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Photoactive decontamination and reuse of face masks

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ABSTRACT

The corona virus disease 2019 (COVID-19) pandemic has led to global shortages in disposable respirators. Increasing the recycling rate of masks is a direct, low-cost strategy to mitigate COVID-19 transmission. Photoactive decontamination of used masks attracts great attention due to its fast response, remarkable virus inactivation effect and full protection integrity. Here, we review state-of-the-art situation of photoactive decontamination. The basic mechanism of photoactive decontamination is firstly discussed in terms of ultraviolet, photothermal or photocatalytic properties. Among which, ultraviolet radiation damages DNA and RNA to inactivate viruses and microorganisms, and photothermal method damages them by destroying proteins, while photocatalysis kills them by destroying the structure. The practical applications of photoactive decontamination strategies are then fully reviewed, including ultraviolet germicidal irradiation, and unconventional masks made of functional nanomaterials with photothermal or photocatalytic properties. Their performance requirements are elaborated together with the advantages of long-term recycle use. Finally, we put forward challenges and prospects for further development of photoactive decontamination technology.

1. Introduction

The COVID-19 pandemic poses serious threat to people's lives and the global economy [1,2]. Globally until June 2022, there have been 525 million confirmed cases, 6.29 million deaths and economic losses of more than $10 trillion, and the numbers are still rising. Recent studies show that respiratory droplets and aerosols produced by coughing, sneezing or talking in close range are the main routes of viral transmission Fig. 1(a) and (b) [3–8]. During the COVID-19 pandemic, it became evident that wearing masks can provide respiratory protection and thus significantly slow down the viral transmission and reduce the infection risk [9,10]. Nevertheless, the outbreak has led to a sharp increase in demand for masks and a serious shortage of the supplies Fig. 1 (c) [11–14]. According to National Geographic, 129 billion masks are consumed worldwide every month. Waste management of a huge number of masks after use has also become a serious issue faced by all countries. Most countries dispose used masks by burning them, which could have an adverse impact on the environment. It may cause secondary transmission of viruses that further threaten the safety of human life [15–17].

Scientists have carried out significant research on the mask decontamination process. Some of which are based on physical methods, such as Ultraviolet germicidal irradiation (UVGI), heat treatment (e.g., dry heat, wet heat), and microwave generated steam treatment [18–20]. Whereas others are based on chemical methods, such as vaporized hydrogen peroxide, hydrogen peroxide gas plasma, ethylene oxide, alcohols, bleach, ozone, etc. [21–24]. Considering the poor decontamination effectiveness, the significant reduction in filtration efficiency of masks after several cycles, and the potential harm to the human body, these methods mentioned above have not been used for actual decontamination of masks [25,26]. Multi-functional masks with the photothermal and photocatalytic inactivation principle attract people's attention because of its unique advantages. Recently, the photoactive nanomaterials for making multi-functional masks mainly focus on plasmonic nanomaterials (e.g., silver, copper ion), inorganic semiconductor materials (MoS_2, TiO_2) and carbon-based materials (graphene). Due to the excellent photothermal and photocatalytic properties of these materials, functional masks made from them have remarkable decontamination effect [27,28]. While the current research of multi-functional masks is still at an initial stage. It thus requires extensive research and production before it is put into practical use.

In this review, we focus on photoactive decontamination methods (e.g., UVGI, photothermal and photocatalytic inactivation) for the recycle of used masks Fig. 2. UVGI has significant viruses and microorganisms'

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inactivation effect that has been widely used in real world [29]. Photothermal inactivation refers to attach nano-materials with excellent super-hydrophobicity and photothermal properties to the surface of the mask, which can raise the surface temperature of mask, and kill COVID-19 by damaging the protein [30–33]. Photocatalytic inactivation is attaching nano-materials with photocatalytic nanomaterials to the surface of masks, which can release reactive oxygen species to allow redox reactions with intracellular components, which destroys the outer structure of cell to kill viruses and microorganisms. To accelerate the research progress, this work summarizes the state-of-the-art situation of photoactive decontamination. The basic mechanism of photoactive decontamination is briefly introduced to fully understand the viruses and microorganisms' inactivation. We then discuss the practical effects and existing problems of these methods for mask decontamination and put forward our own views on this technology for future development.

2. Photoactive decontamination mechanism

Viruses and microorganisms can accumulate on mask surface. Most of them have complete cellular structures and their genetic material is DNA. A few viruses, such as COVID-19 is an enveloped single-stranded RNA virus with no cellular structure, and genetic material is RNA. Depending on the cellular structures and genetic materials, different viral inactivation pathways may be applied. In this section, viruses and microorganisms' inactivation mechanism is discussed in terms of Ultraviolet, photothermal and photocatalytic decontamination.

2.1. Ultraviolet inactivation

Ultraviolet (UV) inactivation is a traditional way to inactivate viruses and microorganisms. UV is the light with a frequency of 750THz–30PHz and a wavelength of 10–400 nm in vacuum. It can be divided into UVA (320–400 nm), UVB (280–320 nm), UVC (200–280 nm), Extreme UV (10–200 nm) Fig. 3(a) [34]. UVC has significant microorganism inactivation effect, which reaches its peak capacity near 254 nm [35,36]. Fig. 3(d) shows the inactivation rate of microorganism under different UV wavelengths. It kills viruses and microorganisms by destroying its genetic material (DNA, RNA). UV photons are directly absorbed by intracellular chromophores, resulting in photoreaction, which can cause DNA damage in microorganisms Fig. 3(b) by the formation of cyclobutane pyrimidine dimers and pyrimidine-pyrimidone (6–4) photoproducts between adjacent pyrimidine bases on the same DNA single chain [37–40]. For viruses whose genetic information is RNA in the case of COVID-19, UV can cause certain damage to RNA, resulting in changes in gene structure and production of non-functional proteins thus inactivate the virus Fig. 3(c) [41,42]. The survival rate of pathogen exposed to UV light can be expressed as the following:

$$S = \frac{P}{PO} = e^{\frac{-Et}{Q}} \tag{1}$$

Where S is the survival rate of pathogen; P is the number of pathogen after UV exposure; PO is the Number of pathogen before UV exposure; E is the effective UV exposure (J/cm^2); t is the Irradiation time (s); Q is the amount of UV radiation required when the pathogen survival rate S is $1/e = 36.8\%$. The formula explains the survival rate of bacteria in a period under effective UV irradiation.

2.2. Photothermal inactivation

Photothermal inactivation consists of the following processes. First, the photothermal material converts the absorbed light into heat energy through the photothermal effect, and then destroys proteins in viruses and microorganisms through high temperature to achieve the purpose of inactivation. Various photothermal mechanisms (e.g., plasmonic localized heating, electron-hole generation and relaxation and thermal vibration of molecules) are shown in Fig. 4 with respect to different photothermal materials upon diverse solar absorption range [43,44]. Light is made up of photons that vibrate at different frequencies and exist as electromagnetic waves [45]. For metallic materials, when the natural frequency of the photon on metal surface is the same as that of the incident photon, Local surface plasmon resonance initiates with the photon-induced coherent oscillation of electrons, resulting in thermal

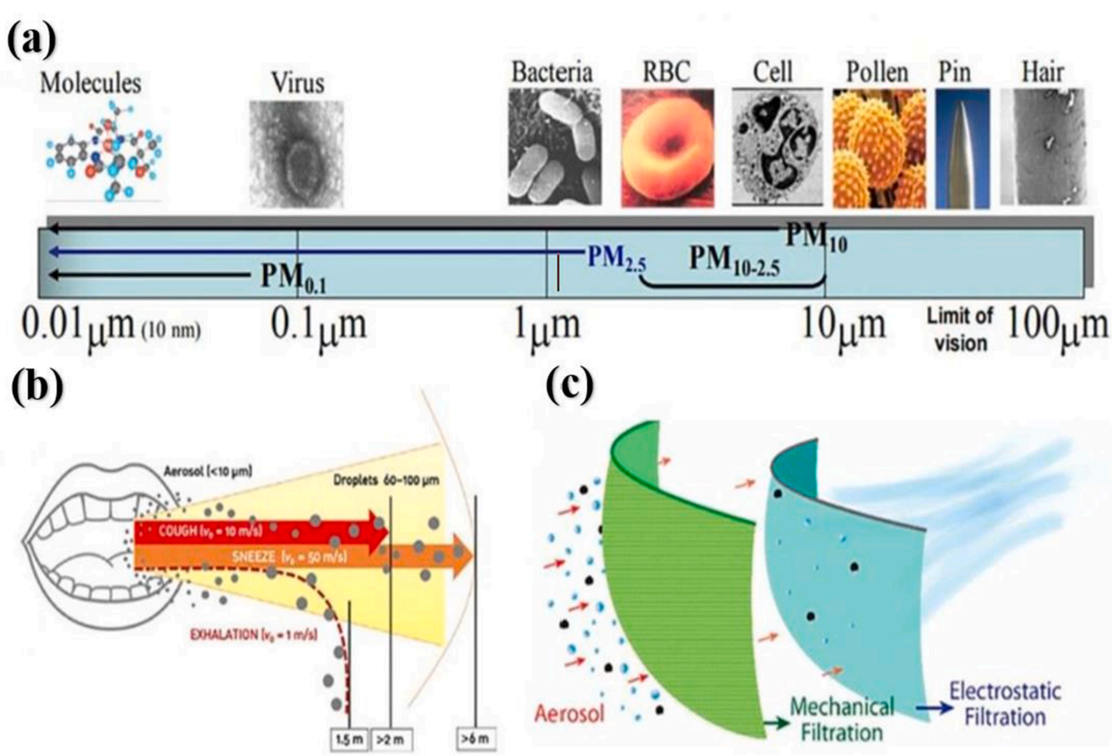

Fig. 1. (a) Size distribution of particulate matters (PMs). (b) A diagram of aerosols and droplet molecules. (c) Diagram of filter mechanism of mask [84].

electron generation and photothermal conversion Fig. 4(a). The mechanism of inorganic semiconductor materials is the optical-stimulated electron diffusing and recombination of carriers that cause the temperature increase Fig. 4(b). Carbon-based materials can promote the photo-excitation of electrons by producing a large number of conjugated π-bonds, when the excited electrons relax to the ground state through electron-electron and electron-phonon scattering, causing the temperature to rise Fig. 4(c) [46,47].

Since proteins in viruses and microorganisms are distributed in various structures of cells in the form of structural proteins or enzymes, which structural and functional proteins are the main targets of heat damage [48,49]. Protein damage can be divided into thermal denaturation and thermal mechanical damage according to different temperatures [50]. Protein thermal denaturation can occur in three different pathways. Firstly, upon thermal denaturation, the structures of protein macromolecules are disrupted and their natural functional properties deprived. Secondly, ribosomes are made up of RNA and proteins, these components are more thermosensitive than DNA and therefore directly affected. Usually, irreversible thermal denaturation damage of the ribosome occurs at temperatures close to the bacterial inactivation temperature. Thirdly, the structure of the detoxifying enzymes are destroyed (such as catalase or superoxide dismutase, proteases, chaperones and DNA repair enzymes), thus making cells inactive [51]. At low temperatures, proteins will suffer thermal denaturation damage for seconds to hours. When the temperature exceeds a certain range, thermal-mechanical damage will occur within nanoseconds. It disrupts cell structure and function by disrupting the permeability of cell membranes. Fig. 4(d) and (e) show mechanism of photothermal inactivation of bacteria and virus [52,53]. The degree of thermal denaturation of proteins is expressed by [54]:

$$\frac{\partial f}{\partial t} = -\frac{K_B T}{\overline{h}} \exp\left(-\frac{\Delta H - T\Delta S}{R_g T}\right) f \tag{2}$$

Initial condition: f (t = 0) =1, Where f is the degree of thermosdenaturation of protein molecules; K_B is the Boltzmann; $\overline{h}$ is the Planck constants; ΔH, ΔS is difference of enthalpies and entropies of initial and activated states, R_g is universal gas constant. The kinetic equation characterizes the degree of thermal denaturation of protein in tissue.

In the case where T is constant, the characteristic time τ_D of thermal denaturation is as follow:

$$\tau_D = \frac{\overline{h}}{K_B T} \exp\left(\frac{\Delta H - T\Delta S}{R_g T}\right) \tag{3}$$

Where τ_D is the time of thermal denaturation, which decreases with the increase of T. The equation shows the time required for thermal denaturation of protein molecules at a given temperature.

2.3. Photocatalytic inactivation

Photocatalysis is an advanced oxidation technology that can degrade

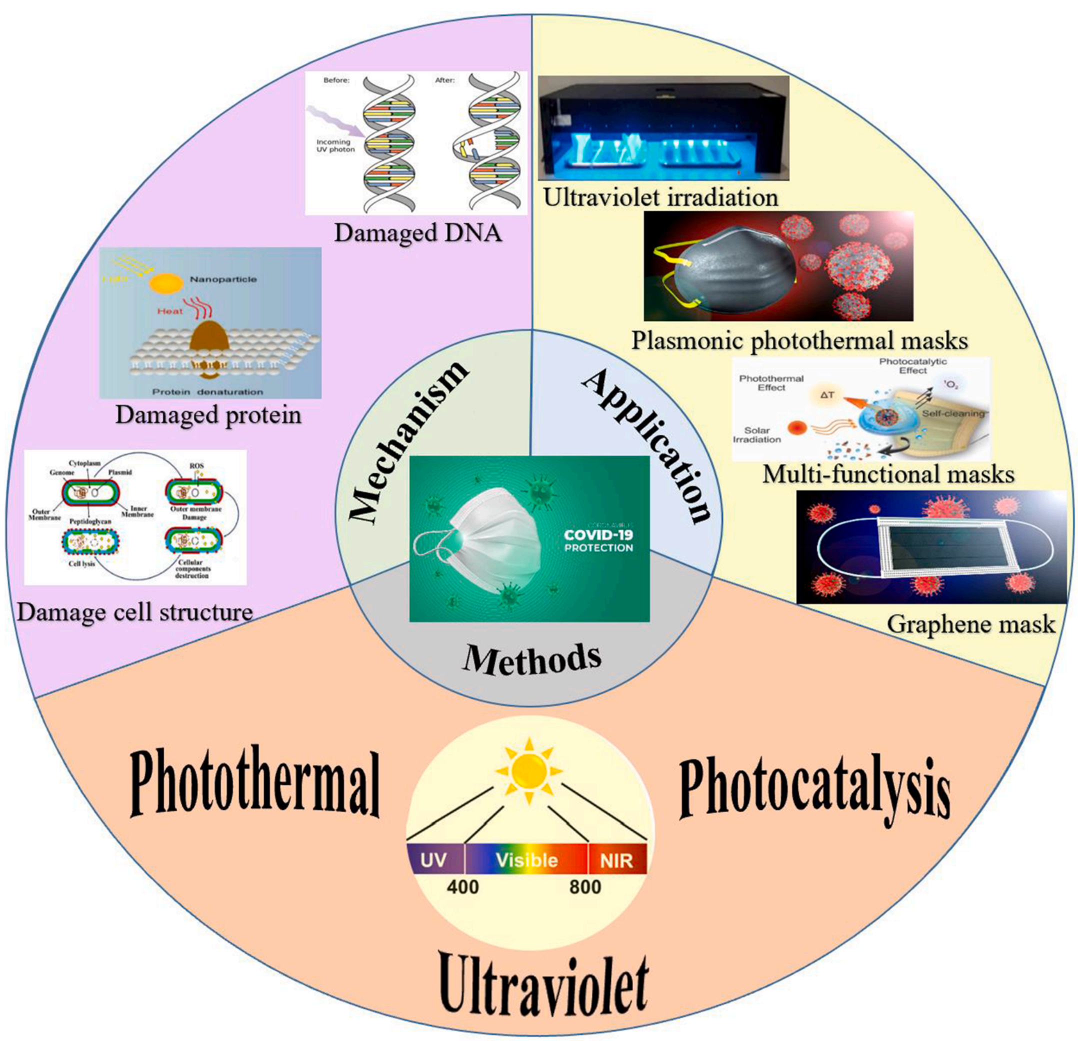

Fig. 2. Three methods based on photoactive decontamination and reuse of masks [28,31,33,50,60,81,89].

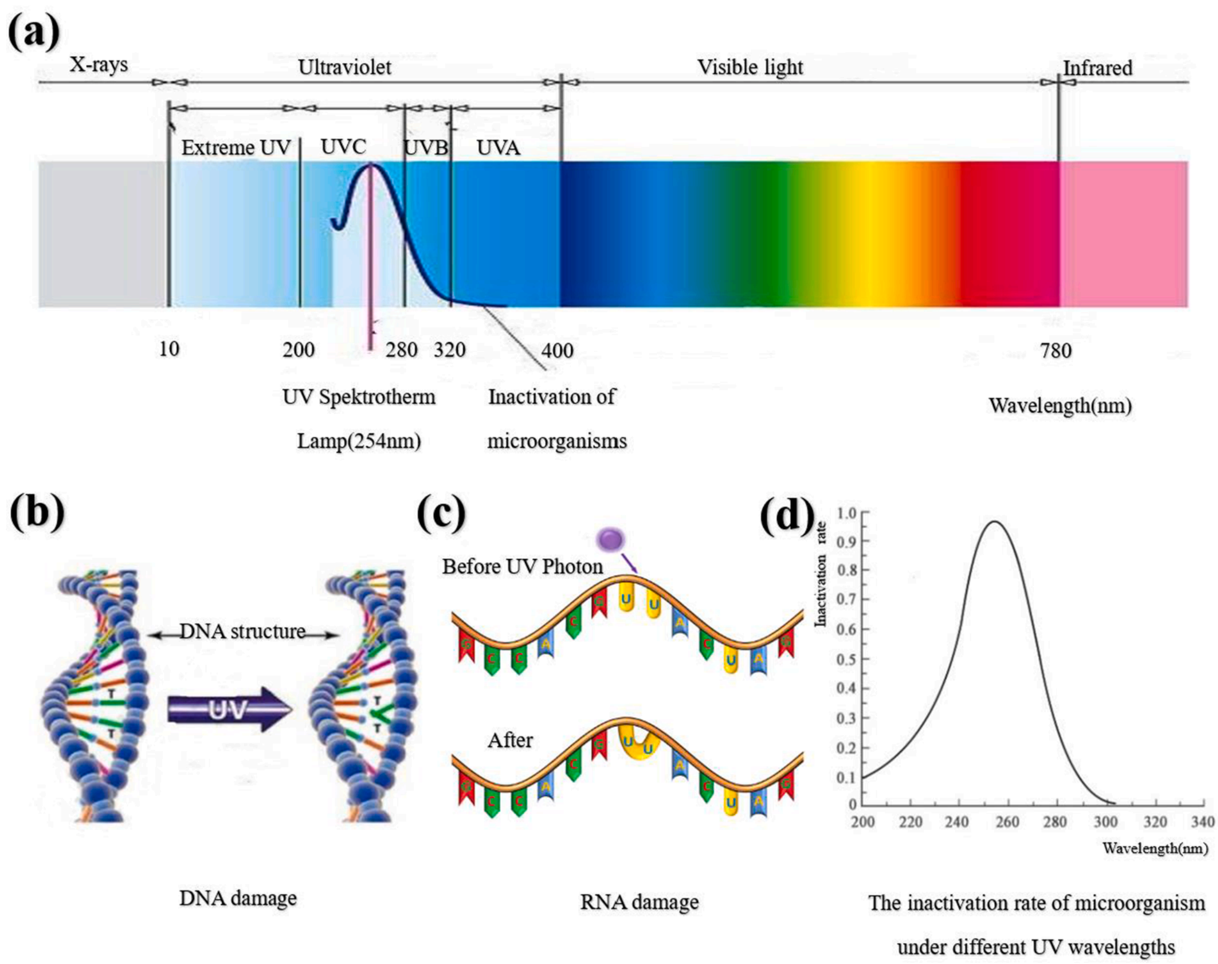

Fig. 3. (a) Schematic diagram of solar radiation spectrum composition. (b) Mechanism of UV damage to DNA. (c) Mechanism of UV damage to RNA [42]. (d) The inactivation rate of microorganism under different UV wavelengths.

pollutants through reactive oxygen species [55]. Fig. 5 shows the detailed mechanism of photocatalytic inactivation. In this approach, reactive oxygen species produced by semiconductor catalyst destroy the cell structure to achieve the purpose of inactivation [56]. Specifically, electrons migrate from valence band to conduction band to generate photogenic electrons (e^-), and corresponding holes (h^+) are generated in valence band. Photogenerated electrons have reducibility that can be captured by dissolved oxygen, to produce various oxidizing groups through the chain reaction to inactive microbial. The holes are oxidizing and directly damaging microorganisms in contact with the photocatalyst, as well as reacting with O_2 or H_2O [57]. The specific redox reaction of this process can be described as [58]:

$$Photocatalyst + h\nu \rightarrow e^-_{CB} + h^+_{VB} \quad (4)$$

$$e^-_{CB} + O_2 \rightarrow \bullet O_2^- \quad (5)$$

$$h^+_{VB} + H_2O \rightarrow \bullet OH + H^+ \quad (6)$$

In redox reactions, the main reactive species are hydroxyl radical ($\bullet OH$), superoxide radical anions ($\bullet O_2^-$), hydrogen peroxide(H_2O_2). The interconversion involved between them are shown as [58,59]:

$$\bullet O_2^- + 2H^+ + e^- \rightarrow H_2O_2 \quad (7)$$

$$H_2O_2 \rightarrow \bullet OH + \bullet OH \quad (8)$$

$$\bullet OH + \bullet OH \rightarrow H_2O_2 \quad (9)$$

Hydroxyl radical is the most important oxidizing species in photocatalytic inactivation of microorganisms. It attacks the peptidoglycan layer, the lipopolysaccharide layer, and the phospholipid bilayers of microbial cell walls. In the presence of O_2, $\bullet OH$ destroys the phospholipid bimolecular to produce H_2O_2 through entering the inner layer, which reacts with nearby phospholipids to form phospholipids free radicals, the unstable phospholipid free radicals are further converted into stable oxidation products. In the process, creating many holes in the cell barrier, thus causing DNA, RNA and ribosomes to flow out of the cell, and eventually killing the viruses and microorganisms. The oxidation potential of superoxide radical anion is 0.65 V and can attack biological macromolecules such as protein and nucleic acid, resulting in the destruction of cell structure and function. The oxidation capacity of hydrogen peroxide is between $\bullet OH$ and $\bullet O_2^-$, and it can destroy cell wall, cell membrane and intracellular substances. But as the microbes oxidize, they rapidly produce catalase, which breaks down H_2O_2 into O_2 and H_2O, allowing the damaged microbes to survive. Therefore, H_2O_2 alone cannot effectively inactivate microorganisms [60].

3. Decontamination and reuse of masks

An effective decontamination method must be able to inactivate the viruses and microorganisms while maintain the integrity of the masks and ensure the wearer safety [19,20]. Besides, this method must have a considerable high recycling rate. Here, we review the practical applications of photoactive decontamination for the recycle of used masks.

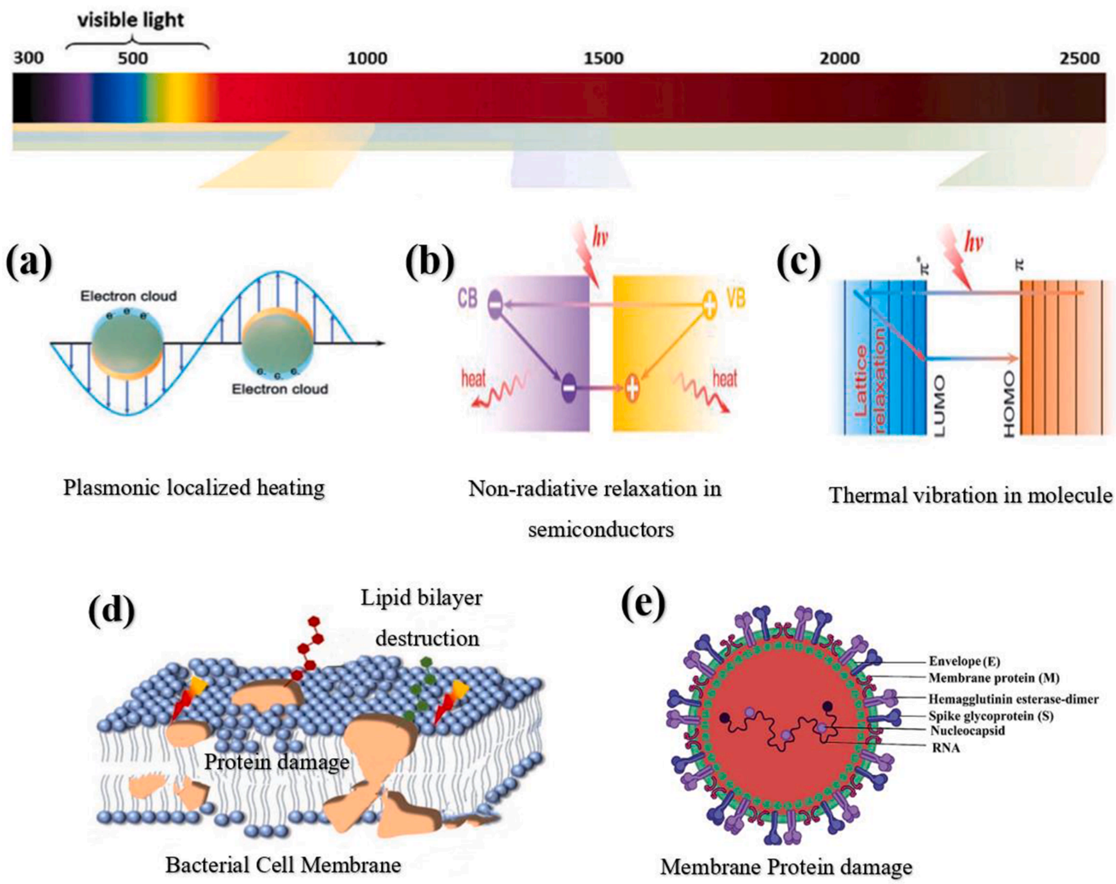

Fig. 4. Photothermal mechanisms for various types of photothermal materials. (a) Plasmonic localized heating. (b) Non-radiative relaxation in semiconductors. (c) Thermal vibration in molecules [43,46]. (d) Mechanism of photothermal sterilization [52]. (e) Mechanism of photothermal inactivation of COVID-19 [53].

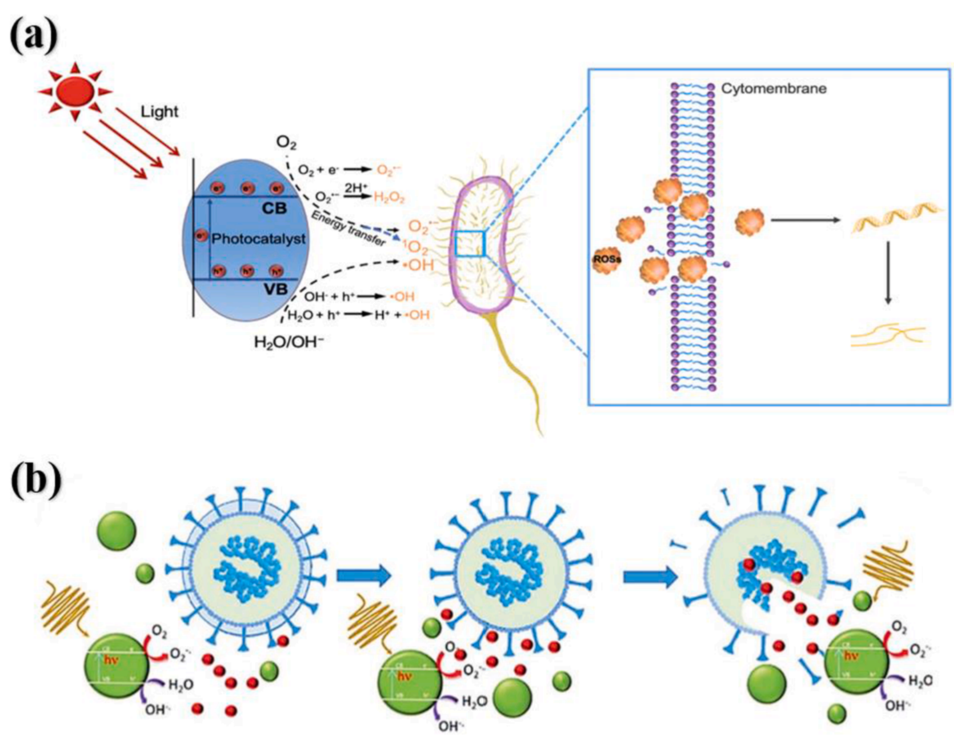

Fig. 5. (a) Photocatalytic disinfection [103]. (b) Principle of photocatalytic inactivation of COVID-19 by nanoparticles [53].

3.1. Ultraviolet germicidal irradiation

UVGI is widely used in drinking water, wastewater and air sterilization as a recognized effective decontamination method [61]. It has been shown that UVC can effectively inactive COVID-19 virus from respirator surface. Since the declaration of the COVID-19 pandemic by World Health Organization in March 2020, the Centers for Disease Control and Prevention has summarized the effectiveness of various mask decontamination methods in disinfecting and maintaining respirator integrity, and UVGI is listed as one of the most promising Filtering Facepiece Respirators (FFRs) decontamination methods for crisis conditions [62,63].

Light source. Common UV light sources include low and medium pressure mercury lamp, light emitting diode, deuterium lamp and microplasma lamp [64]. Low-pressure mercury lamps or UVC-LED is commonly used for decontamination of masks [65–67]. Low-pressure mercury lamp is a common light source, while the application is limited due to short longevity, the production of ozone and secondary pollution caused by mercury-containing waste [68]. UV light emitting diode is small, flexible in design, quick in response, long longevity and free of pollutants. It is a new and promising UV source widely used at present [69,70]. Fig. 6 shows an UVGI device [71].

Decontamination effect. Researchers around the world have done a lot of studies on the UVGI in masks [72]. The results show that the decontamination effect depended on three factors: wavelength, dose and 3D structure of mask [73,74]. The ideal wavelength is 254 nm [29]. COVID-19 was inactivated by 4 $\log_{10}$ upon exposure to a UVC does of 19.5 mJ/cm^2. When the dose of UVC is 10 J/cm^2, UVC can contact with viruses and microorganisms in all parts of the mask, and make their reduction of >5 log10 (The J/cm^2 is widely used in decontamination literature to show UVC flux). At doses up to 6 times higher than the standard dose, the respirator fitting integrity and filtration capacity would not be significantly affected [75]. Studies have shown that the ideal dose of some N95 FFRs is 1.5 J/cm^2 [29]. Under this premise, the optimal irradiation time for mask decontamination using a general commercial UVGI device is 10 min. The different 3D structures will cause different radiation differences, thus affecting the decontamination effect [65]. It is worth noting that in the process of decontamination, as the UVC could not reach the surface of the mask evenly, especially the strap may still have residual viruses, so it needs to be further disinfected. Up to now, there is no literature available for a detailed classification discussion.

Recycling rate. Experts have selected three kinds of commercial respirator masks (e.g., N95 respirator, surgical mask, procedure mask) to conduct experiments and analyze the fractional efficiency and breathing resistance after multiple cycles of decontamination. The fluctuation range of the three commercial respirator masks is small (e.g., 2% for N95, 11% for surgical mask, and 8% for procedure mask), no significant efficiency drop was found after 10 cycles Fig. 7 [76]. It is concluded that the recycling rate of UVGI is 10 times [63,77]. Considering the low recycle rate, a vacuum UV disinfection device was made and tested the disinfection effect of its N95 mask. The results showed that the device could inactivate Escherichia coli cells attached to the surface of masks in a few of seconds, the effective circulation rate of the mask can be increased to about 20 cycles [78]. With the introduction of this device, the potential of UV decontamination may be improved for reuse of masks.

As one of the most promising decontamination methods, UVGI attracts wide attention due to its advantages such as wide application range, compact system and remarkable effect. Since UVC may not be able to reach all parts of the mask evenly to make decontamination complete, this may have certain risks. As we all know, UVC causes certain harm to human body, according to the American Conference of Governmental Industrial Hygienists, the upper daily dose per person is 0.003 J/cm^2 of UV (200–315 nm) [65]. To reduce the harm of UVC on human body when using UVGI equipment for decontamination, we should wear protective equipment to avoid direct contact of UVC with our skin, and the whole decontamination process should be completed away from human. And the current theoretical system for decontamination of UVC in masks is not perfect. These factors limit the development of UVGI in mask decontamination [79–81]. We should focus on the research and development of new UVGI equipment to obtain higher dose and stronger penetration of UVGI in the future. The theoretical research on decontamination of masks should also be paid to make their commercial use possible as soon as possible.

3.2. Photothermal self-cleaning mask

With the global energy shortage, solar energy has attracted widespread attention. Especially the emergence of nanomaterials with excellent photothermal characteristics that have been widely used in seawater desalination, steam power generation, cancer treatment and disinfection [44,82,83]. Since the COVID-19 outbreak, photothermal nanomaterials provides new ideas for the decontamination and reuse of masks [84,85]. Plasmonic nanomaterials (e.g., silver, copper ion), inorganic semiconductor materials (MoS_2) and carbon-based materials (graphene) with excellent super-hydrophobicity and photothermal properties have aroused interests for photothermal decontamination.

Material properties. Nanomaterials have high solar absorption capacity and photothermal conversion capacity [43]. In photothermal decontamination, three types of nanomaterials including plasmonic nanomaterials, inorganic semiconductor materials and carbon-based materials are widely studied to improve the recycling rate of masks. Plasmonic nanomaterials of gold, silver, copper, platinum undergo surface plasmon resonance upon solar radiation to produce a lot of heat [46]. Semiconductor material-MoS_2 consists of covalently bonded Mo and S atoms and is a graphene-like transition metal sulfide 2D layered material [86]. It has been proposed as new photothermal agents with

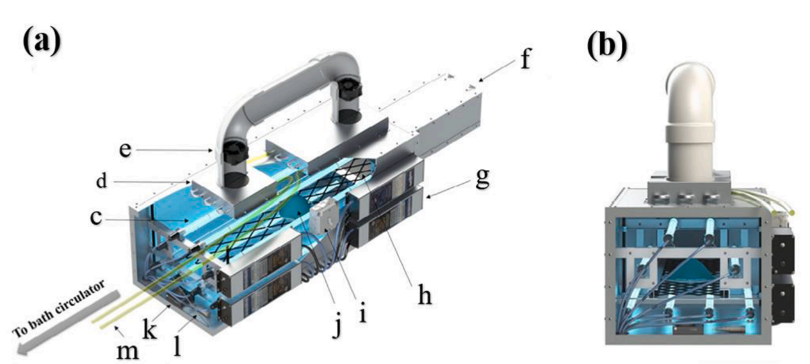

Fig. 6. UVGI device [71]. (a) Top view: c, UV light bulb; d, heat exchanger; e, fan; f, hinged door; g, power supply; h, sliding mesh wire shelf; i, power switch; j, filtering facepiece respirator (example); k, radiometer; l, temperature/humidity probe; m, ethylene glycol supply line. (b) Side view.

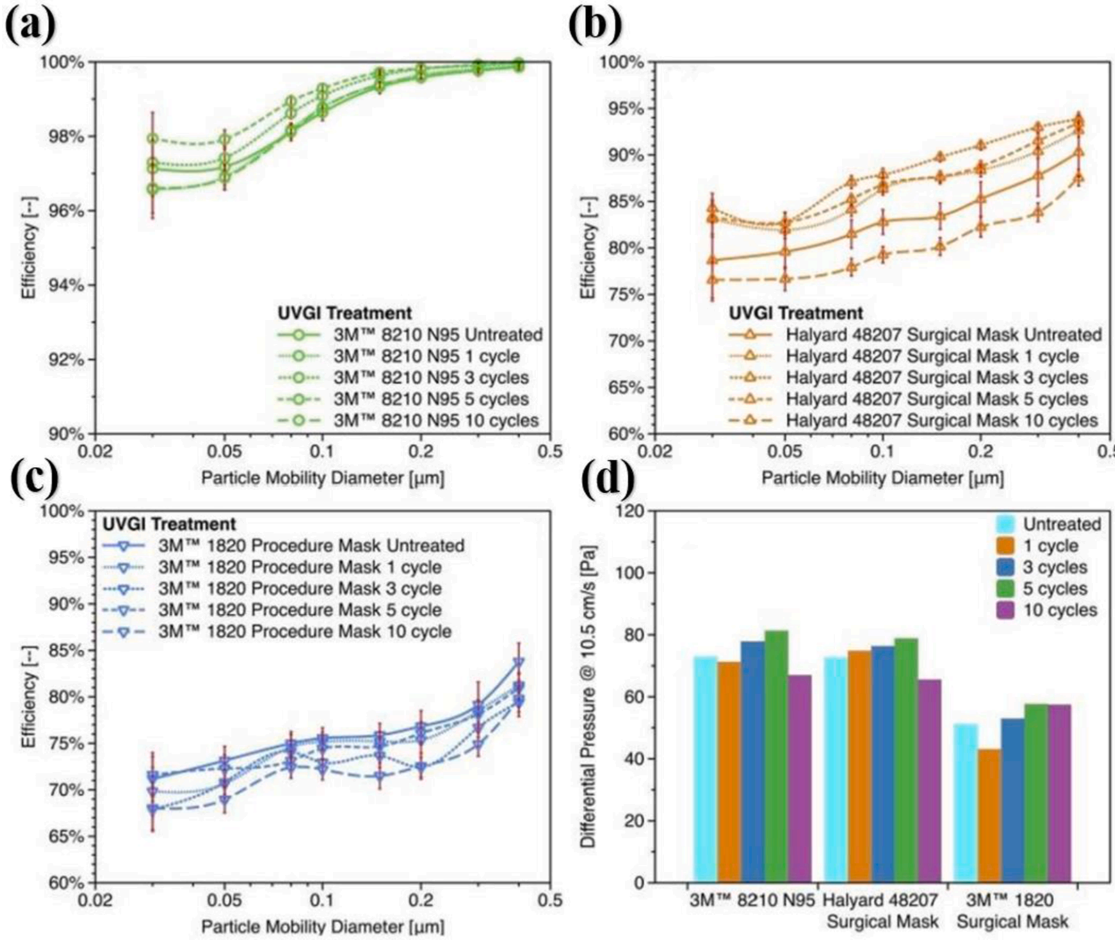

Fig. 7. Fractional efficiency of N95 (a), surgical mask (b), and procedure mask (c) after multiple UVGI treatment cycles. (d) Breathing resistance for 1,3,5,10 cycles [76].

good biocompatibility, electrical conductivity, and low cytotoxicity for mask decontamination. Graphene is a carbon-based photothermal material with a single atomic layer, two-dimensional honeycomb lattice structure, which is made up of a type of carbon atoms linked by a sp^2 hybrid [87,88]. Graphene has good antibacterial activity, with an inhibition rate of about 81% against bacteria, and when exposed to photothermal effects, the efficiency of inactivation can reach 99.998% in 10 min [89]. Graphene oxide revealed a 95.5% inhibition in the E. coli [90]. Meanwhile, Graphene and its derivatives have also been studied due to their excellent electrical conductivity and photothermal properties, and are suggested as the most promising carbon materials for decontamination of masks [91]. Due to their excellent properties, these photothermal materials can attach to the mask surface and quickly heat up upon light irradiation to kill viruses, thus achieving the purpose of mask purification.

Fabrication and structure. For self-cleaning masks made of photothermal materials, the researchers deposited silver nanoparticles on the surface of the N95 mask using laser-induced forward transfer to make a plasmonic superhydrophobic self-decontamination N95 respirator. In addition, laser-induced graphene can be deposited with silver nanoparticles by fine-tuning the laser parameters to improve photothermal and super-hydrophobicity properties of the surface [92]. For MoS_2, someone conceived a four-layer purifying mask containing MoS_2-Fabric-500 (500 means the concentration of nanosheet suspension used for preparation of nanosheets is 500 μg/mL) Fig. 8(c). The four layers are non-woven fabric (Hydrophobic), MoS_2-Fabric-500, melt-blown non-woven fabric, and non-woven fabric (soft-absorbing) [32]. The structure enhances the washing durability and filtration efficiency of the mask. Finally, the researchers created a graphene mask by depositing graphene on the mask surface using a fourth-generation laser deposition process at a sufficiently low temperature [33]. The technology is mature enough and graphene can be attached to the surface without damaging mask.

Decontamination performance. For plasmonic superhydrophobic self-decontamination N95 respirator, the researchers tested its decontamination properties and found that the surface temperature of the mask can be stabilized at 80^{O}C after 60 s upon solar radiation at 1000 W/m^2. According to the latest study, the COVID-19 can be inactivated at 56^{O}C for 15 min [27]. Therefore, it has good inactivation to the COVID-19. The recycling rate is above 100 times. Copper nanoparticles are usually deposited on the mask surface in combination with shellac, a photo-initiator that improves their hydrophobicity and photoactivity. The mask can be rapidly heated up to 70 °C under sunlight to inactivate the microbes or viruses [89]. Although clinical trials have not yet been proposed, the findings provided new clues on plasma mask decontamination. Secondly, the pristine mask reached 40^{O}C after 5 min of solar irradiation, while the temperature of MoS_2-Fabric-500 rose from 23 to 54^{O}C within one minute of solar irradiation and remained at about 80^{O}C after 5 min. The results show that the MoS_2-coated increases the solar absorption by about 5 times Fig. 8(a) and (b). This temperature has a significant effect on inactivating viruses and microorganisms. It also has good recycling rate, doesn't lose decontamination effect while maintaining good permeability and filtration effect after 60 cycles [32]. Thirdly, the researchers also tested the performance of graphene masks and the results showed that respiratory droplets cannot stay on the surface due to graphene's excellent super-hydrophobicity, the

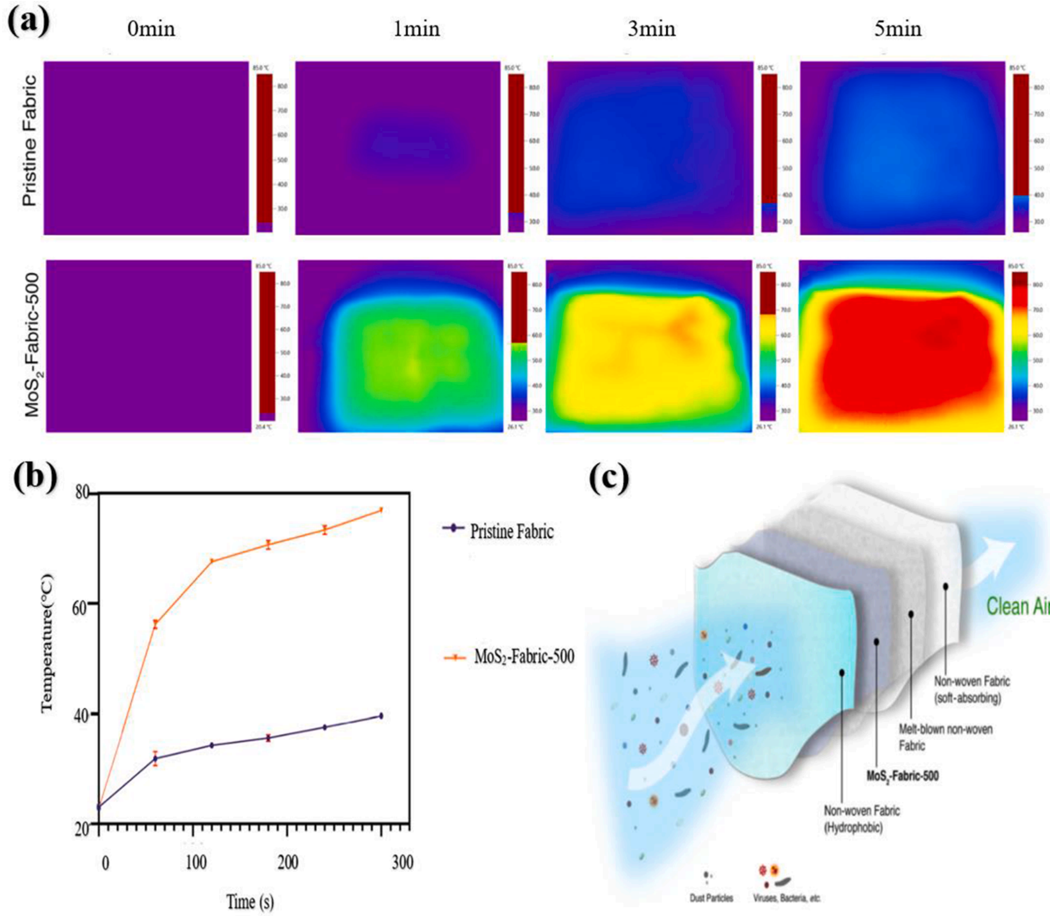

Fig. 8. Photothermal performance of the pristine fabric and MoS_2-Fabric-500 [32]. (a) Infrared camera images after solar illumination. (b) Temperature change within 5 min upon light exposure. (c) The personal protective mask using the MoS_2-Fabric-500.

self-cleaning ability of the mask is significantly improved Fig. 9(a). Graphene-coated masks showed significant advantages in solar spectral absorption and photothermal performance compared to pristine masks Fig. 9(b). The surface temperature of ordinary masks is still below 45^{O}C after 5 min of sun exposure Fig. 9(c–e). The surface temperature of graphene-coated masks increased rapidly to over 70^{O}C after 40 s of sun exposure, and remained at about 90^{O}C after 5 min, which was sufficient to inactivate a large number of viruses. The recycling rate is as high as 200 times [27]. Therefore, graphene shows great potential in decontamination and reuse of masks. Since the temperature variation of the above photothermal self-cleaning masks in the decontamination is largely beyond the range of human normal cells, the entire decontamination process must completed away from the human body.

The photothermal nanomaterials have shown excellent properties in developing decontamination and reuse of masks, especially for Africa with poor health care and plenty of solar energy has a very practical significance. However, the amount of solar intensity that reaches the Earth's surface is affected by a few factors. Therefore, sunlight as an excitation source has certain limitations. While in actual production process, because of considering the difficulty of obtaining a large number of raw materials and the high economic cost, especially the lack of a unified theoretical system for reference, the method is still in the theoretical stage [93]. We should conduct sufficient adaptability test for the decontamination standards of masks, and develop new nanomaterials to meet practical application.

3.3. Photocatalytic functional mask

Photocatalysis as a safe, efficient and environmentally friendly decontamination technology has been widely used in air purification, water purification, self-purification and antifouling fields [94,95]. In the field of decontamination and reuse of masks, silver, copper and TiO_2 nanoparticles with excellent photocatalytic properties have attracted people's attention [53,96,97].

Material properties. Photocatalyst often use semiconductor material to produce reactive oxygen species upon light illumination to kill viruses and microorganisms. Common photocatalytic materials include metal/metal oxides, metal-free, and 2D materials (e.g., MXenes, Metal-Organic frameworks, covalent Organic frameworks) [53]. Metals and metal oxides are traditional photocatalysts, including silver, copper, CuO, TiO_2. TiO_2 has a strong oxidation capacity, good chemical stability, non-toxic, cheap and other excellent characteristics [57]. It is the most widely studied photocatalyst and can be used to inactivate a variety of viruses [98,99]. Metal-free photocatalysts include carbon nanotubes, graphene oxide and g-C3N4, which have stable physical and chemical properties, good electrical conductivity, hydrophobicity, and strong antibacterial activity [58]. The 2D photocatalyst is a layered structure with a large surface area, good electrical conductivity, mechanical properties, and excellent activity against viruses.

Fabrication and structure. For functional masks made of photocatalytic materials, the researchers loaded these metal nanoparticles onto N95 masks through embedding, covering and impregnation. Fig. 10 (d) [92,100]. In addition, someone made a photocatalytic mask made of TiO_2 through a TiO_2 nanowires-based filters [27]. The researchers then created a N-TiO_2/TiO_2 mask to increase photocatalytic performance by adding nitrogen to the surface. The mask uses polyvinyl alcohol, poly (ethylene oxide) and cellulose nanofiber instead of polypropylene as the raw material, then N-TiO_2 and TiO_2 were mixed on the surface of the

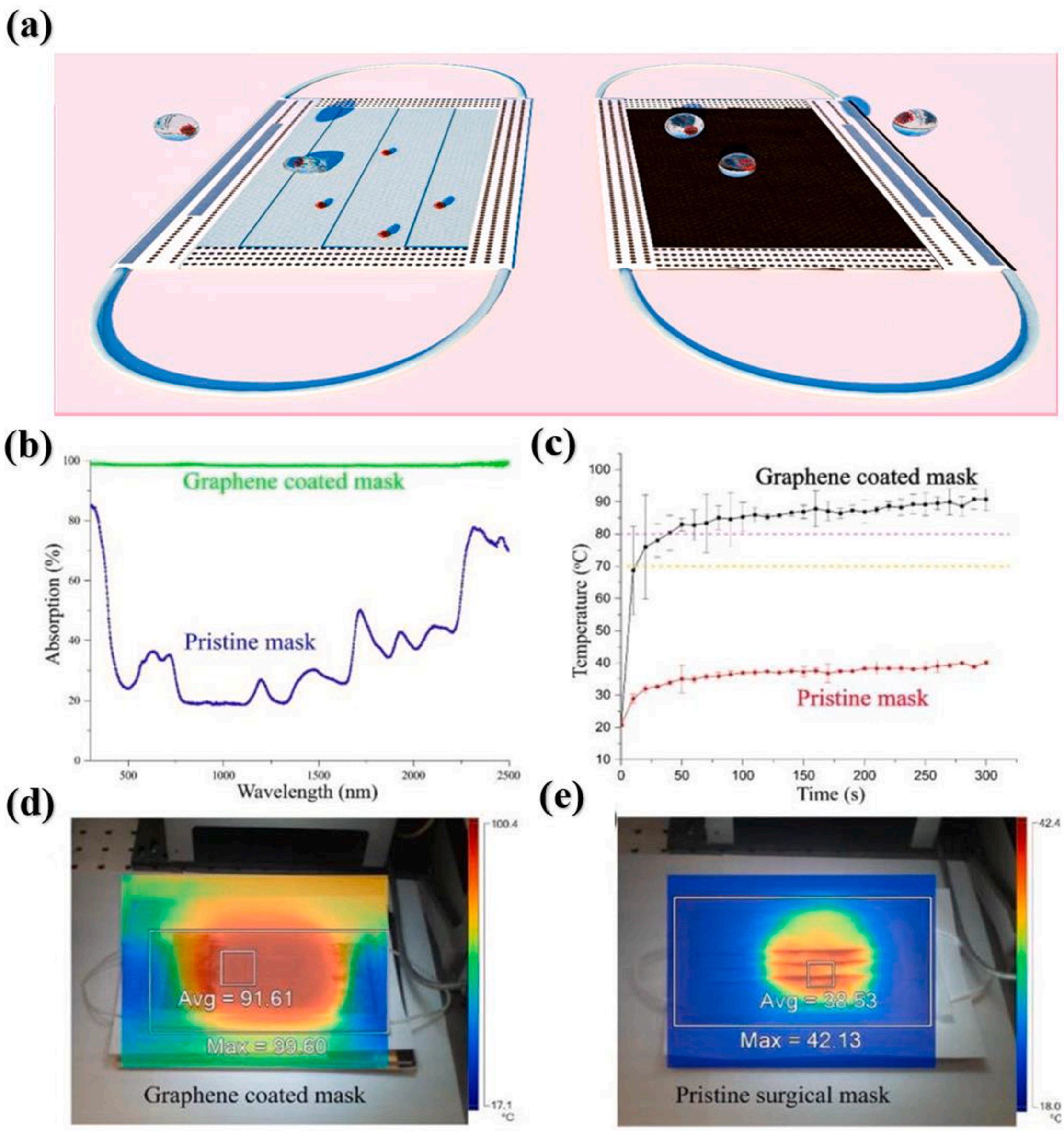

Fig. 9. (a) The pristine mask, the super-hydrophobic and self-cleaning Graphene-coated mask. (b) Optical absorption of pristine and graphene-coated masks. (c) Surface temperature. Infrared camera images of a graphene-coated mask (d) and a pristine mask (e) after 5 min [33].

mask through esterification [101]. Due to the molecular interaction of these three materials, the synthetic mask has a strong electro-spinnability and mechanical performance. They are biodegradable, which can reduce environmental pollution. Above all, adding the nitrogen on TiO_2 surface reduces the band gap of TiO_2 to increase the photocatalytic property of masks. However, light excitation has limited the development of such masks, for which someone made a photocatalytic mask decorated with a mini UV-LED array combined with ZnO/TiO_2 bilayer Fig. 10(a–c) [102]. The mask is composed of four layers, as follows outer layer, photocatalytic filter layer (e.g., polypropylene, ZnO, TiO_2), UV-LEDs layer (e.g., battery (3 V), Mini UV-LEDs) and soft contact layer. The four-layer structure enables photo-induced electrons transfer more effectively, improves photocatalytic efficiency, and the efficiency of mask inactivation is greatly improved due to the presence of UV-LED. Crucially, the mask can be used anytime and anywhere without relying on natural light source.

Decontamination performance. As strong antibacterial agent, silver, copper and other metal nanoparticles release reactive oxygen species that damage DNA, RNA and other cellular structures, especially by destroying the envelope proteins of the viruses to inactivate COVID-19 [66,103,104]. Silver acts as a natural antibacterial agent can make H5N1 that a substitute of COVID-19 completely inactivated in 15 min [105]. And the photocatalytic and photothermal properties of metal nanoparticles can work together to show both advantages in mask decontamination. That gives people enough confidence to inactivate COVID-19. These nano masks have passed all the national Institute for Occupational Safety and Health test standards. Considering the harmful effects of these metal nanoparticles, it is necessary to develop a broad-spectrum disinfectant combined with them to achieve a safe and reliable antiviral effect. The researchers did a lot of research on TiO_2-coating for its decontamination performance and recycling rate. Firstly, the results showed that under UV light (365 nm), almost all bacteria could be inactivated within one minute, and the recycling rate of the mask was more than 1000 times [27]. N-TiO_2/TiO_2 mask was then tested results show that after 10 min of actual sunlight, the efficiency of inactivation of the mask can reach 100%; its filtering efficiency can remain above 90% after continuously wearing for more than 2 h. In addition, the mask has excellent performance in mechanical strength,

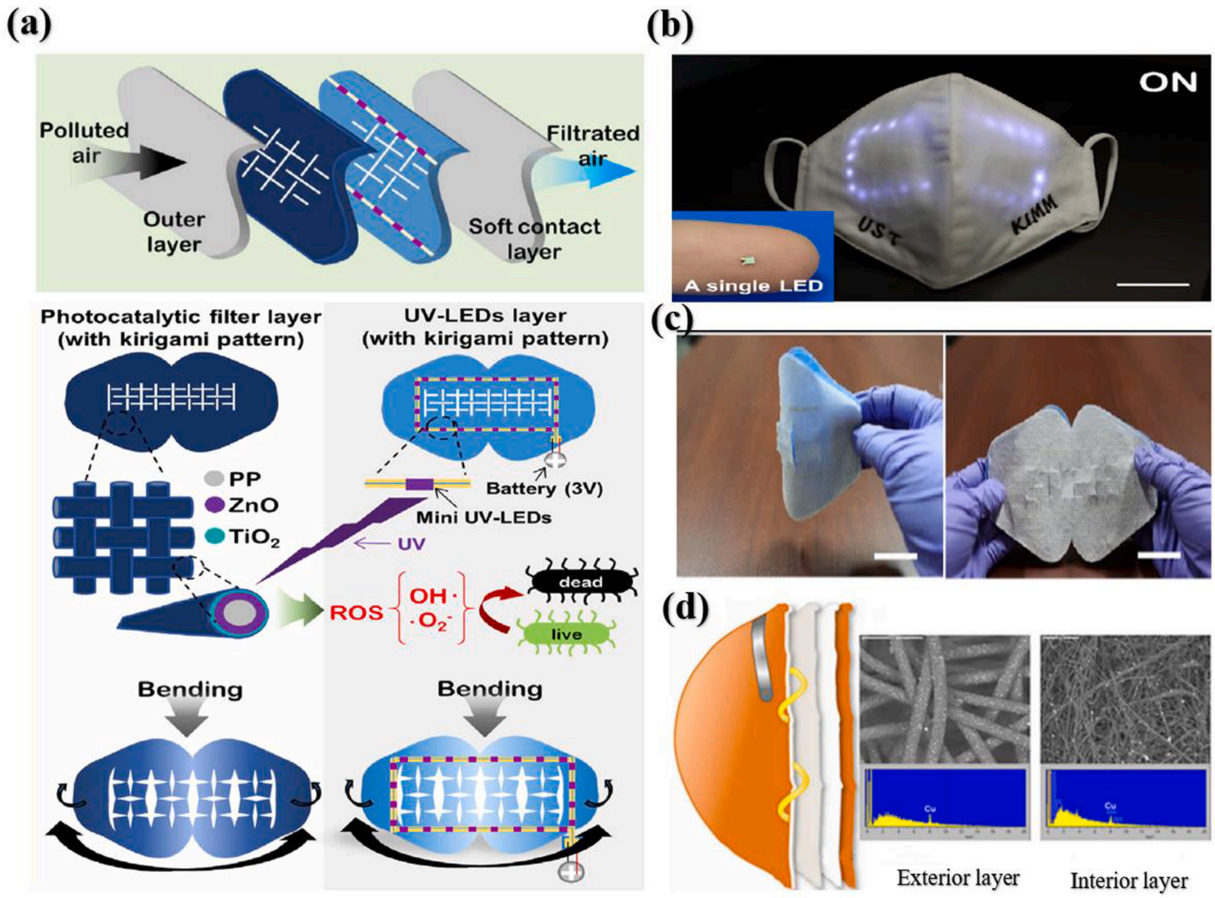

Fig. 10. (a) Photocatalytic mask with a mini-UV-LED array and ZnO/TiO_2 bilayer. (b, c) The real photo of the photocatalytic antibacterial facemask [102]. (d) Copper oxide face masks [66].

breathability, circulation performance, especially its low cost of raw materials, which makes it have the potential of practical application [101]. Finally, the results of the tests on the photocatalytic mask decorated with a mini-UV-LED array combined with ZnO/TiO_2 bilayer showed that it has good filtration efficiency, flexibility, and recycling rate. The most important is the photocatalytic efficiency has been greatly improved. In terms of practical applications, there is still much work to be done.

Photocatalytic functional masks effectively block the transmission of COVID-19 and other viruses in the air, showing great potential in decontamination and reuse of masks [106]. However, their effective inactivation against COVID-19 needs to be further verified. In addition, considering the high production cost, certain harm to human body and the lack of theoretical research, the application of photocatalysis in decontamination and reuse of face masks still needs further discussion. In the future, we should carry out more tests to buildup standards so that photocatalytic decontamination can be used for reuse of masks as soon as possible.

4. Summary and prospects

This work introduces photoactive decontamination methods for reuse of masks, and discusses the mechanism, research progress and development prospects. In these decontamination methods, inactivation performance, filtration efficiency, cycle times, acquisition of raw materials and whether it is harmful to the human body become the priority concerns [107]. UVGI as a common decontamination method, its system compact, low cost, decontamination effect is remarkable. But it can only be obtained by low-pressure mercury lamp or UVC-LED, which brings great inconvenience. With the development of solar energy and the emergence of new nanomaterials, photothermal and photocatalytic decontamination attract people's attention [108]. A large number of materials has emerged including silver, copper nanoparticles, MoS_2, graphene, TiO_2 and other nanomaterials etc. These materials are attached to the surface of the pristine mask to make a new nano-mask with multiple layers. They have strong inactivation performance, good filtration efficiency, and the recycling rate is increased by dozens of times compared with traditional methods. In daily wear, they can be stimulated by sunlight for ease of use. Unfortunately, sunlight has certain limitations due to many factors (e.g., geographical location, climate, diurnal variation) [109]. There are some uncertainties in the production and practical use of nano-masks. Future research should focus on the establishment of a unified theoretical system about antiviral property, self-cleaning, biodegradability, manufacturing, appropriate light sources to promote the application in real life [110].

Here, we list three decontamination methods, as well as their specific examples and actual performance in Table 1 to highlight the advantages and challenges for future development of the technology. Although many efforts have been devoted to finding suitable new materials and testing performance of masks after decontamination and reuse, there are still a lot of gaps to be filled in this domain. The advent of vacuum UV equipment makes us to see the great potential of UV in mask disinfection. With the rapidly development of UVC-LED, there will be new equipment with higher dose and stronger penetration in the future. For multi-functional nano-masks, we should pay more attention to how to achieve low-cost and large-scale production and achieve commercial application as soon as possible. Meanwhile, we should explore more materials with distinct photocatalytic and photothermal properties to

Table 1
The advantages and limitations of photoactive decontamination are evaluated based on data and results from the literature.

Method	Mechanism	Example	Performance	Advantages	Challenges
UVGI	Damage to DNA/ RNA	low-pressure mercury lamps UVC-LED	The best irradiation time is 10 min The recycling rate is above 10 times	• Wide application range • The system is compact • Price is cheap • Significant bactericidal effect	² Not readily available ² Harmful to human health ² Cannot reach all parts of the mask evenly
		vacuum UV disinfection	E. coli inactivated in seconds The recycling rate is above 20 times		
Photothermal	Damage to Proteins	Silver ions	The temperature at 80 ^{O}C after 1 min of solar intensity at 1000 W/m^2 The recycling rate is above 100 times	• Excellent self-cleaning performance • High recycling rate • Environmentally friendly • Significant bactericidal effect	² High production cost ² Difficulty in obtaining large quantities of raw materials ² Lack of a unified theoretical system
		MoS_2	Good washing durability, permeability The temperature at 80 ^{O}C for 5 min The recycling rate is above 60 times		
		Graphene	Excellent photothermal performance The temperature at 90 ^{O}C for 5 min The recycling rate is above 200 times		
Photocatalysis	Generating ROS to damage cell structure	Copper, silver	Passed all the NIOSH test standards	• Short acting period • High recycling rate • Environmentally friendly • Significant bactericidal effect	² High production cost ² Harmful to human health ² Lack of a unified theoretical system
		TiO_2	Bacteria inactivated within one minute The recycling rate is above 1000 times		
		N-TiO_2/TiO_2	Inactivation rate is 100% in 10 min Good permeability and recycling rate		

achieve the syngerstic advantages from different materials. We propose to combine UVC as excitation source to eliminate the dependence of the masks on natural light sources, achieving all-weather use. In sum, we should continue to explore the effectiveness of photoactive decontamination for actual prevention of COVID-19, and conduct further adaptability test for different materials, different mask structures in the future [18,111–114]. Relevant departments should make a detailed classification and introduce standardized procedures to ensure the consistency and reliability of mask decontamination. This review systematically discusses the mechanism, progress, and prospects of the photoactive decontamination approaches to reuse masks, highlighting the advantages and challenges of these methods. It can provide some reference for mask decontamination technology to curb COVID-19 transmission.

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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