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## Review on heterogeneous photocatalytic disinfection of waterborne, airborne, and foodborne viruses: Can we win against pathogenic viruses?



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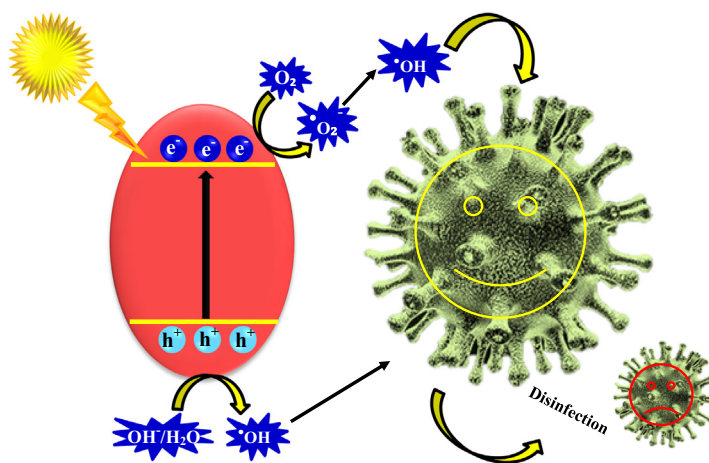
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### HIGHLIGHTS

- Photocatalytic disinfection of waterborne, airborne, and foodborne viruses were reviewed.
- Promising potential of heterogeneous photocatalysis for viral disinfection were discussed.
- Compatibility of photocatalytic disinfection method with sustainable development was discussed.
- Future research headlines about photocatalytic disinfection of different viruses were highlighted.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Microbial pathogenic contaminations have world widely represented a serious health hazard to humans. Viruses, as a member of microbial contaminants, seriously threaten human health due to their high environmental resistance, having small sizes, and causing an extensive range of diseases. Therefore, selecting an appropriate technology to remove viral contaminants from the air, water, and foods is of prominent significance. Traditional methods for viral disinfection have not proven to be highly practical and effective because they need high energy resources and operational expenses. In recent years, semiconductor-based photocatalysis has attracted more attention in the field of microorganism inactivation due to its outstanding performance and mild reaction conditions. Therefore, this review primarily concentrates on the recent development in viral inactivation/disinfection by heterogeneous photocatalysts. Moreover, the photocatalytic viral inactivation of waterborne, airborne, and foodborne viruses is discussed. Given the appealing merits of heterogeneous photocatalytic disinfection of viruses, there is no doubt that this technology will be an impressively active research field and a source of comfort and confidence to humans in battling against viruses.

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## 1. Introduction

Nowadays, microbial pathogenic contaminations with viruses, bacteria, and protozoa have become a growing environmental concern, because these pathogens threaten human health and cause dangerous infectious illnesses [1–3]. Among different kinds of microbial contaminations, viruses have proven as a global challenge due to their small-sized particles, difficult inactivation, high environmental endurance, and also because of an extensive range of illnesses and diseases caused by them [4,5]. Viruses are extremely ubiquitous microorganisms failing to survive outside the host organisms. Moreover, their survival/disinfection is primarily subject to the host-virus dynamics [6]. Viral contaminants, associated with drinking water, breathing air, and food, have become a notable threat due to their adverse effects on the environment and human health. Foodborne, waterborne, and airborne pathogens enter the body through different modes of infection and cause over 15 million deaths around the world annually. Water-borne and foodborne outbreaks correlate with climatic changes and disturbances in the ecosystem. In addition to airborne transmission, these pathogens are also transmitted by direct surface contact [7,8]. In particular, the risk of disease through exposure to the airborne and waterborne viruses is higher than those of other microbial pathogenic contaminants [9–16]. Infectious diseases caused by these viruses are the most widespread and common health risks. Spiraling worries about epidemic and pandemic viral diseases, such as severe acute respiratory syndrome coronavirus (SARS-CoV), swine influenza virus (H1N1), middle-east respiratory syndrome coronavirus (MERS-CoV), and novel coronavirus disease-2019 (COVID-19), have drawn the attention of many scientists for viral treatments [17–23]. Accordingly, to treat the diseases caused by viruses, different methods have been utilized and many attempts have been allocated for disinfection of various viruses presented in the environment [24,25]. For waterborne viruses, there is a diversity of disinfection processes like ultraviolet (UV) disinfection, membrane filtration, and chemical disinfectants (ozone, chlorine dioxide, and chlorine) [26]. In practice, however, these processes suffer from some limitations. The production of noxious byproducts has restricted the use of chemical disinfectants [27]. Membrane methods like nanofiltration and ultrafiltration, due to the small membrane pore sizes relative to the size of viruses, can eliminate viruses efficiently, although these methods are unaffordable and energy consuming [13]. In addition to the high expense of the UV method, some viruses show a high resistance to UV illumination [28,29]. Further, conventional methods for airborne viral disinfection like UV light, thermal treatment, and non-thermal plasma are not highly practical and effective, because they require high energy resources and high operational expenses [30]. Therefore, an effective technology with eco-friendly features, high proficiency, low energy consumption, and affordable expense is required for inactivation of viruses.

Over the past decades, we have witnessed extensive and unprecedented research in the field of advanced oxidation pro-

cesses (AOPs), which are judged to be the most encouraging method for the removal of pollutants, including organic, inorganic, and microbial contaminants, compared with traditional purification procedures [31,32]. In the AOPs, highly reactive oxygen species (ROS) like  $\cdot\text{OH}$ ,  $\cdot\text{O}_2^-$ ,  $\text{h}^+$ , and  $\text{HO}_2$  are produced, which have large oxidizing ability. These species can oxidize organic contaminants to  $\text{CO}_2$  and inorganic ions, reduce inorganic contaminants to nontoxic ions, and inactivate microorganisms producing no noxious compounds [33,34]. Of these AOPs, semiconductor-assisted photocatalysis is introduced to be the most desirable method due to its proven ability in the purification of an immense range of contaminants [35,36]. Photocatalysis is an extremely effective and promising technology, because it requires only solar light (or artificial light) and a photoactive material. The heterogeneous photocatalytic procedure begins with the absorption of the utilized light with a higher amount of energy than the photocatalyst band gap, which transfers the valence band (VB) electrons into the conduction band (CB), leading to production of charge carriers ( $\text{e}^-/\text{h}^+$  pairs). The photoexcited charge carriers migrate to the surface of the photoactive material and take part in the reduction and oxidation (redox) reactions. The holes in VB and the electrons in CB can thermodynamically oxidize water molecules and reduce  $\text{O}_2$  to produce ROS, respectively. Subsequently, the reactions of harmful microorganisms and environmental pollutants with these radicals result in disinfection and elimination of contaminants found in the environment, respectively [37–40].

## 2. Inactivation of viruses by heterogeneous photocatalysis

After viral inactivation on  $\text{TiO}_2$  photocatalyst discovered by Sierka and Sjogren in 1994, heterogeneous photocatalysis has been given widespread recognition as an outstanding technology in the field of viral disinfection [41]. The ROS created by photocatalytic processes destroy the shell and/or capsid of viruses, resulting in release of genetic materials, minerals, and proteins inside viruses. Additionally, organic compounds presented in the structure of viruses could be completely mineralized, which causes their inactivation/disinfection. As shown in Fig. 1, Zhang et al. suggested three mechanisms for viral disinfection in photocatalytic processes, which include physical damage of viruses, metal ion toxicity obtained from metal-including photocatalysts, and chemical oxidation by ROS generated over the photocatalysts [5]. These mechanisms are affected when the photocatalyst surface and the virus come into contact, which leads to an increase of the photocatalytic efficiency. The contact built up between the viral cells and the photocatalyst particles in suspension may supply an extended surface area for production of more ROS [42,43].

It is witnessed that relevant publications in the field of viral inactivation through heterogeneous photocatalysis are increasing with time, confirming the rising popularity of the field.

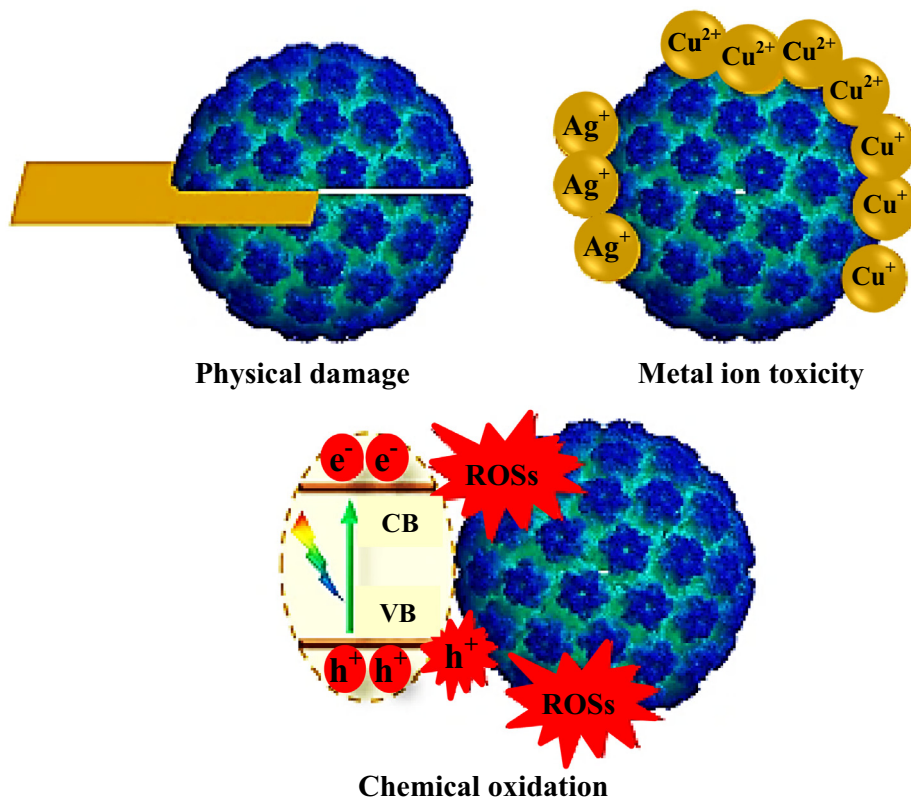


Fig. 1. Three main mechanisms of viral inactivation induced by heterogeneous photocatalysts (Reproduced with permission from reference [5] Copyright 2019 Elsevier).

The photocatalytic disinfection of viruses mainly takes place by chemical oxidation initiated by ROS over heterogeneous photocatalysts. The disinfection mechanism includes decomposition of the cell wall and the cytoplasmic membrane as a result of the generation of ROS like  $\cdot\text{OH}$  and  $\text{H}_2\text{O}_2$  [44], through several steps as follows:

- 1) Electron/hole ( $e^-/h^+$ ) pairs are produced after excitation of the selected photocatalyst and transfer of charges to its surface.
- 2) The holes in VB react with surface adsorbed  $\text{OH}^-$  or  $\text{H}_2\text{O}$  species to generate hydroxyl radical ( $\cdot\text{OH}$ ), which subsequently oxidize the chemicals presented in the virus (especially the shell and capsid) adsorbed on the photocatalyst surface.
- 3) The electrons in CB, after reaction with  $\text{O}_2$ , produce highly efficient radicals ( $\cdot\text{O}_2^-$ ,  $\cdot\text{OH}$ , and  $\cdot\text{OOH}$ ), and then, the generated ROS initiates reactions, leading to destruction of the virus adsorbed on the photocatalyst surface.

As stated, the diverse highly efficient species, produced on the photocatalyst surface, can oxidize viruses adsorbed on the photocatalyst surface, leading to their disinfection [45]. Fig. 2 demonstrates the formation of  $e^-/h^+$  pairs, recombination step, generation of ROS, and viral disinfection. Finally, the photocatalytic disinfection efficiency of viruses is obtained using Eq. (1):

$$Q = \log N_0 - \log N_t = -\log \frac{N_t}{N_0} \quad (1)$$

where  $N_t$  and  $N_0$  stand for concentrations at the time  $t$  and the initial time, respectively, and  $Q$  is the microorganism removal efficiency [46].

The heterogeneous photocatalytic performance of viral disinfection principally pertains to the capability for retardation of  $e^-/h^+$

pairs from recombination and the ability to fully utilize sunlight. Regrettably, the photocatalytic ability of most semiconductors is trivial because of several disadvantages including poor capability for  $e^-/h^+$  separation, fast recombination of charges, and low utilization efficiency of solar light [47,48]. Up to now, diverse photocatalysts such as  $g\text{-C}_3\text{N}_4$ ,  $\text{CuO}$ ,  $\text{ZnO}$ ,  $\text{TiO}_2$ , and  $\text{Ag}_3\text{PO}_4$  prepared with different morphologies, structures, and procedures have been used for the inactivation of viruses due to their nonhazardous nature and high stability [49–51]. Moreover, they are eco-friendly and are used in biomedical fields such as drug delivery systems, biological sensors, cell imaging, and the photodynamic therapy of cancer [52]. However, the practical and large scale utilization of the mentioned semiconductors in photocatalysis is normally hindered by the rapid recombination of charges, inadequate visible-light absorption, and a low specific surface area. In the past years, considerable efforts have been made to overcome the mentioned shortfalls and increase the photoactivity of sole semiconductors through extrinsic and intrinsic doping [53,54], surface modification [55], sensitization [56], and coupling with other semiconductors to form heterojunctions [57]. Therefore, by considering the actual state of the review, this study focuses on a survey of the photocatalytic inactivation of waterborne, airborne, and foodborne viruses using semiconductor-assisted photocatalysis and the perspective of this important research field to tackle issues related to the spread of different viruses worldwide. Thus, in the following sections, we will review the literature on photocatalytic viral inactivation for waterborne, airborne, and foodborne viruses.

### 2.1. Waterborne pathogenic viruses

Waterborne pathogenic viruses (like enteroviruses, adenoviruses, noroviruses, and rotaviruses) are usually found in groundwater, surface water, and even treated drinking water,

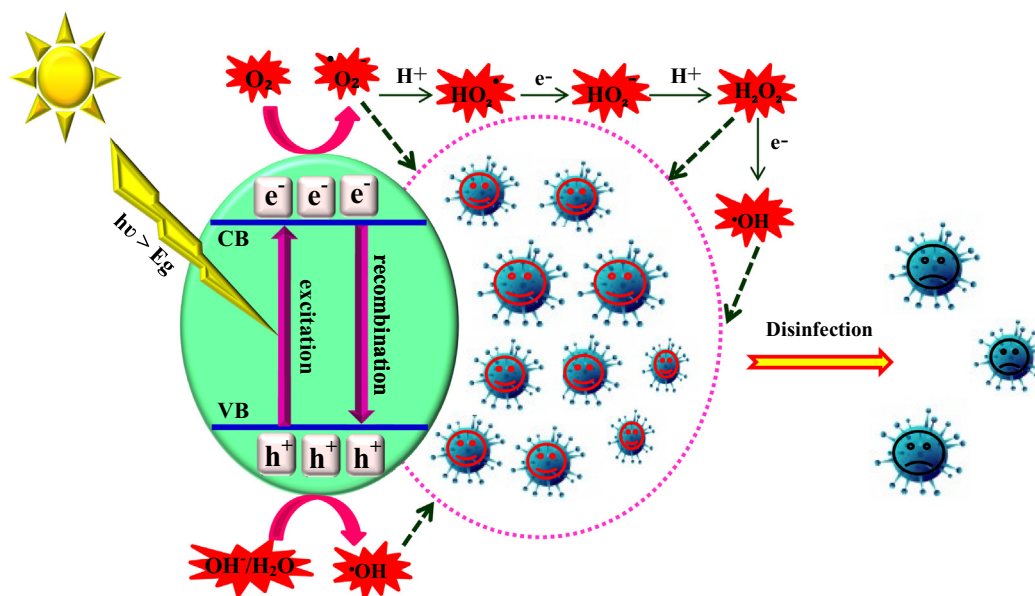


Fig. 2. Disinfection mechanism of viruses by photocatalysts.

which could pose serious hazards to human health [58–60]. For this reason, most studies have been focused on the antiviral ability of various photocatalysts against waterborne viruses [61–63]. In 1994, Sierka and Sjogren as pioneers in managing the photocatalytic inactivation of viruses explored MS2 disinfection, as a waterborne virus, with  $\text{TiO}_2$  [41]. Near-UV photocatalytic inactivation was performed in  $\text{TiO}_2$  suspensions. The phage MS2 disinfection level reached to 99.9% after adding  $2 \mu\text{M}$  of  $\text{FeSO}_4$ . The increased MS2 disinfection level might be described by impressive targeting of  $\text{OH}$  oxidation directed by  $\text{FeSO}_4$  adsorbed to MS2. In 1998, in another research, Lee et al. used Bacteriophage Q $\beta$ , as a model waterborne virus [64]. They concluded that UV illumination on  $\text{TiO}_2$  suspension was more effective in virus disinfection than only UV illumination. Accordingly, after 2 min of irradiation,  $3.5\text{-log}_{10}$  Q $\beta$  disinfection was obtained by UV illumination on  $\text{TiO}_2$ , while UV disinfected only  $2\text{-log}_{10}$  Q $\beta$ . In another research, Koizumi and Taya investigated the photocatalytic disinfection of phage MS2 over  $\text{TiO}_2$ , in different situations [65]. It was observed that the considerable disinfection of MS2 occurred only with the presence of light and  $\text{TiO}_2$ . Concerning the efficacy of pH on MS2 disinfection, the rate constant was determined to show an outstanding property with the maximal amount at pH 6.0 ( $9.1 \times 10^{-2} \text{ s}^{-1}$ ).

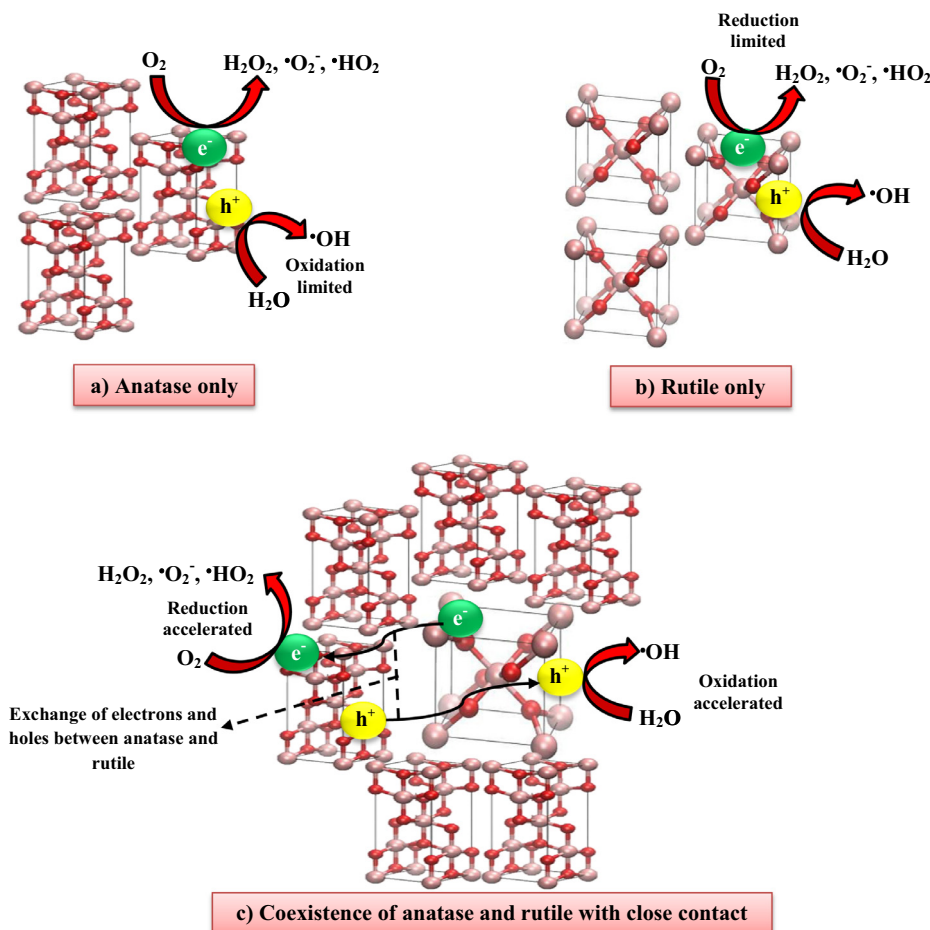
Noroviruses (NVs) are identified as major waterborne viruses, which cause outbreaks of gastroenteritis. Hence, in 2005, Kato et al. explicated methods to quantitatively specify NVs in wastewater and determine the probability of the inactivation procedure [66]. It was found that the UV-assisted  $\text{TiO}_2$  system was effective in disinfection of viruses. In this study, the UV-assisted  $\text{TiO}_2$  system was a developed inactivation system wherein  $\cdot\text{OH}$  species, created through the oxidative decomposition of  $\text{H}_2\text{O}_2/\text{OH}$  species, led to disinfection of viruses. After that, in 2006, the photocatalytic disinfection of MS2 was carried out with the mixture of rutile and anatase-type  $\text{TiO}_2$  upon black-light illumination [67]. As illustrated in Fig. 3, due to the coexistence of two types of  $\text{TiO}_2$ , they can be in close contact, which may facilitate the exchange of  $\text{h}^+$  and  $\text{e}^-$  among these phases with the balanced acceleration of reduction and oxidation rates. As a consequence, the quantum yield can increase production of ROS.

In another research, Sang et al. inactivated rotavirus, astrovirus, and feline calicivirus using a  $\text{TiO}_2$  film under visible light [68]. They displayed that under the activation of  $\text{TiO}_2$  with visible light

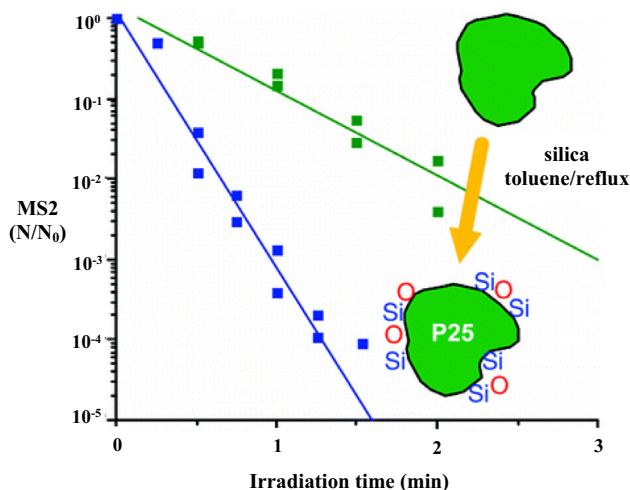
through a fluorescent white lamp,  $\cdot\text{OH}$  and  $\text{O}_2^-$  species are generated in a significant amount. The authors inferred that virus disinfection over this photocatalyst may be related to the production of these ROS. They also underscored the potential and importance of the fabricated  $\text{TiO}_2$  film in the future specific treatment of enteropathogenic viral infection. In another attempt, Li et al. fabricated palladium-modified/nitrogen-doped TiO (denoted as  $\text{TiON}/\text{PdO}$ ) nanocomposite via a sol-gel method [69]. In the fabrication of this nanocomposite, the palladium additive appeared as PdO. For the first time, a great amount of coliphage MS2, as a nonpathogenic virus, was inactivated upon visible-light irradiation. In this study, highly reactive  $\cdot\text{OH}$  was generated by  $\text{TiON}/\text{PdO}$  under visible light to disinfect MS2 phage. In 2010, a specific procedure was presented for identical viral and bacterial adhesion on the selected photocatalysts. *Bacillus thuringiensis*, *Mycobacterium smegmatis*, and vaccinia viruses were disinfected after adhering to the  $\text{TiO}_2$  and  $\text{Pt}/\text{TiO}_2$  photocatalysts [70]. An enhanced disinfection rate was observed on the  $\text{Pt}/\text{TiO}_2$  upon UVA illumination. A disinfection rate of 99.8% and 90% was obtained in 30 min of the light illumination on the  $\text{Pt}/\text{TiO}_2$  and  $\text{TiO}_2$  photocatalysts, respectively. The outcomes illustrated that  $\text{TiO}_2$  or  $\text{Pt}/\text{TiO}_2$  photocatalytic filters are able to disinfect viral microorganisms and successfully decompose them into inorganic products.

Another research group in 2010, illustrated that boosted photocatalytic efficiency over  $\text{TiO}_2$  for bacteriophage MS2 virus disinfection was obtained through adding  $\text{SiO}_2$  [71]. They reported that by adding  $\text{SiO}_2$ , the virus deposition increased on the photocatalyst. The increased photoactivity for the  $\text{TiO}_2\text{-SiO}_2$  composite could be related to the reduced recombination of the charge carriers, production of a higher concentration of  $\cdot\text{OH}$ , and higher adsorption ability of MS2 to the photocatalyst surface. Moreover, as can be viewed in Fig. 4, the  $\text{TiO}_2\text{-SiO}_2$  photocatalysts were better than  $\text{TiO}_2$  and the rate constant for the  $\text{TiO}_2\text{-SiO}_2$  photocatalyst fabricated with refluxing method was  $3.1 \text{ min}^{-1}$ , which was almost 3-folds premier than that of  $\text{TiO}_2$  ( $0.95 \text{ min}^{-1}$ ). Hence, the enhanced ability of this photocatalyst for MS2 disinfection makes it a more noteworthy alternative for using as an antiseptic.

In plasmonic photocatalysts, metal noble particles are dispersed over photocatalysts, which possess outstanding properties due to the surface plasmonic resonance (SPR). A further combination of light with metal particles at special photon energies is because of



**Fig. 3.** Possible mechanism for enhancement of photocatalytic disinfection of viruses caused by contacting between anatase and rutile phases of  $\text{TiO}_2$  (The modified illustration with permission from reference [67] 2006 Elsevier).



**Fig. 4.** Photocatalytic inactivation of MS2 by  $\text{TiO}_2$  (P25) (green,  $R^2 = 0.935$ ), and  $\text{TiO}_2$  (P25)- $\text{SiO}_2$  (blue,  $R^2 = 0.970$ ) photocatalysts (Reproduced with permission from reference [71] Copyright 2011 Elsevier). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the excitation of the electron in noble particles under the light illumination, introduced as SPR. The individual capability of noble metal particles for light absorption and scattering depends on the particle geometry and metal type. Recently, it has been illustrated that plasmon-excited nanoparticles can be an effective resource of

hot electrons. Under optical excitation, any plasmon quantum can decay either nonradiatively into an electron-hole pair or radiatively into a photon (scattering). Hence, this process can be completely impressive and if a nearby semiconductor as an electron acceptor exists, hot electrons can move into its electronic states [72,73]. Photocatalysis can benefit from the SPR in different ways. First, the resonance wavelengths for Ag and Au nanoparticles can be manipulated to be in the range of visible or near-UV lights, based on the shape, size, and surrounding media. Second, the SPR can remarkably improve the visible-light harvesting ability of the wide-band gap photocatalysts [74,75].

Liga et al. studied silver-doped  $\text{TiO}_2$  nanoparticles (denoted as  $n\text{Ag}/\text{TiO}_2$ ) to disinfect MS2 [76]. The disinfection rate of MS2 increased with the increase of the Ag amount. These photocatalysts were excited by visible light through SPR generated by the silver nanoparticles. They showed that the  $n\text{Ag}/\text{TiO}_2$  photocatalyst remarkably increased the photocatalytic disinfection of the virus through enhancing  $\cdot\text{OH}$  generation in addition to slightly enhancing virus adsorption. Liga et al. also synthesized  $\text{SiO}_2$ - $\text{TiO}_2$  photocatalysts through modifying the  $\text{TiO}_2$  surface with  $\text{SiO}_2$  [77]. Although the  $\text{SiO}_2$ - $\text{TiO}_2$  photocatalysts slightly decreased  $\cdot\text{OH}$  generation, they presented excellent photocatalytic disinfection rates for MS2, due to the increased MS2 adsorption. These outcomes suggested that modifying  $\text{TiO}_2$  surface to enhance adsorption of viruses is a major method in developing photocatalytic disinfection performance.

In another research, Zuo et al. used Phi X174 and MS2 viruses as viral disinfection models [78]. They applied three disinfection

procedures (UV, chlorine, and UV/TiO<sub>2</sub>) to eliminate the abovementioned viruses. Based on the obtained results, the successful disinfection in the presence of the UV-assisted TiO<sub>2</sub> system was observed for the mentioned viruses from water sources. Li et al. for the first time evaluated the photocatalytic disinfection of MS2 virus on g-C<sub>3</sub>N<sub>4</sub>, as a metal-free semiconductor, upon visible-light excitation [79]. Briefly, the inactivation process was as follows: By preparing 1 × 10<sup>8</sup> PFU/mL of the primary virus, the MS2 stock suspension was diluted into 100 mL of PBS. Then, the obtained g-C<sub>3</sub>N<sub>4</sub> photocatalyst was appended for inactivation of the virus. The suspension was stirred at 25 °C. Before illumination, to reach an adsorption–desorption balance, the reaction was left in the dark upon stirring for 30 min. Viruses were sampled at different irradiation times using a 300 W Xenon lamp, and then were enumerated immediately to stop any further inactivation. A reaction solution containing the sample and viruses, without the light irradiation, was utilized as a dark control. Moreover, as a light control experiment, a suspension of viruses without the photocatalyst was illuminated under the same circumstance. Upon the light illumination for 5 h, the ability of g-C<sub>3</sub>N<sub>4</sub> was compared with those of other visible-light-induced systems, like N-TiO<sub>2</sub>, Bi<sub>2</sub>WO<sub>6</sub>, and Ag@AgCl photocatalysts in the viral disinfection. Accordingly, g-C<sub>3</sub>N<sub>4</sub> disinfected >7 log of the virus, while the Bi<sub>2</sub>WO<sub>6</sub> and N-TiO<sub>2</sub> photocatalysts reduced the amount

of the virus only ~4 log and ~1 log, respectively (Fig. 5a). The g-C<sub>3</sub>N<sub>4</sub> photocatalyst demonstrated long-term and durable anti-virus efficacy against MS2. As demonstrated in Fig. 5b, the disinfection of this virus by this photocatalyst was explained as nonselective reactions initiated by e<sup>-</sup>, ·OH, and ·O<sub>2</sub><sup>-</sup> species, which finally led to removal of virus without regrowth. Thus, it was inferred that g-C<sub>3</sub>N<sub>4</sub> and g-C<sub>3</sub>N<sub>4</sub>-based photocatalysts are excellent selections for inactivation of different viruses.

In 2018, Cheng et al. prepared Ag<sub>3</sub>PO<sub>4</sub>/g-C<sub>3</sub>N<sub>4</sub> (denoted as AgCN) nanocomposites through a hydrothermal procedure [49]. The photocatalytic inactivation was studied with bacteriophage f2, as a viral model. Meanwhile, the mechanism of boosted inactivation by the mentioned binary photocatalyst was evaluated through radical quenching tests, denoting that ·OH and h<sup>+</sup> played major roles in the inactivation process. The photocatalytic disinfection efficiency of f2 virus through the mentioned binary photocatalysts reached 6.5 log in 80 min upon visible-light excitation. This impressive enhancement was related to the synergistic effects of Ag<sub>3</sub>PO<sub>4</sub> and g-C<sub>3</sub>N<sub>4</sub> for the supreme segregation of the charge carriers and broad visible-light absorption. To describe the improved photocatalytic performance of the mentioned binary photocatalysts, a photocatalytic Z-scheme mechanism was suggested, as represented in Fig. 6. The selected virus was decomposed by the ROS

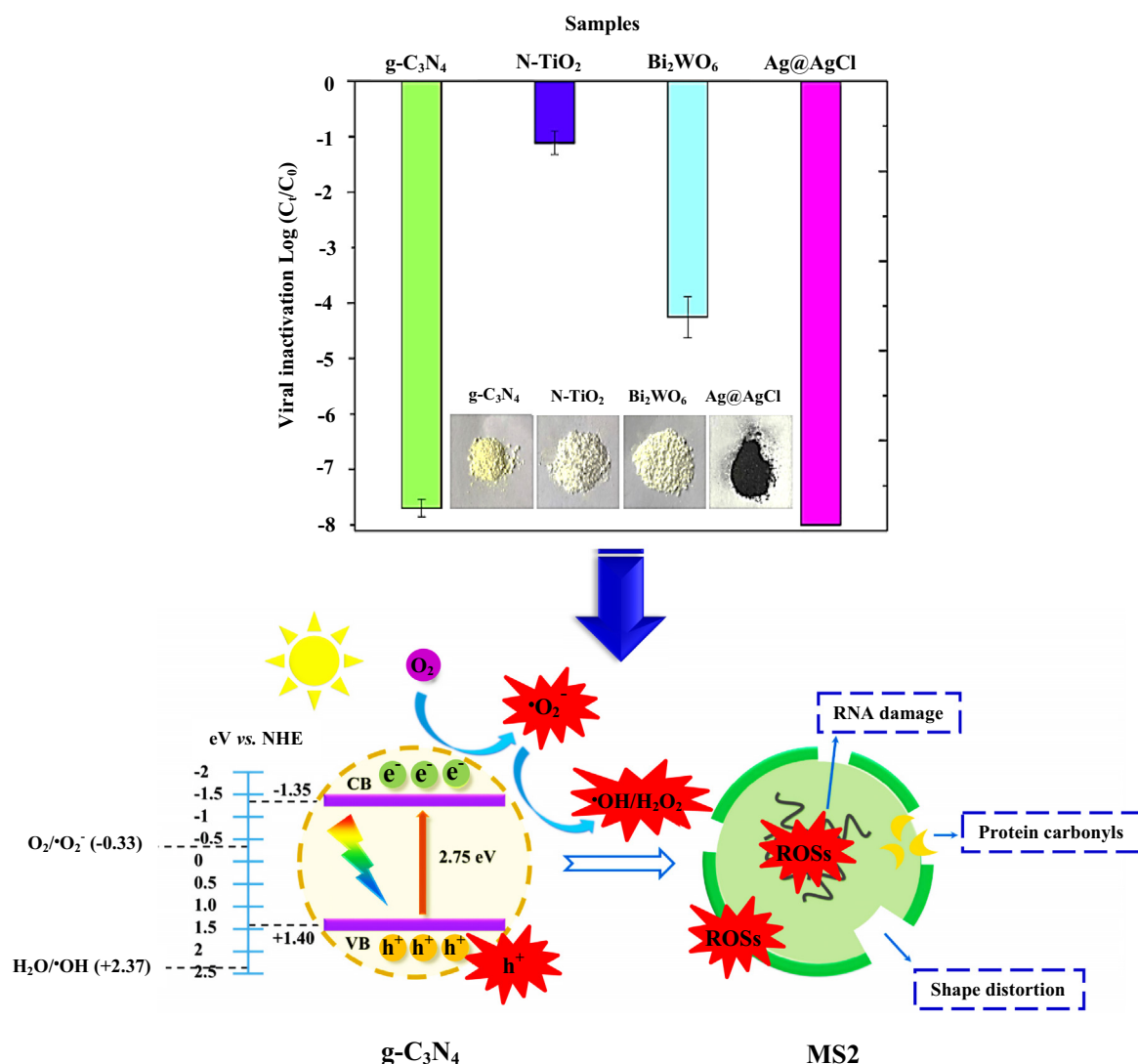
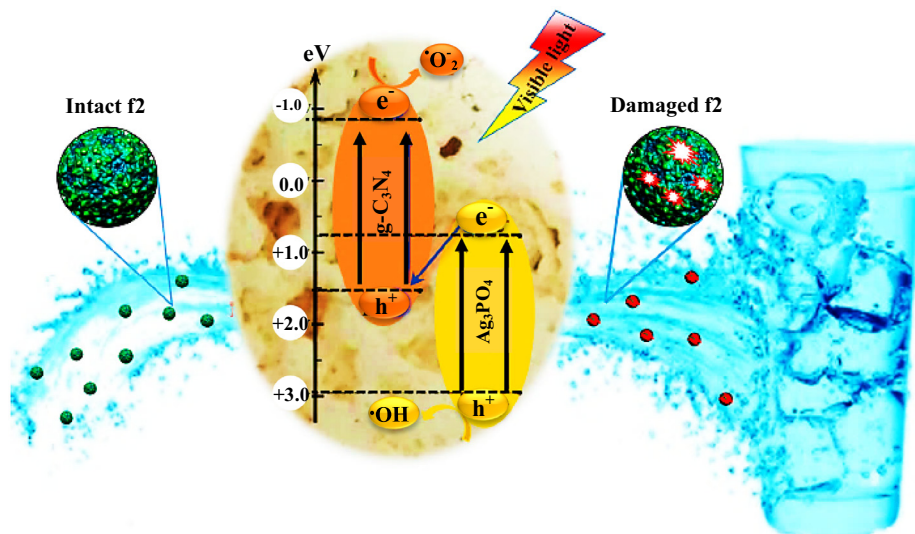


Fig. 5. (a) Comparison between the photocatalytic performance of g-C<sub>3</sub>N<sub>4</sub>, N-TiO<sub>2</sub>, Bi<sub>2</sub>WO<sub>6</sub>, and Ag@AgCl photocatalysts for MS2 inactivation under 300 min visible-light irradiation. (b) Schematic illustration of proposed mechanism for the viral inactivation by g-C<sub>3</sub>N<sub>4</sub> (Reproduced with permission from reference [77] Copyright 2016 Elsevier).



**Fig. 6.** The possible mechanism for photocatalytic inactivation of bacteriophage f2 by AgCN photocatalysts under visible light (Reproduced with permission from reference [49] Copyright 2018 Elsevier).

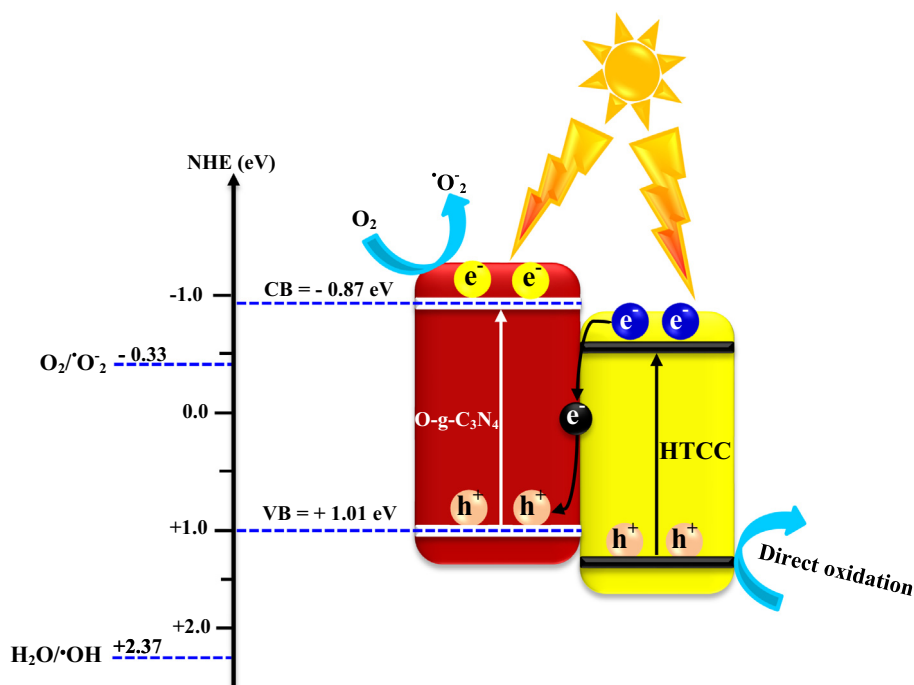
produced after efficiently separation of the charge carriers of  $g-C_3N_4$  and  $Ag_3PO_4$  components. This work completely created a type of promising nanocomposite for disinfection of different viruses present in contaminated water sources.

In another attempt, some novel metal-free nanocomposites of oxygen-doped  $g-C_3N_4$ /hydrothermal carbonation carbon (denoted as  $O-g-C_3N_4$ /HTCC) microspheres were successfully constructed through a simple two-step method [13]. The optimum nanocomposite had strong visible-light absorption and showed outstanding virucidal efficacy for HAdV-2, which disinfected 5-log in 2 h of the light illumination. The boosted viral disinfection ability of the optimum nanocomposite was related to the Z-scheme mechanism for separation of charges, which significantly developed charge segregation (Fig. 7). Furthermore, the Z-scheme mechanism sim-

plified the generation of  $\cdot OH$ , leading to the lethal rupture of the rigid capsid of HAdV-2.

### 2.2. Airborne pathogenic viruses

The emission of airborne microorganisms through animal feeding operations has prompted growing worries in the field of epidemiology and health [80]. Airborne microorganisms may create negative immune reactivity in animals and trigger inflammatory respiratory dysfunction in humans. Moreover, several pathogenic species are suspected to be airborne transmittable species among farms [81,82]. Several infectious viruses have been discovered at the outlet of animal houses, and other extremely infectious illnesses are spread via aerial transmission. Hence,



**Fig. 7.** The possible Z-scheme mechanism proposed for the  $O-g-C_3N_4$ /HTCC photocatalyst (The modified form with permission from reference [13] 2019 Elsevier).



impressive procedures are needed to hinder pathogen transmission and decrease microbial emissions, and thus safeguard human and animal health.

Although many studies about the photocatalytic disinfection of bacteria have been carried out, few investigations have been reported about disinfection of airborne viruses. Hence, in a research conducted in 2012, Nakano et al. observed that TiO<sub>2</sub> thin film significantly disinfected the influenza virus through degradation of viral proteins. They realized that the degradation relied on the illumination time of UV and its intensity [83]. Despite the partial intensity of UVA, a viral decrease of almost 4 log<sub>10</sub> was seen during the illumination time. These outcomes demonstrated that the TiO<sub>2</sub> thin film could be applied to disinfect the influenza virus in the air. As a result, TiO<sub>2</sub> might be an efficient photocatalyst for disinfection of other airborne viruses and it can be applied to hinder viral transition through air. In addition, Dai-koku et al. constructed a porous ceramic substrate coated with nanosized-TiO<sub>2</sub> and used it for disinfection of airborne influenza infection [84]. The airborne infectivity of the influenza virus was attenuated within 5 min through this photocatalytic system under black light. The photocatalytic air cleaner impressively inactivated airborne influenza virus infection. Moreover, as known, air contamination created by fine particulate matters (PM<sub>2.5</sub>), bioaerosols, and volatile organic compounds, is a major risk to health. In 2017, Shiraki et al. constructed a photocatalytic air cleaner to decrease the contamination levels of indoor air. They studied the photocatalytic activity using UV-LED [85]. For this purpose, they fabricated a TiO<sub>2</sub>-coated aluminum plate system as a photocatalyst. This photocatalytic air cleaner was utilized for inactivation of the aerosol-associated influenza virus. This photocatalytic system effectively disinfected aerosol-associated influenza virus, showing that it could detoxify and clean the air in a closed place.

Doss et al. introduced the first LED photocatalytic system constructed by TiO<sub>2</sub>/β-SiC solid alveolar foams for air purification from airborne viruses such as T2 bacteriophage [12]. They demonstrated that the purification efficiency associated with the elimination of this virus resulted from the passive filtration effect and the photocatalytic ability of the TiO<sub>2</sub>/β-SiC solid alveolar foams. Moreover, it was reported that utilizing 56 LEDs versus 40 LEDs significantly improved the logarithmic reduction. These outcomes demonstrated the potential application of LEDs and solid alveolar foam as an impressive and energy-saving method to disinfect viruses via a photocatalytic procedure.

Although some UV-based inactivation procedures have been introduced for viral disinfections, these techniques often need long illumination periods or use of the recirculating mode due to their low photon energy. Vacuum UV (V-UV) was lately discovered to be a highly effective light source. In a research conducted by Kim and Jang [18], the photocatalytic processes were investigated by V-UV with short illumination times to simultaneously disinfect MS2 as an airborne virus (nearly 90% disinfection efficiency at a VUV illumination time of 0.009 s) and remove the produced ozone toward an air inactivation system. In this study, the Pd-TiO<sub>2</sub>/VUV system demonstrated the ability for simultaneous MS2 disinfection and ozone elimination and the photocatalytic ability was efficient regardless of relative humidity.

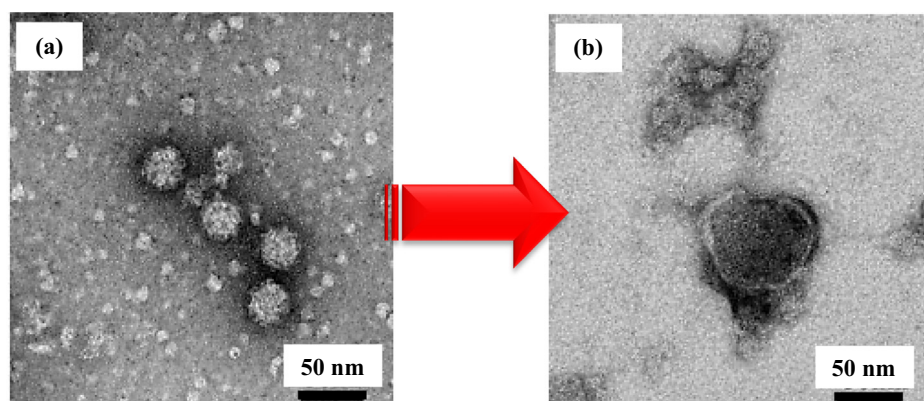
In another study carried out by Choi and Cho, novel visible-light-driven nanocomposites based on some metals (Mg, Fe, and Mn) deposited on TiO<sub>2</sub> were investigated for their antiviral ability against airborne viruses such as influenza H1N1 [86]. Under wavelengths higher than 410 nm supplied with fluorescent lamps, >99% of the virus was inactivated within half an hour. Thus, they concluded that the mentioned nanocomposites could be satisfactorily utilized to decrease viral transmission.

### 2.3. Foodborne pathogenic viruses

Human norovirus (denoted as HuNoV) is the main cause of viral gastroenteritis [87,88]. Hence, it is necessary to determine intervention procedures to decrease the danger of foodborne diseases. The inactivation yield of disinfection procedures is hard to investigate for vegetables and fruits, due to their irregular surface characteristics and inconsistent degree of pollution [89,90]. Park et al. investigated the disinfection efficiency of murine norovirus 1 (MNV-1), as a HuNoV, by a constructed solidified agar matrix (SAM) as a simulated blueberries under UVA, UVB, and UVC irradiations in the absence and presence of TiO<sub>2</sub> [91]. Among them, UVC with TiO<sub>2</sub> obtained a good level of virus decrease for both externally inoculated and internalized MNV-1. Furthermore, the Weibull model was used to explain the disinfection mechanism of MNV-1, which proved an excellent fit to the data. There are many studies which agree with the Weibull model, as a better fit than first-order models for kinetic analysis of disinfection processes. More importantly, the Weibull model has been extensively utilized because of its simplicity and flexibility [92,93]. A good correlation was quantified between the viral disinfection and the steady-state concentration of ·OH through a probe compound, indicating that the generated ·OH was the main species for MNV-1 disinfection. It was found that UVC in the absence and presence of TiO<sub>2</sub> was more efficient for MNV-1 disinfection than UVA and UVB irradiations. Hence, the UVC/TiO<sub>2</sub> inactivation system can disinfect the virus found inside and on the surface of blueberries, which is an impressive alternative technique to common chlorine inactivation for decreasing the danger of HuNoV infection in various foods. Moreover, the viral disinfection procedure presented by this research group indicated that the use of SAM as an efficient simulated food for evaluation of the yield of disinfection procedures indicated favorable outcomes.

As mentioned, HuNoV is the main cause of foodborne diseases, which can also associate with shellfish consumption [94]. Kim et al. injected MNV-1 inside SAM for virus internalization and specified the effect of high hydrostatic pressure (HHP) and UV-assisted TiO<sub>2</sub> [95]. The internalized MNV-1 decreased by 5.5-log<sub>10</sub>, when HHP was followed by the UV-assisted TiO<sub>2</sub> system, suggesting a synergistic disinfection effect. Moreover, as can be viewed in Fig. 8a, untreated MNV-1 particles were round with a 35–40 nm diameter, while the TEM image of the treated MNV-1 virus demonstrated considerable virus deformation due to a synergistic efficacy of the inactivation procedure. This suggested that the outer surface was degraded (Fig. 8b). As a result, a hurdle strategy of the HHP-UV-assisted TiO<sub>2</sub> combined method proved efficient for internalized MNV-1 via a simulated food.

A summary of details about photocatalysts and operational parameters applied for viral disinfection is presented in Table 1. Furthermore, we know that heterogeneous photocatalytic processes are non-selective technology for degradation of pollutants and inactivation of microorganisms. Up to now, a wide range of organic contaminants and microorganisms have been removed/inactivated over photoactive materials. Despite non-selectivity in viral disinfections, the most important issue is the lack of any research about heterogeneous photocatalytic disinfection of novel viruses. As a consequence, more scientific activities in the field of heterogeneous photocatalytic disinfection of new viruses should be stimulated to obtain more insights about the exact potential of this technology to tackle the diseases caused by these viruses. After designing and fabricating more efficient photocatalysts, these photoactive materials could be used for inactivation of waterborne viruses in water decontamination plants and fabrication of more effective filters to disinfect airborne viruses. Additionally, walls of infectious parts of hospitals can be covered with photoactive mate-



**Fig. 8.** (a) TEM analysis of purified MNV-1 (untreated) and (b) HHP-UV-assisted  $\text{TiO}_2$  treatment (Reproduced with permission from reference [93] Copyright 2017 Elsevier).

**Table 1**  
Summary of utilized photocatalysts for various viral disinfection.

Photocatalyst	Virus	Operational condition		Light source	Disinfection efficiency	Type of virus	Ref.
		Catalyst loading (mg/L)	Virus level (PFU*/mL)				
$\text{TiO}_2$	Phage MS2	1000	$6 \times 10^4$	UV	2.8-log in 65 min	waterborne	[41]
$\text{TiO}_2$	Phage MS2	1000	$6 \times 10^5$	18 W BLB* lamp	1.8-log in 180 min	waterborne	[61]
$\text{TiO}_2$	Bacteriophage Q $\beta$	1000	$1 \times 10^6$	UV lamp	3.5-log in 2 min	waterborne	[64]
$\text{TiO}_2$	Phage f2	1000	$10^{10}$ – $10^{11}$	6 W black light lamp	6-log in 15 min	waterborne	[78]
$\text{TiO}_2$	Influenza virus	No data	$4.0 \times 10^8$	1 mW black light	Eliminated in 5 min	airborne	[83]
$\text{TiO}_2$	Influenza virus	No data	0.0 or $0.1 \text{ mg ml}^{-1}$	20 W black light	4-log in a short irradiation time	airborne	[84]
$\text{TiO}_2$	H1N1	No data	No data	UV-LED lamp	Eliminated in 7 min	airborne	[85]
$\text{TiO}_2$	MNV-1	No data	No data	UV lamp	3.2-log in 10 min	foodborne	[91]
$\text{TiO}_2$	MNV-1	No data	No data	UV lamp	>5.5-log in 15 min	foodborne	[95]
$\text{TiO}_2$	MS-2 bacteriophage	No data	$2 \times 10^5$	4 W BLB lamp	2-log in 109 min	waterborne	[96]
$\text{TiO}_2$	Phage f2	100	>20	4 W UV-Clamp	5–6-log in 160 min	waterborne	[97]
$\text{TiO}_2$	Murine norovirus	10	$1 \times 10^8$	UV lamp	3.3-log in 24 h	waterborne	[98]
Pd- $\text{TiO}_2$	MS2	No data	2.30 ( $\pm 1.27$ ) $\times 10^8$	VUV	90% in 0.009 s	airborne	[18]
Cu- $\text{TiO}_2$ nanofibers	Bacteriophage f2	50	$1 \times 10^4$	Xe lamp	4.0-log in 120 min	waterborne	[46]
Fe, Mg, and Mn-loaded $\text{TiO}_2$	H1N1	No data	100 $\mu\text{l}$	Fluorescent lamp	99% in 30 min	airborne	[86]
Cu- $\text{TiO}_2$ nanofibers	Bacteriophage f2	10	$1 \times 10^8$	Xe lamp	> 5-log in 240 min	waterborne	[99]
Mn- $\text{TiO}_2$	Phage MS2	100	$1 \times 10^5$	150 W Xe ozone-free lamp	4-log in 60 min	waterborne	[100]
$\text{TiO}_2/\beta\text{-SiC}$	T2 Bacteriophage	T2	No data	$6 \times 10^6$	56 LEDs	3-log in 60 min	airborne
$\text{TiO}_2/\text{CuO}$ films	Phage T4	No data	$8 \times 10^9$	40 W UVA lamp	9.9-log in 80 min	waterborne	[50]
$\text{SiO}_2\text{-TiO}_2$	Phage MS2	100	$3 \times 10^7$	8 W UVA lamp	5-log in 1.8 min	waterborne	[71]
nAg/ $\text{TiO}_2$	Phage MS2	100	$3 \times 10^7$	8 W UVA lamp	9.9-log in 80 min	waterborne	[76]
g- $\text{C}_3\text{N}_4$	Phage MS2	150	$1 \times 10^8$	300 W Xe lamp	8-log in 300 min	waterborne	[79]
g- $\text{C}_3\text{N}_4$	Phage MS2	135.4	$1 \times 10^8$	Xe lamp	8-log in 240 min	waterborne	[101]
$\text{Ag}_3\text{PO}_4/\text{g-C}_3\text{N}_4$	bacteriophage f2	100	$3 \times 10^7$	8 W UVA lamp	6.5-log in 80	waterborne	[49]
g- $\text{C}_3\text{N}_4/\text{EP}^*$	MS2	0.06	$1 \times 10^8$	300 W Xe lamp	8-log in 240 min	waterborne	[102]
O-g- $\text{C}_3\text{N}_4/\text{HTCC}^*$	HAdV-2	3	No data	7 W white LED* lamp	5-log in 120 min	waterborne	[13]
$\text{TiON}/\text{PdO}$	Phage MS2	100	$3 \times 10^8$	1000 W Xe arc lamp	1.5-log in 60 min	waterborne	[69]
G- $\text{WO}_3$ films	Phage MS2	No data	$2 \times 10^6$	Mercury lamp	5.9-log in 180 min	waterborne	[103]
FeO	Phage MS2	5	$1 \times 10^6$	Simulated solar	5-log in 30 min	waterborne	[104]
C60/ $\text{SiO}_2$	Phage MS2	300	$5 \times 10^6$	UVA, FL*, BLB	[UV]: 3.55-log in 75 min [FL]: 2.8-log in 75 min [BLB]: 2.3-log in 75 min	waterborne	[105]
C70/ $\text{SiO}_2$	Phage MS2	300	$3 \times 10^8$	Vis, Sunlight	[Vis]: 4.35-log in 90 min [Sunlight]: 4.4-log in 90 min	waterborne	[106]
Rh-Sr $\text{TiO}_3$	Phage Q $\beta$	3000	$5 \times 10^7$	Vis	5-log in 120 min	waterborne	[107]

[\*]: PFU = plaque forming unit; HRV-Wa = human rotavirus type 2 Wa; Xe = Xenon; BLB = black-light-blue; EP = expanded perlite; FL = Fluorescent light; HTCC = Hydrothermal carbonation carbon; LED = Light emitting diode.

rials to sustainably disinfect/inactivate viruses adhered over them using the irradiations applied for lightning of these parts. Furthermore, on streets of cities, photoactive materials may be used to sustainably inactivate/disinfect viruses using solar energy, without using any compounds currently used for inactivation of viruses.

### 3. Conclusions and future perspectives

Given the fact that viruses are potential dangers to human health, their removal from water, air, and foods is of prominent concern for researchers worldwide. Luckily, semiconductor-based photocatalysis has indicated a potential alternative technology with valuable merits of the facility, high efficiency, and energy-saving procedure to inactivate various viruses present in water, air, and foods. This is the first review on the development of heterogeneous photocatalytic disinfection of waterborne, airborne, and foodborne viruses. The research domains recommended below can open up new opportunities for exploring the potential application of the photocatalytic viral inactivation technology in addressing new challenges provoked by viral epidemic and pandemic cases.

Although utilized photocatalysts have presented promising results for disinfection of different viruses, more efficient photocatalysts are still needed to be applied for viral disinfections. Therefore, it is urgently necessary to explore ideal materials for photocatalytic disinfection processes with relatively high redox potential, low price, and long-term durability. To use sustainable resources in the photocatalytic viral inactivation processes, it is highly desired to develop more efficient visible/solar-light driven photocatalysts to tackle viral issues. In our opinion, recently developed photocatalysts based on  $g\text{-C}_3\text{N}_4$ , metal-organic frameworks, layered double hydroxides, and MXenes will be hot research topics as viral disinfection materials in the next decade. Furthermore, magnetically separable materials to simplify the separation of utilized photocatalysts from the aquatic systems are another bottleneck for the semiconductor-based photocatalytic viral disinfection procedures. To maximize the light/oxygen utilization to produce more ROS, floating photocatalysts are promising choices. In addition, contrary to waterborne viruses, the research on photocatalytic viral disinfections for airborne and foodborne viruses is in its infancy. Hence, more studies should be conducted to illustrate the potential application of the heterogeneous photocatalysis technology to disinfect these viruses. In spite of the non-selectivity of photocatalytic disinfection of viruses, the most important issue is the lack of any research about heterogeneous photocatalytic disinfection of novel viruses such as SARS-CoV and COVID-19. Therefore, future scientific studies should be undertaken on the field of heterogeneous photocatalysis processes to gain more insights into the exact potential of this technology to tackle new viral diseases. Consequently, there is no doubt that the heterogeneous photocatalysis viral disinfection technology, with many appealing merits, will be an impressively active research field in the future to provide comfort and confidence to humans worldwide.

### CRedit authorship contribution statement

**Aziz Habibi-Yangjeh:** Conceptualization, Writing - review & editing, Supervision. **Soheila Asadzadeh-Khaneghah:** Writing - original draft, Methodology. **Solmaz Feizpoor:** Writing - original draft, Methodology. **Afsar Rouhi:** Writing - review & editing.

### 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.

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