research to develop new products and applications of these doped and 2-D nanomaterial fabricated TiO₂ nanohybrid in food preservation needs to continue to increase in number and variety. Current research in this area suggests that there are more potentials to prepare visible light active photocatalysts by modifying TiO₂ for food application.

Overall, the visible light active TiO₂ nanohybrids have a great potential in food preservation applications. To make further inroads in this area, the interdisciplinary collaborations between experts in the fields of

material science, chemical engineering, chemistry, and nanotechnology is a need of the time. Application of doped and 2-D nanomaterial fabricated TiO₂ in food preservation may only enter the market after approval. It is necessary to monitor the safety of new products for the consumer and for the environment. In addition, dedicated studies are required to enhance the application of photocatalytic activity of modified TiO₂ in food preservation. We hope that this brief review contributes to boost the enthusiasm in developing efficient photocatalysts to solve some pressing global problems, especially global food security.

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Availability of data and materials

Not applicable.

Funding sources

This work was supported by the World Academy of Sciences [TWAS grant number 19-237 RG/CHE/AS_G-FR3240310129, 2019].

Declaration of competing interest

The authors declare that they have no competing interests.

Acknowledgements

Not applicable.

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