



Review article

Photocatalytic microbial disinfection under indoor conditions: Prospects and challenges of near IR-photoactive materials

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ABSTRACT

The accumulation of microbes especially in the air and in water bodies is causing the major disease outbreaks. Indoor environment remediation methods are necessary today to clean up these microbes. Among the remediation methods available, in situ generation of highly reactive and oxidizing radical species by advanced oxidation processes (AOPs) inactivate most of the microbes unselectively. Of these AOPs, photocatalytic microbial disinfection especially under indoor conditions is of great interest to maintain microbe-free indoor environment. For efficient microbes' inactivation under indoor conditions, the near IR and IR response of the photocatalysts must be improved. Though the photocatalytic disinfection of microbes using semiconductor-based photocatalysts has been extensively investigated, most of the photocatalysts that have been investigated are either weakly responsive or totally not responsive to IR photons due to inappropriate bandgap energies. Several strategies have been investigated to enhance the light harvesting properties of semiconductor based photocatalysts under indoor conditions and make them active to near IR and IR radiations. This review summarizes the recent progress in the field of materials for photocatalysts employed for microbial removal in indoor environments over the past decade as well as outlines key perspectives to enlighten future researches. The paper details the fundamentals of photocatalysis and basic properties of photocatalytic materials in the disinfection of common microbes under indoor conditions. The applications of photocatalytic materials in the disinfection of microbes in indoor environmental conditions are discussed and reviewed. Finally, the remaining challenges and future strategies/prospects in the design and synthesis of IR (and near IR) responsive photocatalysts are discussed.

1. Introduction

Sustaining of worldwide health security is of great challenge with ever increasing populations, recent global developments and owing to uncertain global climate changes. One such health security concern is the biohazards (i.e. medical waste, microorganisms or toxins) which pose a threat to the health of living organisms that could cause a variety of diseases to humans and animals. Common infectious diseases in humans and animals are caused by pathogens such as cryptosporidium parvum, *Helicobacter pylori*, *E. coli* O157:H7, swine influenza virus H1N1, severe acute respiratory syndrome coronavirus (SARS-CoV), rotavirus, norovirus, COVID 19, tuberculosis, and nontuberculous mycobacteria (e.g., *M. chelonae*) are of growing concern to the general public and especially for the infection-control authorities (Weber and Rutala, 2001). Several outbreaks of pandemics such as the Spanish flu

of 1918–1919 (H1N1), which was considered by far the most lethal flu pandemic infecting about a quarter of the global population and killing more than 40 million people (Johnson and Mueller, 2002), H5N1 strain of avian flu (de Jong and Hien, 2006), the Severe Acute Respiratory Syndrome coronavirus (SARS-CoV) (Delgado-Roche and Mesta, 2020), have been experienced in the past and recently COVID 19 in 2020. Henceforth, increasing concerns about these pandemics have attracted worldwide attention in disinfection of microorganisms.

In order to prevent the transmission of diseases and infection, the proper control of microorganisms is essential as most micro-organisms are known to survive on surfaces for extended periods of time. Disinfection is defined as the treatment of surfaces/equipment using physical/chemical means such that the amount of microorganisms present is reduced to an acceptable level (van Asselt and te Giffel, 2005). The common physical methods are temperature, desiccation, osmotic

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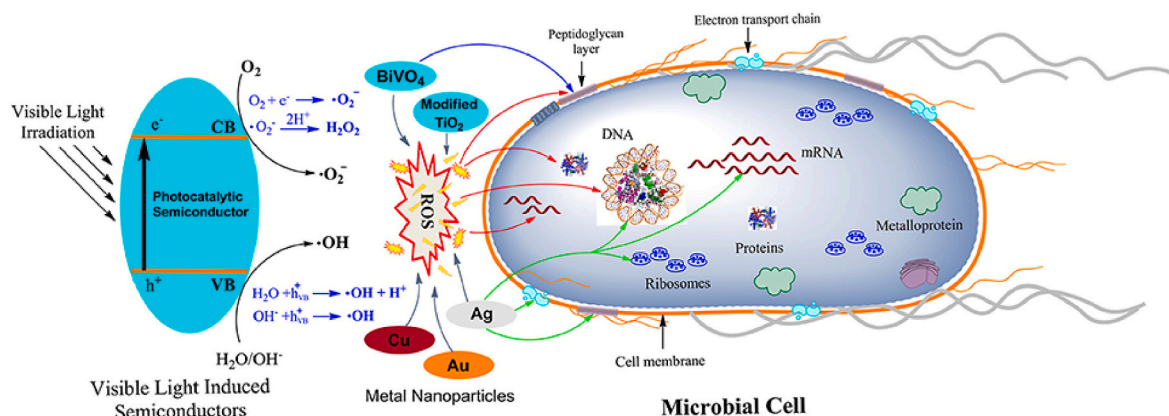
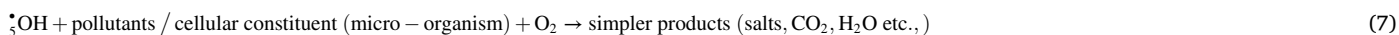
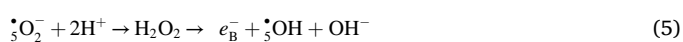


Fig. 1. The possible mechanisms of antimicrobial activities exhibited by different photocatalytic semiconductors. In the left side of the figure, the activation of the photocatalytic semiconductor by visible light is shown. Red colored arrows point the targets of reactive oxygen species (ROS) generated by various semiconductors. The blue color arrow represents the target of BiVO_4 . Ag, Cu, and Au metal nanoparticles are also known to generate ROS and targets different parts in the cell. The green color arrow represents targets of Ag nanoparticles. Different targets in the microbial cells are labeled within the cell. (Adapted from (Regmi et al., 2018) open access, Copyright 2018, Frontiers in chemistry).

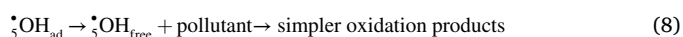
pressure, radiation, and filtration while chemical methods include the use of disinfectants, antiseptics, antibiotics, and chemotherapeutic antimicrobial chemicals. Though the current disinfection processes such as chlorination, ozone, and ultraviolet are effective in removing microorganisms to a certain extent, these methods results in the formation of harmful by-products, i.e. production of strong carcinogens and trihalomethanes, haloacetic acid, bromate in the chlorination process (Alkhudhiri, 2021). Though, the ultraviolet and ozone methods are effective, their high cost, energy consumption and also harmful nature make them non-environmental-friendly microbe disinfection methods. Nevertheless, most of pathogens are susceptible to currently available disinfectants processes, innovative environmental-friendly microbe disinfection methods without secondary pollution and high cost are the requirement of the present day. Essentially, these microbe disinfection methods should be healthy and not impede the normal life-quality of occupants and keeping the ecosystem healthy. In this respect, semiconductor based photocatalytic oxidation process is one of the main advanced oxidation processes (AOPs), which has proven to be efficient

and $\cdot\text{OH}$ ROS species are 10^{-5} , 10^{-6} and $\sim 10^{-9}$ s respectively (Attri et al., 2015). These highly oxidative reactive species attack and damage the cell wall/membrane of microorganism and destroy them (Cai et al., 2019; Dalrymple et al., 2010; Nosaka and Nosaka, 2017; Regmi et al., 2018).



in degrading a wide range of pollutants and disinfecting a variety of pathogens, including bacteria, viruses and fungi (Akerdi and Bahrami, 2019; Chan et al., 2011; Duan et al., 2021; Mazivila et al., 2019). The major advantage of photocatalytic disinfection of pathogens over the classical purification techniques is that pathogens can be completely eliminated by the inhibition of their proliferation, disinfection and degradation of the toxins and by-products produced by pathogens (Hu et al., 2022; Yang et al., 2021a).

In photocatalysis, as shown in Fig. 1 and reactions (1) to (8), upon irradiation of semiconductor by UV, visible or NIR/IR light depending on the band gap energy (E_{BG}) of the semiconductor, photo-generated electrons (e_{CB}^-) and holes (h_{VB}^+) are formed in the conduction band (CB) and valence band (Ahire et al.) respectively. Consequently, photo-generated electrons react with dissolved oxygen to produce reactive oxygen species (ROS) such as oxygen radicals ($\cdot\text{O}_2^-$), singlet oxygen (${}^1\text{O}_2$) while photo-generated holes react with water or adsorbed OH groups to produce hydroxyl radicals ($\cdot\text{OH}$) and the solar-driven photocatalytic generation and effects of various reactive oxygen species is reviewed by Liu et al. (2021b) The corresponding half-life of $\cdot\text{O}_2^-$, ${}^1\text{O}_2$



The fundamentals of photocatalytic microbes' disinfection mechanisms have been described and surveyed by Dalrymple et al. (2010). With the exception of viruses, as most common pathogens i.e. bacteria and fungi have same cell structure, their disinfection proceeds in a similar way. Though the exact mechanism of cell death in photocatalysis based on semiconductor based nanoparticles is currently unknown, as described by Regmi et al. it could be multiple modes of actions which could be due to oxidative stress induction by the oxidation of cell by photogenerated ROS leading to the peroxidation of lipid membrane and then attacking proteins that would depress the activity of certain periplasmic enzymes and finally interact with DNA and damage it (Fig. 1) (Dalrymple et al., 2010; Regmi et al., 2018).

As shown in Fig. 1, microbes degradation mechanisms can be explained as follows: (i) in the oxidative stress induction mechanism, ROS exert a different level of stress reactions to the peptidoglycan layer, electron transport chain system, genomic materials (DNA, RNA),

proteins, ribosomes etc., in the cell damaging process. Moreover, ROS also enter the cell membrane and depress the activities of various proteins essential for physiological processes in the cell, while increasing the expression pattern of oxidative stress-induced genes (Bains et al., 2019; Cabisco Català et al., 2000; Padmavathy and Vijayaraghavan, 2011; Ray et al., 2018); (ii) metal ion release; - the metal ions that would release from metal oxide semiconductors can be percolated through the cell membrane and attack the -SH, -NH and -COOH group of nucleic acid and protein and finally damage them (Daub et al., 2020); (iii) non-oxidative mechanism; - without oxidative stress induction, microbes are inactivated by decreasing the critical cellular metabolism i.e. protein, amino acid, nucleotide, energy, and carbohydrate metabolism while the non-oxidative stress cell death mechanism is poorly understood (Leung et al., 2014). In the case of viruses disinfection by ROS, the protein capsid of virus is attacked by ROS resulting in photodegradation of the protein capsid and subsequent destruction of genome by ROS leading to the death of virus (Costa et al., 2012; Habibi-Yangjeh et al., 2020a; Zhang et al., 2019).

2. Microbial disinfection under indoor conditions

Indoor conditions microbial disinfection by AOT is important in places such as clinics, offices, gyms, hospitals, industries, and buildings because it is impossible to completely remove microbes with common cleaning and detergents. As people spend approximately 85% of their time indoors, there is a high risk of microbe exposure because the air we breathe in indoor environments is frequently contaminated. Non-thermal plasma (NTP), thermal treatment, use of antimicrobial material-embedded filters, ultraviolet (UV) light, and photocatalysis (Chirumbolo et al., 2023a; Mohite et al., 2022; Xu et al., 2011; Yu et al., 2009) are the promising indoor air purification techniques for the disinfection of indoor microbes. Each technique has many disadvantages, i.e. in NTP method, formation of secondary pollutants (e.g., ozone, CO, or NO_x) (Ryan et al., 2010), thermal treatment method consumes much power to apply thermal energy at high temperature (Hwang et al., 2010), frequent replacement of antimicrobial material-embedded filters, etc. Hence, photocatalytic disinfection in indoor condition is an innovative and promising technology, and also a good alternative to overcome the limitations of the aforementioned techniques. Moreover, it has many advantages including non-selective disinfection of pathogens, relatively low cost and simplicity in the operation and maintenance (Szeto et al., 2020). Though water disinfection has received considerable attention, microbial disinfection has received less attention. Microbial disinfection under indoor conditions is distinct in that photocatalyst excitation is limited by low light intensity, necessitating the use of high-absorption coefficient light harvesting materials. Furthermore, biological indoor air treatment must have the ability to cleanse vast amounts of air in tiny spaces. Despite the fact that AOT based methods that used NIR/IR active photocatalysts in indoor conditions have many advantages, such systems have not been fully investigated. Inactivation of airborne bacteria by photocatalysts has demonstrated greater capability than inactivation of airborne fungi and viruses. This is due to differences in resistance abilities such as bacterial and viral cell composition, complexity, structure, and resistance. (Ahmadi et al., 2021) Given that pathogenic microbial infections can be spread in three ways: through droplets, direct contact, and airborne transmission, focusing on microbial infection reduction through these channels is highly recommended. The development of purifiers that need shorter time is better as compared with conventional air purifiers. (Ahmadi et al., 2021; Habibi-Yangjeh et al., 2020b). However, the photocatalytic disinfection mechanism is still in its infancy, and in these disinfection methodologies, the effective catalyst dose, light intensity, and contact time must all be known. (Dalrymple et al., 2010b; Ojha, 2020; Zhang et al., 2020).

As the world was impacted by the pandemic virus spread known as COVID-19, attention has recently been focused on the introduction and

improvement of devices used for bacterial disinfection in urban areas. With this global challenge, scientists and researchers focused on pandemic sanitization strategies to keep people alive. This research urged the development of efficient indoor disinfection in larger scale public crowded areas, such as public transportation, supermarkets, hospitals, and banks. U. Tirelli et al. reported on a recently patented effective adhesive photocatalytic membrane made of nanosized TiO₂-Ag nanoparticulate (WiWellTM), which was used to study its activity in public transportation areas. This study found a significant reduction in microbial pollution. (Umberto et al., 2022). This resulted in securing congested urban environments and maintaining a clean and healthy environment for the general public, ranging from children to adults. (Chirumbolo et al., 2023b). Painting with photocatalytic paints or coating with photocatalytic ceramics in an indoor environment, on the other hand, allows for the neutralization of microbes in the air. Hence, in this review our focus is on the recent progress of NIR-driven photocatalysts design and applications for microbial disinfection that would stimulate for future material design for efficient NIR driven photocatalysts. Because the disinfection of pathogens by oxidative stress induction by photogenerated ROS in indoor environmental conditions is the primary focus of this review, the discussion is limited to applications of photocatalytic materials in the disinfection of microbes, primarily with NIR and IR radiation, though UV and visible light active photocatalytic disinfection of microbes is briefly discussed when necessary. The review was structured in such a way, bandgap engineering, an upconversion strategy, the plasmon effect, and sensitization methods to harvest NIR/IR radiations for microbial disinfection is discussed and finally addressed the challenges and prospects for future development of NIR-driven photocatalysts for microbial disinfection under indoor conditions.

2.1. Photocatalytic materials in the disinfection of microbes under indoor conditions

TiO₂-based nanomaterials have been established as promising photocatalysts disinfection of microorganism (Reddy et al., 2017). However, the use of pure TiO₂ in indoor conditions as an effective photocatalyst is restricted owing to fact that the TiO₂ can only be activated by lights in the near-UV region due to its large band gap (Kumar and Devi, 2011; Raza et al., 2019). Low-band gap semiconductors that can harvest visible and near IR radiations are the most appropriate materials to be used as photocatalysts in indoor conditions (Mavridi-Printezi et al., 2021; Yang et al., 2021a). In recent years, emerging of new types of photocatalysts that are active under visible and near-IR lights resulted in achieving a reasonable progress in the photocatalytic disinfection of microorganisms in indoor conditions (Guillard et al., 2008; Pelaez et al., 2012). i.e. Chemically exfoliated MoS₂ (ceMoS₂) and functionalized Nano-MoS₂ have been successfully employed as a NIR driven microbe disinfection as an alternative to common near IR catalysts such as TiO₂, owing to its high surface-area-to-mass ratio, colloidal stability in aqueous media and importantly, its ability to harness NIR photons efficiently (Chou et al., 2013; Yin et al., 2016). In addition, the modification of high band gap semiconductors to shift their light absorption capacity towards visible light also resulted in development of novel photocatalysts that are active under near IR radiations (Giovannetti et al., 2017; Jing et al., 2013; Kumar and Devi, 2011; Majumdar and Mahanta, 2020; Park et al., 2013; Reddy et al., 2016; Wang et al., 2015).

2.2. Disinfection of microbes with near IR and IR light active catalysts

Photocatalytic oxidation involves an interaction between the photocatalyst, light and the pollutant and the photocatalyst must be excited by light irradiation and the pollutant must be adsorbed on the photocatalyst surface to be removed. The solar spectrum contains 5% UV (300–400 nm), 45% visible (400–700 nm), and 50% infrared, near-infrared (IR, NIR; >700 nm). As a result, semiconductors with large

band gaps (3.3 eV) absorb UV photons, whereas semiconductors with small band gaps (2.0–2.5 eV) absorb visible light (400–700). So far, studies have mostly used low solar energy, leaving NIR, which accounts for a larger portion of the solar spectrum. (Sun et al., 2022b; Yang et al., 2021a; Nawaz et al., 2021). Because IR/NIR light is more prevalent indoors throughout the day, disinfecting microbes with near IR/NIR light active catalysts has an advantage over visible light active photocatalysts. Though most researchers have focused on photocatalysts that extend from the UV to visible region, the trend has now shifted to effective utilization of NIR light, which accounts for approximately 50% of solar light. NIR responsive photocatalysts will be burgeoning in near future in the field of bacteria inactivation due to progress of novel NIR active photocatalysts for harnessing NIR/IR radiation and also due to minimum photodamage to biological tissues in the AOT process initiated by NIR/IR catalysts (Sun et al., 2022a; Yang et al., 2021a; Yin et al., 2018).

Due to the expensive and less abundance of bare noble metals, they are considerably less competitive in the means as an antibacterial agent. However, studies have proved that even noble metals cause invasive effects on human health and the environment. Therefore, the development of non-precious metal-based UV to NIR active photocatalysts to inactivate bacteria using solar energy was found to be more cost-effective. Although the less focused NIR irradiation is found of a much cheaper light activation method as compared to UV and Vis light (Sun

et al., 2022b). The NIR techniques that have been employed for the microbe disinfection can be categorized into either heat-based or AOT-based mechanisms as schematically shown in Fig. 2. In the heat-mediated which used to transform energy of NIR into heat generation followed by reactive oxygen species (ROS) generation can be used in photothermal therapy (PTT), photodynamic therapy (PDT) and synergistic therapy. Significantly, these therapies widely used in wound healing, in tissue infection treatments related with antibacterial studies. Optimal PTT and PDT cause for effective antibacterial activity (Han et al., 2020; Ren et al., 2020; Yang et al., 2021b; Zhou et al., 2021). In the case of AOT-based microbial disinfection method, the following strategies have been employed; (i) Defect engineered photocatalysts in which the position of the bands or create intermediate states by doping or constructing vacancies, (ii) energy upconversion process based on upconversion materials which have ability to convert NIR light into UV and visible light, (iii) Based on Surface Plasmon Resonance (Kaye et al.) in which SPR substrate has great potential to absorb and utilize the NIR light due to resonance with incident light at specific frequencies and (iv) Sensitization process based on intrinsic narrow band gap semiconductors or photosensitizers, such as dye and black phosphorous which can absorb NIR light, they are promising in sensitizing semiconductor photocatalysts under NIR light irradiation (Cao et al., 2022; Li et al., 2021a; Rao et al., 2022; Suryani et al., 2018; Wang et al., 2021b, 2022b).

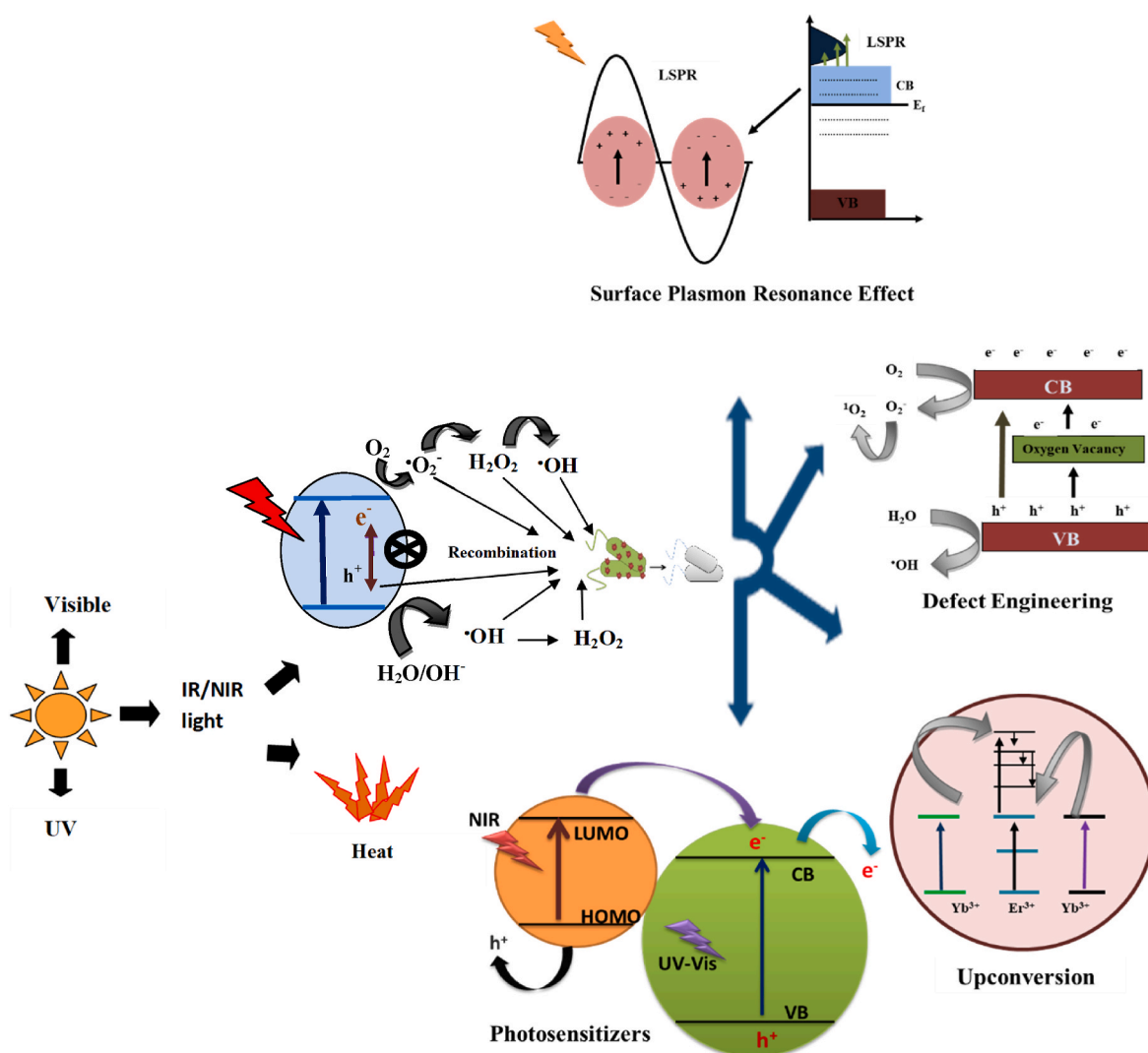


Fig. 2. Categorization of NIR active different type of photocatalysis (Han et al., 2020; Li et al., 2021a; Sun et al., 2022a; Yang et al., 2021b; Zhou et al., 2021).

It is known that noble metals such as Ag and Au have been implied as developed NIR photocatalytic findings for wiping out of pathogens, whereas vital inactivation against pathogens is observed. Additionally, greater photothermal characteristics are revealed with respect to local surface plasmon resonance by noble metals (Yang et al., 2021a). Due to the high cost and less abundance of bare noble metals, they are considerably less competitive in the means of as an antibacterial agent. However, studies have proved that even noble metals cause invasive effects towards human health and environment. Therefore, the development of non-precious metal-based UV to NIR active photocatalysts to inactivate bacteria using solar energy was found to be more cost-effective (Wang et al., 2017). Furthermore, NIR-IR based AOT methods in microbe disinfection have not been fully utilized and in this review, we will discuss these strategies and their roles in the photocatalytic process in details.

2.2.1. Defect engineered photocatalysts for bacteria inactivation

The strategy of introducing defects in photocatalysts is vital for improving the near-IR and IR light harvesting properties of semiconductors (Osada et al., 2002; Yin et al., 2018). As shown in Fig. 3a, vacancies can cause the formation of defect states in semiconductors that are located between the VB and CB and hence defect engineering has been reported to result in the formation of new energy levels, causing the band gap of materials to narrow as well as effective excited charge separation (Wang et al., 2020a). Catalysts with vacancies are found to be more advantageous in the extension of the photogenerated charge carriers although, it is uncertain whether every type of elemental vacancies able to enhance the photocatalytic efficiencies or not (Sun

et al., 2019). Heavily doped semiconductors catalysts with oxygen vacancies and enhanced free carrier concentration i.e. MoO_{3-x} , $\text{Mo}_x\text{W}_{1-x}\text{O}_3$, BiO_{2-x} , TiO_{2-x} and WO_{3-x} known to have non-metallic plasmonic and exhibit LSPR effect and higher light absorption in the NIR region (Yin et al., 2018). Some of the reported photocatalysts developed via defect engineering are listed in Table 1.

In an attempt to enhance the IR response, defects have been introduced by treating BiOBr with NaOH to form BiOBr-0.01 and the brown colored BiOBr-0.01 shows enhanced near-IR photocatalytic activity for the microbial disinfection due to extended light absorption and efficient charge separation (Wu et al., 2016). On the other hand, Yin et al. pioneered the introduction of a novel photocatalyst which was based on plasmonic semiconductor for efficient inactivation of bacteria (Yin et al., 2018). The use of IR responsive plasmonic semiconductors such as MoO_{3-x} , $\text{Mo}_x\text{W}_{1-x}\text{O}_3$, BiO_{2-x} can be advantages due to stronger light absorption in the NIR region than the plasmonic metal, in addition to their decrease toxicity of to the organism. Overall, the results proved that 99.2% of *E. coli* and 97.0% of *S. aureus* were killed by the heavily doped MoO_{3-x} decorated with Ag under NIR light irradiation due to plasmonic absorption of MoO_{3-x} . As shown in Fig. 3b, the transfer of hot charge carriers as well as heat generated in MoO_{3-x} with the NIR irradiation to Ag causing the increase of temperature in Ag particles that would result in the killing of bacteria due to protein denaturation and loss of enzyme activity (Yin et al., 2018). At the same time, photo-generated OH reactive species kill the bacteria by damaging the cell wall. The common low charge separation properties of plasmonic oxide catalysts has been minimized by coating a carbon layer on WO_3 (WO_{3-x}/C) for photothermal synergistic disinfection of *E. coli* under

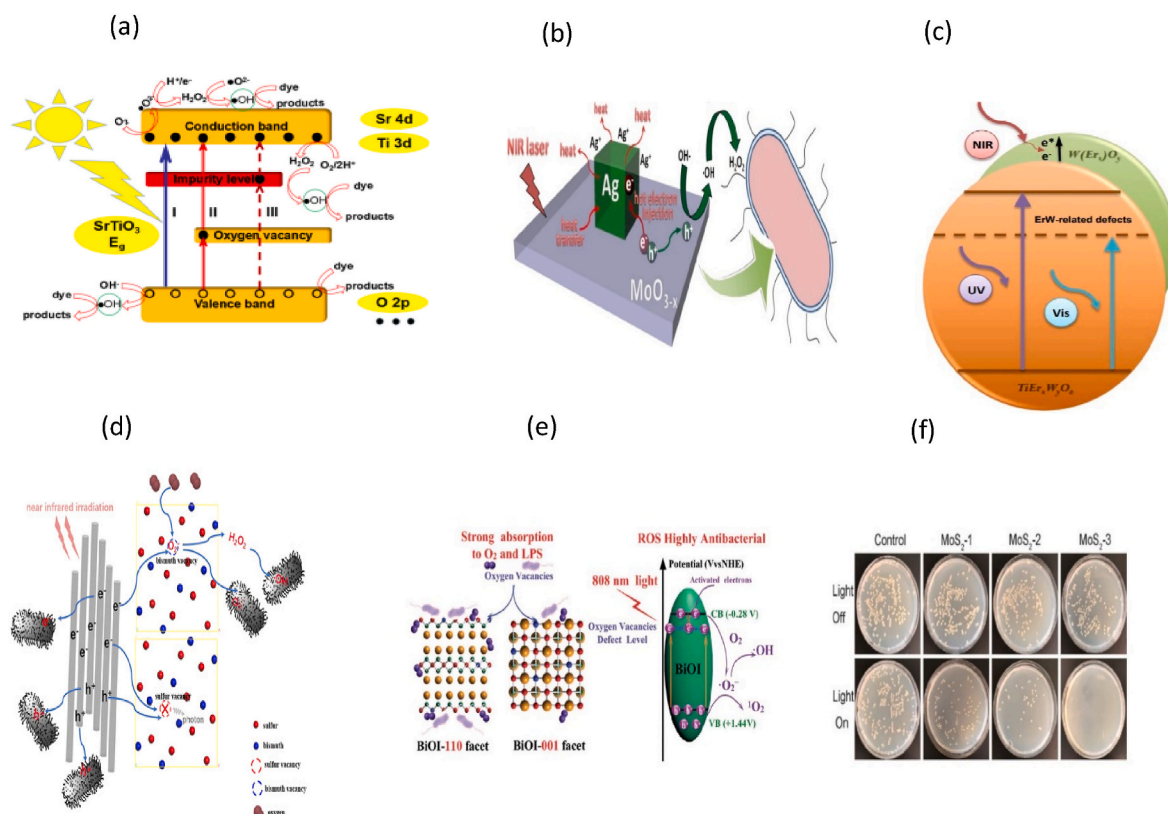


Fig. 3. (a) Photocatalytic mechanism for the congo red dye degraded by pure SrTiO_3 , O (oxygen vacancy)— SrTiO_3 , and I (impurity)— SrTiO_3 under simulated sunlight irradiation (Adapted with permission from (Wang et al., 2020a), copyright 2020, Springer Nature). (b) Schematic illustration of the photo-catalytic antibacterial mechanism of $\text{MoO}_{3-x}\text{-Ag}$ under NIR laser irradiation (Adapted with permission from (Yin et al., 2018), copyright 2018, Elsevier). (c) Main light absorption events occurring in Sn-Ti samples (Adapted with permission from (Kubacka et al., 2018), copyright 2018, Elsevier). (d) Proposed mechanism of NIR-driven photocatalytic inactivation of *E. coli* by bismuth-deficient Bi_2S_3 (Adapted with permission from (Sun et al., 2019), copyright 2019, John Wiley and Sons). (e) Schematic illustration of possible photocatalytic antibacterial mechanism (Adapted with permission from (Sun et al., 2020), copyright, 2020, John Wiley and Sons). (f) Pictures of the bacterial colonies (Adapted with permission from (Wu et al., 2022), copyright 2022, Chemical Engineering Journal).

Table 1
Summary of photocatalysis developed via defect engineering for bacterial inactivation.

Photocatalyst	Light irradiation conditions	Application	Model Bacteria used	Eff.%	Ref
MoO _{3-x} -Ag	300-W Xenon lamp 0.5 W/cm ² 808 nm	As an antibacterial agent	<i>E. coli</i> <i>S. aureus</i>	99.2 97.0 Within 10 min	Yin et al. (2018)
BiO _{2-x} nanoplates and persulfate	300 W Xenon lamp with a 700 nm cutoff filter	Persulfate activation under NIR Bacterial inactivation	<i>E. coli</i>	Up to 7log Within 40 min	Sun et al. (2022a)
Bi ₂ S ₃ nanorods	Xenon lamp with a700 nm long-pass filter	Bacterial inactivation activity	<i>E. coli</i>	Up to 7log Within 40 min	Sun et al. (2019)
BiOBr-0.01	Xenon lamp $\lambda > 700$ nm	Bacterial disinfection Organic dye decomposition	<i>E. coli</i>	Up to 7log Within 15 min	Wu et al. (2016)
WO _{3-x} /C	Xenon lamp with a700 nm filter 2000 W/m ² -light intensity	photothermal synergistic disinfection Organic degradability such as RhB	<i>E. coli</i>	Within 40 min	Zhang et al. (2020)
WO _{3-x} and Er Co-doped TiO ₂	950/975 nm (near IR)	Inactivation of microorganisms	<i>E. coli</i> <i>S. aureus</i>		Kubacka et al. (2018)
BiOI nanosheets BI-110	808 nm light irradiation	As an antibacterial agent Inactivation of multidrug resistant bacteria	<i>E. coli</i>	BI-110 shown higher inactivation than BI-001 Within 15 min	Sun et al. (2020)
MoS ₂	808 nm NIR laser	Bacterial Inactivation	<i>E. coli</i>	100% of bacteria were disappeared from the colony with MoS ₂₋₃	Wu et al. (2022)
Ni/rGO	808 nm NIR light 2.0 W/cm ²	Pathogenic bacteria contained water purification	<i>E. coli</i> <i>Bacillus subtilis</i>	99.6 99.5 Within 8 min	Zhang et al. (2021b)
AgVO ₃ /BiO _{2-x}	300 W xenon light 880–930 nm	full spectrum solar light for photocatalytic disinfection enriched with wound healing properties	Methicillin-resistant <i>Staphylococcus aureus</i> (MRSA)	bacteria can be almost complet-ely killed within 30 min	Wang et al. (2021c)

infrared light by Zhang et al. (2020).

Plasmonic WO_{3-x} and Er Co-doped TiO₂ has been employed by Anna Kubacka to enhance the IR response of high-band gap TiO₂ and noted the enhanced photoactivity in the elimination of microorganisms with the IR radiations in which doped WO_x absorbs IR photons as well as a visible light active cation while Er is a near IR active cation.(Fig. 3c) (Kubacka et al., 2018). Such a co-doping was reported to be advantage in introducing disordered mixed oxides in anatase structure and defects present in surface and bulk have key different roles in producing charge carriers involved in the microorganisms attack.

The beneficial factor in extending the lifetime of photogenerated electrons by intruding vacancies was demonstrated by Sun et al. and the defect type-dependent photocatalytic disinfection of microbes was reported in their study by employing Bi₂S₃ nanorods with bismuth or sulfur vacancies. While both vacancies enhance the IR-driven photocatalytic bacterial inactivation, Bi vacancies outperformed the NIR-driven photocatalytic bacterial inactivation efficiency due to increased charge densities of Bi₂S₃ due to B vacancies. As shown in Fig. 3d, these B vacancy sites extend the lifetime of photoexcited charges by efficient transfer of electrons to the bismuth vacancy sites suppressing the electron-hole recombination (Sun et al., 2019). The synergic effect of vacancies and facets engineering for microbial disinfection was reported by Sun et al. in which they demonstrated the crystal facet engineering as a promising way to develop highly active IR-drive photocatalysts. As shown in Fig. 3e, the first principle calculation and also the experimental results revealed strong adsorption energies of O-defective BiOI with facets to LPS and O₂ than the BiOI with facets, due to the unique electronic structures of O-defective BiOI with facets, resulting in the formation of highly concentrated single oxygen species leading to its high bacterized properties (Sun et al., 2020). On the other hand, the excellent photothermal and photocatalytic activity for the microbe disinfect was also reported by Zhang et al. by creating the appropriate oxygen vacancy density in rGO, in which Ovs were found to enhance the NIR light absorption and photogenerated electron-hole pairs separation (Zhang et al., 2021b). Despite oxygen vacancy engineered materials found to be efficiently disinfect microbes with IR and near IR photons, the charge

separation in defect engineered materials were reported to inferior to that of excellent photocatalysts (Huang et al., 2021). Hence to address the inferior charge separation and diminish the electron-hole recombination, Wang et al. designed heterostructures with BiO_{2-x} and vanadate quantum dot (QD). A close interfacial contact between the vanadate QDs and BiO_{2-x} resulting in an efficient charge transfer process leading to enhance the IR photon driven microbe disinfection (Wang et al., 2021c).

In most of the near-IR driven photocatalytic systems that employed for microbe inactivation, microbes are attacked by reactive radicals such as •O₂⁻, ¹O₂ and •OH, but short lifetime of those radicals, limiting the efficiency (Gorle et al., 2018; Regmi et al., 2018). Instead, Sun et al. used vacancy-rich BiO_{2-x} photocatalyst with a persulfate activator as a more stable activator than •OH radicals which possess a comparable oxidizing power to that of •OH and reported enhanced microbe disinfection (Sun et al., 2022a). Similar to oxygen vacancy assisted IR driven disinfection properties of semiconductors, Wu et al. reported molybdenum sulfide (MoS₂) NMs with different concentrations of sulfur vacancies (Vs) for the efficient bacterial inactivation in which sulfur vacancies enhances the light absorption as well as decreasing the charge recombination (Wu et al., 2022). As shown in Fig. 3f, the amount of sulfur vacancies plays a significant role and with an appropriate amount of sulfur vacancies a rapid microbes removal has been reported.

Despite the bandgap engineering of photocatalysts resulting in broad solar light harvesting from UV to NIR regions, the progress in the development of NIR active photocatalysts are still infancy due to major challenges of achieving enhance charge separation and transportation. Hence, one should pay attention to both light harvesting properties as well as charge separation and transportation in developing IR-driven photocatalysts by defect engineering strategy. Especially, in the case of non-metallic plasmonic semiconductors which exhibit LSPR effect due to extra high oxygen vacancies and enhanced free carrier concentration could in principal could be developed as efficient NIR/IR driven photocatalysts for microbe disinfection by enhancing both IR light harvesting as well as charge separation/transport properties.

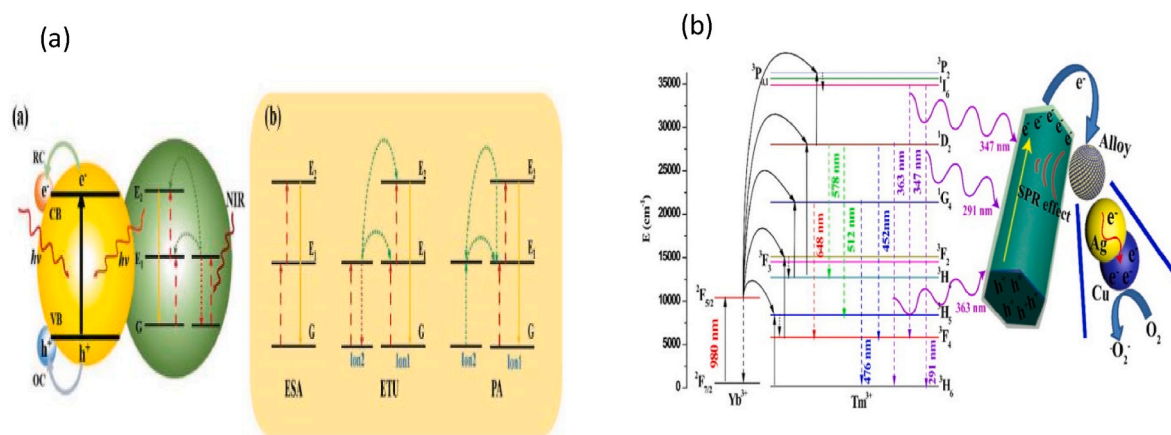


Fig. 4. (a) Mechanism diagram of an upconversion process in photocatalysis, (b) Schematic of the upconversion processes (Adapted with permission from (Yang et al., 2021b), copyright 2021, John Wiley and Sons). (b) Possible mechanism for photocatalytic disinfection (Adapted with permission from (Zhang et al., 2018a), copyright 2018, Elsevier).

2.2.2. Up-conversion driven photocatalysts for bacteria inactivation

There have been a number of studies based on NIR light induced photocatalysis which were expanded in the conversion of NIR photons into visible photons by using upconversion (UC) nanocrystals which were integrated with semiconductors (Tian et al., 2019; Yang et al., 2021b). As shown in Fig. 4a, in the upconversion process, the conversion of longer wavelength (NIR) into shorter wavelength (UV/VIS) can be obtained through Lanthanide-doped materials (Yang et al., 2021b) i.e. NaYF₄ is considered as an efficient host material for UC and further doping with rare earth ions such as Er³⁺/Tm³⁺/Yb³⁺ led to tremendous UC efficiency. The rapid recombination of charge carriers with respect to inadequate charge separation is the most challenging problem that has to be addressed in the application of UC process and found to be partially overcome by metal doping, such used to capturing electrons and eventually speed up the electron migration speed (Zhang et al., 2018a, 2018b). Though the microbial disinfection by the UC process is also related to induced oxidation of cell by photogenerated ROS, the whole process is primarily depend on the efficiency of UC (Jin et al., 2019). However, a little attempt on the use of UC process for microbe disinfection under indoor conditions.

In the upconversion catalytic process, the catalytic activity is largely depending on the efficiency of UC luminescence conversion. UC materials such as YF₃ and NaYF₄ are inefficient host material for UC luminescence conversion and hence their IR driven photocatalytic activity is reported to be poor. By combining NaYF₄ with the nanoporous crystallized TiO₂ inverse opals as host material, Zhang et al. demonstrated efficient upconversion of NIR light into UV photons producing strong ROS and enhanced photocatalytic driven microbe disinfection with IR photons (Zhang et al., 2018b). The activity has been highly depended on the charge transfer and separation in which a monolayer of NYF on TiO₂ reported to be the optimum. For further enhancement of charge transfer and separation from NaYF₄ to TiO₂, Zhang et al. deposited silver-copper bimetallic alloy nanoparticles on NaY₄/TiO₂ catalyst and with NIR irradiation, Ag-Cu alloy coated NYFT exhibited higher photocatalytic activity mainly owing to the synergistic effect of up-conversion (UC) material and electron capturing as well as surface plasmon resonance (Kayes et al.) effect of alloy NPs as shown in Fig. 4b (Zhang et al., 2018a).

In an another report, Zhou et al. demonstrated enhanced light energy transfer from UC material to TiO₂ nanoparticles by coupling the reduced TiO₂ nanoparticles (R-TiO₂) with the UC material (Zhou and He, 2021). In this process, after excitation of Yb³⁺ by IR radiation, the excited electrons in Yb³⁺ would transfer to the H, S, or F states in Er³⁺ followed by releasing energy, emitting at 523 nm, 542 nm, and 658 nm, respectively. As the R-TiO₂ contains the sub-bandgaps states that are close

contact with the UC material can efficiently harvest visible light generated by UC process and generate RO species. In a similar way, by incorporating Ag₃PO₄ in to the NaYF₄:Yb,Tm@TiO₂/Ag₃PO₄, a facile charge transfer and hence efficient microbial degradation has been reported due to the formation of a TiO₂-Ag₃PO₄ heterojunction (Linghu et al., 2022). The exceptional performance has been attributed to the improves FRET efficiency as a result of a unique core-shell structure between TiO₂ and NaYF₄:Yb,Tm, and the heterojunction between TiO₂ and Ag₃PO₄, which exhibited wide spectral response capability and effectively facilitated separation of photogenerated charges, increasing the amount of generated ROS.

Looking into nanometer scale and unique characteristics of up-conversion photoluminescence (UCPL), carbon quantum dots (CDs) have the ability to convert NIR light to violet and visible light, thus CDs are able to trigger photocatalytic materials using NIR light. Additionally, irreversible recombination of electrons and holes is identified as a major limitation factor of photocatalytic material. Herein, Jin et al. reported about, facile methodology which was used to synthesise ternary composite (TNT) loaded with the gold nanoparticles and CDs (TNTs/Au/CDs). Specifically, CDs upconversion property and Au Nps catalytic property eventually enhances the photocatalytic property of the ternary composite, which produces reactive oxygen species (ROS) under 808 nm in NIR radiation, whereas Au NPs produces hyperthermia. These modifications produce an effective killing of bacteria within a shorter period in terms of eradication of bacteria membrane. As a result, the antibacterial efficiency of *S. aureus* and *E. coli*, accounted as 96.19% and 99.89% respectively, less than 808 nm in 15 min spurring of NIR light (Jin et al., 2019). The upconversion driven photocatalysts for bacteria inactivation are briefly summarized in Table 2.

The UC process that contains UC elements has been successfully demonstrated for biomedical application and near-infrared II (NIR-II) phototherapy systems (Fang et al., 2021; Jia et al., 2022; Qin et al., 2021; Wang et al., 2021a; Zhang et al., 2021a). However, NIR driven phototherapy applications especially tissues and bone infection in clinical applications is beyond the scope of this review and not discussed here. The success of IR driven UC process for the microbe removal is highly depended on the light energy transfer from the UP material to the associated semiconductor photocatalysts. However, as the energy transfer efficiency is low due to the loose contact between the UCs and photocatalyst, a proper contact between UCP and photocatalysts should be developed by using new designing strategy.

2.2.3. Surface plasmon resonance based bactericidal activity

As compared to upconversion nanocrystals, plasmonic photocatalysts have the ability to extend the NIR light absorption range and

Table 2

Summarizes the advancement of different types of upconversion materials which used so far for the bacterial inactivation.

Photocatalyst	Light irradiation conditions	Application	Model Bacteria used	Eff.%	Ref
NaYF ₄ : Yb ³⁺ , Er ³⁺ (NYF) with porous TiO ₂	980 nm laser excitation	Inactivation of bacteria		100% within 11 h monolayer photocatalysts	Zhang et al. (2018b)
β-NaYF ₄ : Yb ³⁺ , Tm ³⁺ @TiO ₂ (NYFT) @Ag–Cu	980 nm laser excitation	Water disinfection	<i>E. coli</i>	100% within 8 h	Zhang et al. (2018a)
TNTs/Au/CDs	808 nm	Bacteria eradication	<i>E. coli</i>	99.89%	Jin et al. (2019)
	0.6 W/cm ²		<i>S. aureus</i>	96.19%	
βNaYF ₄ :Yb,Er,Gd@Reduced TiO ₂	980 nm laser (1 W)	Inactivation of bacteria	<i>E. coli</i>	98.1% within 12 min	Zhou and He (2021)
NaYF ₄ :Yb,Tm@TiO ₂ /Ag ₃ PO ₄	980 nm laser and a xenon lamp	microbial degradation	Minimum bactericidal concentrations	50 µg mL ⁻¹	Linghu et al. (2022)
			<i>E. coli</i>	50 and 100 µg mL ⁻¹	
			<i>S. aureus</i>		
TiO ₂ :FYH/Cur/BMP-2	NIR-II laser 0.6 W/cm ²	anti-biofilm	<i>E. coli</i>		Zhang et al. (2021a)
		anti-inflammatory clinical potential in orthopedic applications	<i>S. aureus</i>		
Gold silver nanocages (GSNCs)	laser device	As a multimodal antibacterial agents	<i>E. coli</i>		Qin et al. (2021)
	2 W/cm ²		<i>S. aureus</i>		
FeSe ₂ nanosheets (NSs)	1120 nm laser	synergistic cancer therapy			Fang et al. (2021)
	0.8 W/cm ²				
Single organic small molecule-based nanoparticles (CNPs)	NIR-II (1000–1350 nm)	As efficient photothermal antibacterial agent	<i>S. aureus</i>	100%	Jia et al. (2022)
β-NaYF ₄ :Yb,Er,Gd nanorods@1T/2H–MoS ₂	980 nm	photocatalytic sterilization	<i>E. coli</i>	99.3% within 15 min	Qiao et al. (2020)

hence plasmonic-photothermal effect causes bacteria eradication. Shape controlling of noble metal has been recognized as the most efficient method for extension of visible region towards near infrared region. However, most noble metal such as Ag, Au is toxic and expensive (Yin et al., 2018). As compared to other metals, noble metals such as Silver are mainly used in medical and industrial scales due to their inhibitory effect on numerous pathogenic bacteria. They are in use in wide therapeutic applications as they owe unique properties such as large surface area and the surface atoms covered with fractions. Antibacterial activity of Ag⁺ gets dominated when their particle size is small and releases many ions, rather than nanosilver particles (Fanoro and Oluwafemi, 2020; Slavin et al., 2017). Similarly, Gold nanoparticles have diverse applications in the areas such as nanomedicine, disease diagnosis, and gene expression and therapy. As compared to AuNPs synthesized via one plant extract, a mixture of plant extracts showed higher antibacterial effects (Fanoro and Oluwafemi, 2020). In recent years, the attention has been much drawn towards photocatalysts such as Ag₂S consisting of lower band gaps (1.0 eV) under visible and NIR light. The most common obstacle in the use of plasmonic noble metals in IR driven microbe disinfection is the rapid recombination of electron and hole pairs and

significant decreasing the antimicrobial activity has been addressed by introducing co-catalysts (McEvoy and Zhang, 2014; Rtimi et al., 2019; Yang et al., 2021b).

As prepared Ag₂S@WS₂ by a simple solution method in which the co-catalyst WS₂, which has superior photoelectric property and which also can bind tightly on the in-situ grown Ag₂S particles owing to their similarity as metal sulfides enriched with superb photocatalytic and photothermal activity towards bactericidal activity (Lin et al., 2019). As expected the heterostructure had significant electron mobility and electro-hole pair recombination as well as the extension of life span under NIR irradiation. In comparison with other studies, herein within 20 min higher efficacy was obtained under 808 nm NIR radiation, whereas inactivation of *S. aureus* 99.93% and 99.84% against *E. coli* accounted accordingly (Lin et al., 2019). As shown in Fig. 5a, the reactive species generated via plasmonic effect involves in microbe degradation reactions. Moreover, Xiong et al. synthesized Ag₂S nanoparticles decorated nanocubes (derived from a zeolitic imidazolate framework) via ultrasonic process and solvent reaction in order to use as photodynamic and photothermal agent as a good antibacterial agent which comprised of low toxicity, bio-compatibility and with higher NIR

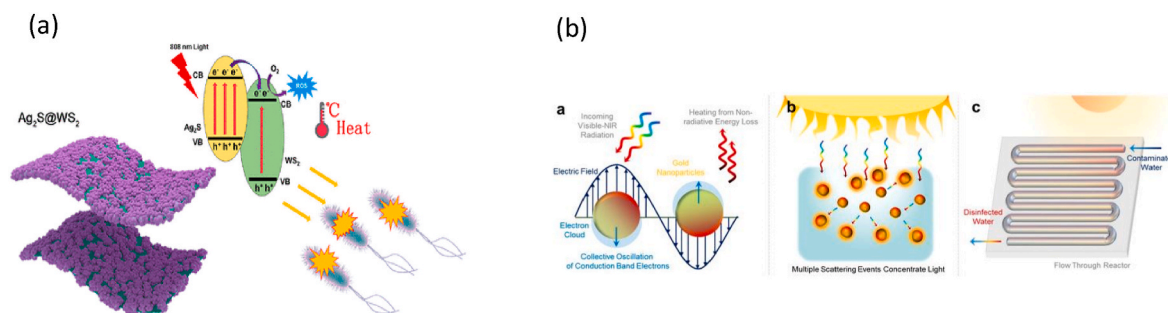


Fig. 5. (a) Ag₂S nanoparticles decorated WS₂ system generates ROS and heat to kill bacteria in a short period under NIR irradiation. (Adapted with permission from (Lin et al., 2019), copyright 2019, American Chemical Society). (b) (a) Photothermal conversion mechanism for surface plasmonic Au nanoparticles. Incoming photons with a corresponding resonant frequency interact with an electric field surrounding the nanoparticle to produce a collective oscillation of conduction band electrons. Energy build-up at the surface of the particle is released in the form of heat, leading to high surface temperatures. (b) Under low-intensity noncoherent solar radiation, heat is generated through the concentration of light by multiple scattering events. (c) A possible photothermal material disinfection reactor schematic. Photothermal nanoparticles are coated inside a transparent substrate with a tortuous flow path employed to increase contact time. Compound parabolic reflectors, or other light concentrating features, could be used to increase solar radiation intensity. (Adapted with permission from (Loeb et al., 2018), copyright 2018, American Chemical Society).

response (Xiong et al., 2019). In an attempt to enhance the antimicrobial activity of SPR based Ag–Cu NP alloy has been coupled with UC properties of NaYF₄ coated TiO₂ and the reported higher microbe disinfect ability has been attributed to enhanced charge transfer and separation from NaYF₄ to TiO₂ and then to Ag–Cu alloy (Zhang et al., 2018a). By coupling UC NaYF₄ material and SPR Ag–Cu NP, light harvesting in near IR region is greatly enhanced in addition to the enhanced charge separation. Though, codoping of the anatase structure with tungsten and erbium reported to enhance the IR driven bacterized due to the plasmonic effect of the Er–W, the SPR activity of Er–W is not clearly demonstrated (Kubacka et al., 2018).

As shown in Fig. 5b, another application of plasmonic materials for the direct inactivation of bacteria and viruses is to convert the solar-to-thermal energy by concentrating the light within a small spatial domain, that would resulting in localized and intense heating leading to inactivates microorganisms in close proximity (Chen et al., 2014; Li et al., 2019; Loeb et al., 2018; Qiao et al., 2020; Xu et al., 2019). It had been demonstrated the elimination of microbes through solar-to-thermal conversion by surface plasmon resonance (Kayes et al.) effect of Au nanorod-carbon black composites and Ag₂S (Jin et al., 2019; Loeb et al., 2018; Wu et al., 2021). The process is highly effective compared to other thermal treatment methods and hence this method can eliminate vast majority of resistances pathogens. In a similar manner, Yin et al. designed plasmonic MoO_{3-x} nanosheets supported Ag nanocubes to convert the solar-to-thermal energy as high-efficient Near-infrared (NIR) light driven antibacterial agent in which heavily doped MoO_{3-x} semiconductor and Ag metal harvest NIR light (Yin et al., 2018). In addition to killing bacteria via the photothermal effect of MoO_{3-x}, charge carriers generated by absorption of IR photons by MoO_{3-x} efficiently separated through the MoO_{3-x}-Ag interface, generating free radicals that lead to the destruction of the bacteria. Similarly, Lie et al. designed near-infrared (NIR) activated catalyst consisted of two-dimensional (2D) MXene and one-dimensional (1D) cobalt nanowires (CoNWs) for microbe degradation in which CoNW function as both trapping of photogenerated electrons and plasmonic material enhancing the photothermal effect and the electron-hole separation (Liu et al., 2021a). Table 3 lists the surface Plasmon resonance-based materials which shows bactericidal activity.

2.2.4. Sensitization method in photocatalysts for bacteria inactivation

In the sensitization process, photoexcited electrons and holes produced via under IR light irradiation of photosensitizers which are coated on a suitable substrate i. e TiO₂ are captured by the surrounding oxygen

atoms and adsorbed OH groups respectively to generate ROS, thereby killing bacteria rapidly. However, the poor low ROS yield is the main drawback of the IR photosensitization process that leads to poor efficiency. Teng et al. fabricated a device that consists of MnO₂, IR780 and polydopamine (PDA) on the Ti plate in which each component function as photothermal material, a photosensitizer that absorb NIR photons and absorbance and the binding material respectively and under the irradiation of 808 nm NIR light, a rapid degradation of common microbes such as *S. aureus* and 99.89% *E. coli* has been reported (Teng et al., 2020). G. Gorle et al. and team researched about, for the first time effective photosensitizers which used for bacteria wiping out along with NIR triggered photocatalytic cationic polyethyleneimine (PEI) wrapped Bi₂Se₃ nanoplates (Bi₂Se₃NPs/PEI). Bacteria eradication of *E. coli* and *S. aureus* at 80 ppm was 97% and 99% respectively. It is a clear study that for the first time it has shown higher capability to be used as an antibacterial agent and efficient photocatalyst which can be used for water purification. Gorle et al. suggested future applications of this photocatalyst in order to apply for methyl orange and Congo red to find their adsorption efficiencies (Gorle et al., 2018). The advancement of different types of sensitization methods which induce the bactericidal activity are described as follows (Table 4).

The system composed of MoS₂(S)–Ag₃PO₄ on Ti found to function as a similar manner and NIR light irradiation, an efficient removal of *S. aureus* and *E. coli* has been reported (Xia et al., 2022). The Ti–MoS₂(S)–Ag₃PO₄ catalyst exhibited a higher photocatalytic performance under IR irradiation owing to that the modification of the electronic as well as optical properties of MoS₂ by the addition of Ag₃PO₄ nanoparticles. Though these nanostructures modified Ti has been designed for the application in manufacturing of biomedical equipment or surgical instruments, a similar system can be successfully designed for microbial disinfection in air.

Hybrid systems that compose of heterojunctions of two different materials such as Ag₂S/Ti₃C₂ (Wu et al., 2021), Bi₂S₃/Ti₃C₂T_x (Li et al., 2021b) and Ti₃C₂T_x@CuS (Huang et al., 2022; Li et al., 2021c; Wang et al., 2022a; Wang et al., 2022b; Wu et al., 2021), and have been tested in an attempt to improve the IR response and the charge separation. As shown in Fig. 6a, the low-band gap material function as NIR active material while the Schottky heterojunctions formed between high-band gap and IR sensitive materials facilitate the charge transfer (Wu et al., 2021). Consequently, the observed enhancement of microbe disinfect ability of Ag₂S/Ti₃C₂, Bi₂S₃/Ti₃C₂T_x and Ti₃C₂T_x@CuS can be attribute to the synergic effect of enhanced photocatalytic and photothermal performance through a continuous flow of NIR-excited electrons

Table 3

Summarizes the advancement of different types of Surface Plasmon Resonance based materials which used so far for the bacterial inactivation.

Photocatalyst	Light irradiation (nm)	Application	Model Bacteria	Eff. %	Ref
MoO _{3-x} -Ag	808 nm NIR laser, 0.5 W/cm ²	As antibacterial agent	<i>E. coli</i> <i>S. aureus</i>	99.2% 97.0%	Yin et al. (2018)
Er–W codoping of TiO ₂ -anatase	950/975 nm (near IR)	Inactivation of microorganisms	<i>E. coli</i> <i>S. aureus</i>		Kubacka et al. (2018)
TNTs/Au/CDs	808 nm, 0.6 W/cm ²	Bacteria Inactivation	<i>E. coli</i> <i>S. aureus</i>	96.19% 99.89%	Jin et al. (2019)
Ag ₂ S@WS ₂	NIR (808 nm) irradiation, 1 W/cm ²	As antibacterial agent	<i>E. coli</i> <i>S. aureus</i>	99.93% 99.84%	Lin et al. (2019)
Au nanorod-carbon black composite materials	875 nm	Thermal inactivation of microorganisms	<i>Escherichia coli</i> K-12 bacteriophages MS2 PR772		Loeb et al. (2018)
Ag ₂ S/NCs	808 nm laser source at 1 W/cm ²	As antibacterial agent	<i>S. aureus</i>	97.3% 20 min	Xiong et al. (2019)
Au/dark-TiO ₂	980 nm laser, 0.68 W/cm ²	Destroy drug-resistant bacteria	<i>E. coli</i>	~50% after 60 min	Xu et al. (2019)
Ag ₂ S/Ti ₃ C ₂	808 nm laser, 0.67 W/cm ²	Treatment for bacterial infections	<i>S. aureus</i>	99.99% 20 min	Wu et al. (2021)
MXene/CoNWs	808 nm NIR light 1.5 W/cm ²	Drug-free antibacterial therapy	<i>S. aureus</i> <i>E. coli</i>	92.74% 80.10% 20 min	Liu et al. (2021a)

Table 4

Summarizes the advancement of different types of Sensitization methods which used so far for the bacterial inactivation.

Photocatalyst	Light irradiation conditions	Application	Model Bacteria used	Eff. %	Ref
Ag ₂ S/Ti ₃ C ₂	808 nm NIR, 0.67 W/cm ²	Treatment for bacterial infections	<i>S. aureus</i>	99.99% 20 min	Wu et al. (2021)
PDA/IR780@MnO ₂ -Ti	808 nm NIR, 0.5 W/cm ²	Kill bacteria on biomedical devices and implants in a short time.	<i>E. coli</i>	99.89% 99.94% Within 15 min	Teng et al. (2020)
Ti-MoS ₂ (S)-Ag ₃ PO ₄	808 nm NIR light 0.4 W/cm ²	Rapid eradication of bacteria on medical tools and superficial implants	<i>S. aureus</i> <i>E. coli</i>	99.76 ± 0.15% 99.85 ± 0.09%	Xia et al. (2022)
Urchin-shaped Au@Bi ₂ S ₃	808 nm laser, 2.0 W/cm ²	As an antibacterial agent Applications in medical treatment or environmental remedy	<i>S. aureus</i> <i>E. coli</i>	100%	Wang et al. (2020b)
Bi ₂ S ₃ /Ti ₃ C ₂ T _x	808 nm laser, 0.7 W/cm ²	Effective eradication of bacterial infection	<i>S. aureus</i> <i>E. coli</i>	99.86% 99.92% within 10 min	Li et al. (2021b)

including those hot electrons produced by local surface plasma resonance (LSPR) from Ag₂S to Ti₃C₂ at the interface between them as a result of the formation of Schottky heterojunction. The Schottky junction with a built-in electric field can be effectively prevent the backflow of electrons and boosts the charge transfer and separation.

In a similar manner, Bi₂S₃ which is a known semiconductor that has been used for microbe disinfection by local photothermal effects as well as ROS production via NIR irradiation coupled with Au to enhance the NIR light absorption and minimize the rapid photo-induced electron hole recombination. Hence, Wang et al. synthesized Au@Bi₂S₃ core-shell Schottky junction to facilitate electron-hole separation and was able to demonstrate the enhancement of the NIR light absorption and to minimize the photo-induced electron hole recombination and thus enhance microbial disinfection activities. (Fig. 6c) (Wang et al., 2020b). In another study, ZnO@Ag nanocomposite were synthesized by varying ratios of ZnO NPs with silver nanoparticles (Ag NPs). Herein, ZnO@8% Ag showed higher efficiency which over 99% of inhibition of *S. aureus* under PTT and PDT. Electron-hole recombination was prevented by the Ag in the nanocomposite which used to maintain efficient electron flow via ZnO to Ag. As per study the molecular mechanism of biofilm inhibition remain to study. As per shown in Fig. 6b, both Ag and ZnO consist of different bandgap energies, while considering the energy level of the CB of ZnO and the Fermi level of Ag acts as a sink which cause for prevention of recombination as per discussed earlier (Obeng et al., 2022).

In the recent decade, scientists were fully focused on visible and UV light-induced catalysts due to their significant ability to activate smaller molecules. Those findings were applied in a way such as water, air disinfections, therapeutic treatments as well as in dye degradation strategies. Over the last 5 years, they have paid attention to utilizing NIR light, the majority of the solar spectrum in a proper way. For fulfillment

of that aspect, studies were focused on material development, which gave rise to pioneers in the last few years with amazing outcomes. This helped out to development and efficient disinfection of microbes with higher efficiencies as compared to previous other studies which were based upon visible light. As future aspects, this can lift to the next level by applying these findings in real-world applications.

3. Prospective and summary: Challenges and opportunities for the future research

A proper control of microorganisms is essential to prevent the transmission of diseases and infection. Most of pathogens are susceptible in addition to the formation of harmful by product formation and high cost of the currently available disinfectants processes. On the other hand, AOT process based on light-harvesting semiconductor photocatalysts proven to be efficient in eliminating a wide range pathogens completely which is innovative and environmental-friendly method without producing secondary pollutants. As a result, microbial disinfection by AOT process under indoor conditions is of great interest to maintain microbe-free indoor environment and in order to achieve this goal, the NIR and IR response of the photocatalysts must be improved. In this review, we summarized the strategies that have been reported microbial disinfection with NIR/IR responsive catalysts under indoor conditions. In NIR/IR-driven photocatalytic microbial disinfection process, bandgap engineering, an upconversion strategy, the plasmon effect, and sensitization methods are the major strategies that have been employed to harvest NIR/IR radiations. However, due to less research has been carried on the NIR-driven photocatalysts for microbial disinfection; the process is still in its early stages.

Overall, the progresses in the development of NIR active photocatalysts by methods described are still infancy due to major challenges

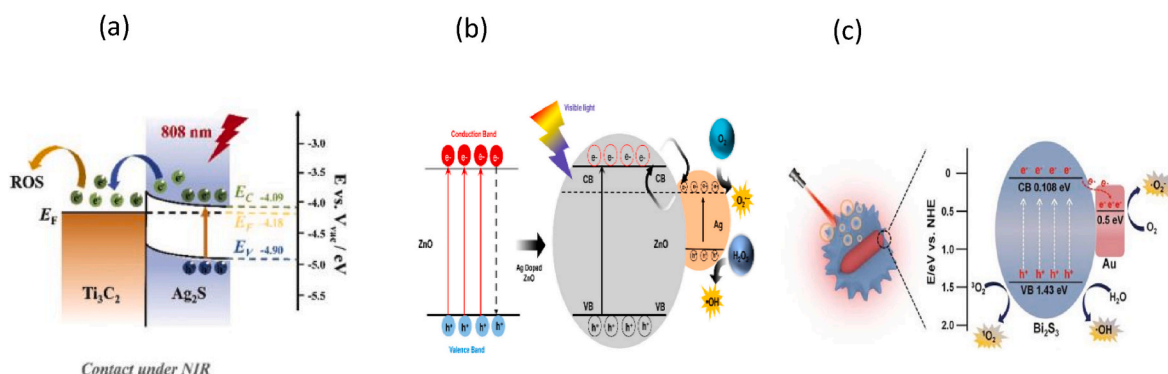


Fig. 6. (a) Schematic diagram of the changes in the energy band structure and internal electric field near the interface of the two phases under different conditions (before contact, contact in darkness and contact under NIR) for Ti₃C₂ and Ag₂S, and the specific process of ROS production under photocatalysis (Adapted with permission from (Wu et al., 2021), copyright 2021, Elsevier). (b) Schematic representation of the movement of electrons in ZnO@Ag under visible light. (Adapted with permission of open access from (Obeng et al., 2022), copyright 2022, Frontiers). (c) Mechanism of ROS produced by urchin-shaped Au@Bi₂S₃ core-shell structures (Adapted with permission from (Wang et al., 2020b), Copyright 2020, Elsevier).

of achieving enhance charge separation and transportation. Hence, one should pay attention to light harvesting properties as well as charge separation and transportation in developing IR-driven photocatalysts. In the case of bandgap engineering process, promising results have been noted with non-metallic plasmonic semiconductors which exhibit LSPR effect and in principal could be developed as efficient NIR/IR driven photocatalysts for microbe disinfection. Combination of metallic and non-metallic plasmonic materials is found to be an appropriate approach achieving extended light absorption properties as well as efficient excited charge carrier separation properties.

In the application of UC process for microbial disinfection is the least investigated method and also least efficient method compared with other microbial disinfection methods under indoor conditions. The rapid charge carrier recombination due to inadequate charge separation is the most challenging problem has been partially addressed by metal doping that eventually speeds up the electron migration speed due to capturing of electrons. Additionally, integrating UC materials with alloy NPs having the surface SPR effect is also of a promising way to minimize the excited charge carrier. In the case of microbe disinfection by plasmonic photocatalysts, the ability of plasmonic materials to extend the NIR light absorption is high compared to other methods. On the other hand, due to plasmonic-photothermal effect there is a possibility to direct inactivation of microbes by concentrating the light within a small spatial domain, that would resulting in localized and intense heating leading to inactivates microorganisms in close proximity. In addition to the photothermal effect of, charge carriers generated by absorption of IR photons by photocatalysts generating free radicals that lead to the destruction of the bacteria. The most common obstacle in the use of plasmonic noble metals in IR driven microbe disinfection is the rapid recombination of electron and hole pairs and significant decreasing the antimicrobial activity has been addressed by introducing co-catalysts. Another promising approach that can be employed for microbial disinfection under indoor condition is to couple with NIR/IR absorption materials with a suitable photocatalytic system. The main drawback of the IR photosensitization process is the poor low ROS yield. To enhance the ROS yield, heterojunctions of two different materials provided a good opportunity to improve the IR response and the charge separation and hence ROS yield. In such a system, it is necessary to choose the correct low-band gap material that enhances the harvesting of NIR/IR photons and high-band gap material to form Schottky heterojunctions to facilitate charge transfer. In a similar manner, Bi_2S_3 which is a known semiconductor that has been used for microbe disinfection by local photothermal effects as well as ROS production via NIR irradiation coupled with Au to enhance the NIR light absorption and minimize the rapid photo-induced electron hole recombination. Hence, Wang et al. synthesized $\text{Au@Bi}_2\text{S}_3$ core-shell Schottky junction to facilitate electron-hole separation and was able to demonstrate the enhancement of the NIR light absorption and to minimize the photo-induced electron hole recombination and thus enhance microbial disinfection activities.

Overall NIR/IR driven photocatalytic microbe disinfection under indoor conditions is yet to be developed. The lack of progress in developing NIR/IR-driven photocatalytic microbial disinfection process is mainly associated with poor charge separation and transportation which is common to bandgap engineering, an upconversion strategy, the plasmon effect, and sensitization methods employed. Similarly, poor NIR/IR absorbance capacity of the photocatalytic systems has to be improved greatly to enhance the overall microbial disinfection capacity. Hence it is indispensable to address these issues and together with introducing co-catalysts to the systems may lead to efficient NIR/IR photocatalytic systems for microbial degradation under indoor conditions. As we discussed earlier, research areas must be broadly addressed about the development of eco-friendly, cheaper, engineered catalytic disinfection devices which can be used in urban contexts to certify the healthy environment around crowded public areas as well as in small scale places. Already European countries have pioneered this area and practically applied this concept in their cities. Via material

development, those findings must be applied as devices to ensure the quality of experiments. Though it is not covered and is beyond the scope of this review, the reactor design (the reactor design and working regime, volume and flow rate, irradiation period and intensity, and so on) should be taken into account because it has a significant impact on photocatalytic performance.

4. Conclusion

Despite the photocatalytic microbes disinfection under indoor conditions with NIR/IR active photocatalyst has many advantages; a little investigation has been carried out. Inefficient photoexcited charge separation is one of the major reasons for not achieving a reasonable performance and one should pay especial attention how to enhance the charge separation. Out of the upconversion, defect engineering, surface plasmon effect and sensitization methods employed for microbial disinfection with IR photons, defect engineering and upconversion processes found to possess many advantages over surface plasmon and sensitization methods. Heavily doped or oxygen vacancies generated semiconductors that function as plasmon semiconductors in addition to their inter-band gap excitations are promising materials to be developed as NIR/IR driven photocatalytic disinfection of microbes. On the other hand, as the microbe disinfection under indoor conditions were confined to catalytic activity investigation and hence in-depth study of the process which may be provided the necessary driving force to enhance the activity and achieving progress in the future. Additionally, it may necessary to search for novel materials that can harvest NIR/IR radiations for microbial disinfection under indoor conditions.

Author contributions

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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