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REVIEW

Progress and Perspective of Antiviral Protective Material

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Abstract
Public health events caused by viruses pose a significant risk to humans worldwide. From December 2019 till now, the rampant novel 2019 coronavirus (SAR-CoV-2) has hugely impacted China and over world. Regarding a commendable means of protection, mask technology is relatively mature, though most of the masks cannot effectively resist the viral infections. The key material of the mask is a non-woven material, which makes the barrier of virus through filtration. Due to the lack of the ability to kill the viruses, masks are prone to cross-infection and become an additional source of infection after being discarded. If the filteration and antiviral effects can be simultaneously integrated into the mask, it will be more effcient, work for a longer time and create less difficulty in post-treatment. This mini-review presents the advances in antiviral materials, different mechanisms of their activity, and their potential applications in personal protective fabrics. Furthermore, the article addresses the future challenges and directions of mask technology.

Keywords Protective material · Antiviral · Fiber · Nanotechnology

Introduction

Emerging infectious diseases caused by viruses have constituted the forefront of global health concerns [1]. At present, China and the world are experiencing the outbreak of atypical pneumonia caused by the zoonotic 2019 novel coronavirus, SAR-CoV-2 (2019-nCoV). As of Feb 16, 2020, there have been more than 60,000 cases of this 2019 coronavirus disease (COVID-19) confirmed in mainland China, including more than 1000 deaths [2]. The SARS-CoV-2 viruses are generally spherical with some pleomorphism, the diameter varies from 60–140 nm, and the surface covered by distinctive spikes, with an average lenght of 9–12 nm [3, 4]. In perspective, two other novel coronaviruses (CoVs) have caused two large-scale pandemics in the last two decades, namely, severe acute respiratory syndrome coronavirus (SARS-CoV; in 2002) and Middle East respiratory syndrome coronavirus (MERS-CoV; in 2012) which both have been seen in many countries [4].

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COVID-19 (like many other diseases) can be transmitted from an infected person through exhalation or emittion of body fluids or aerosol particles containing the virus, which then attach to the surfaces and subsequently touched by receiver person. Aerosolized pathogens are the leading agent of the respiratory infections and their body-to-body transmissions cycle. The parameters behind respiratory protection and airborne transmission intertwine in a complex system that can be broken down into four bidirectional components: (1) release, (2) infection, (3) filtration, and (4) protection (Fig. 1). Aerosols play a prominent role in spreading of viruses in the air. Aerosol particles with different sizes can infect the host's respiratory tract through different mechanisms (da < 10 μm, alveolar regions; $10 <$ da < 100 μm, upper respiratory tract) [5]. Therefore, additional studies are urgently needed to curb the spread of viral infections. The use of respiratory protection devices has been shown to be an effective non-pharmaceutical intervention to reduce the spread of respiratory viruses, primarily when used by individuals in enclosed spaces, in close contact with a person revealing pandemic-like symptoms.

Herein, we describe the ways and mechanisms of virus transmission and summarize the problems, faced by respiratory protection devices technology. Meanwhile, we briefly review the recent research progresses in antiviral nanomaterials, including their main physicochemical characteristics,

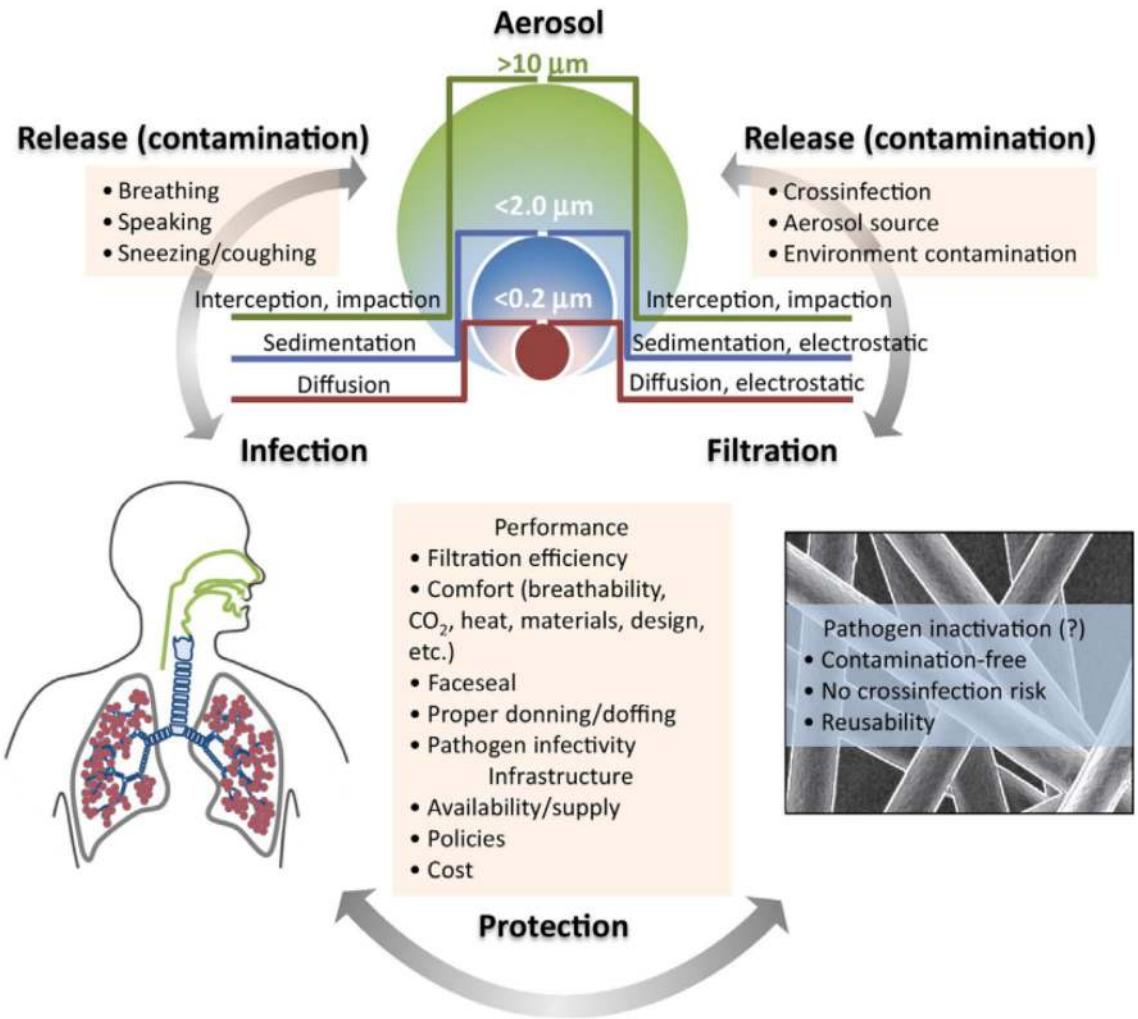

Fig. 1 Respiratory protection and airborne transmission intertwine system. Panel in this figure is reproduced with permission from Ref. [5]. Copyright 2017 Elsevier

the various mechanisms of antiviral function of these materials, and the effect of the combination of antiviral nanomaterials and textiles on perotection performance of related face masks. Lastly, the challenges and future perspectives of the application of nanotechnology in antiviral textiles are discussed.

Current Protect Tools Based on Non-woven Fabrics

Current personal protective tools (medical masks and protective clothing) are used to effectively filter the particles in the air and block the droplets, blood, body fluids, secretions, and so on. The objects of protection are generally infectious microorganisms, bacterial particles in the air, and aerogels containing pathogens [6]. The medical protective masks are typically made of multiple nonwoven layers, including functional wet-resistant spunbonded nonwoven layer, melt-blown nowoven layer, and skin-friendly spunbonded nonwoven layer. The primarily filtering mechanisms of the medical protective masks are interception, inertial impact, and electrostatic deposition. The filtration efficiency of ordinary filtering materials can only reach up to 85% [7]. In order to ensure the filtration performance of surgical masks, electret treatment is essential. After the electret treatment, the filtering material will have a positive charge, through which the filtration efficiency can be increased to over 95%. Since the trapped objects (such as bacteria, viruses and aerosols) are negatively charged, they will be blocked or trapped by created electrical field when they are carried by air flow through the positively charged fibers [7, 8] (Fig. 2).

In most of the regular protective masks (such as N95 masks), the protection performance is mainly determined by the filtration characteristics of the filled non-woven layer (including filtration thickness, packing density, fiber

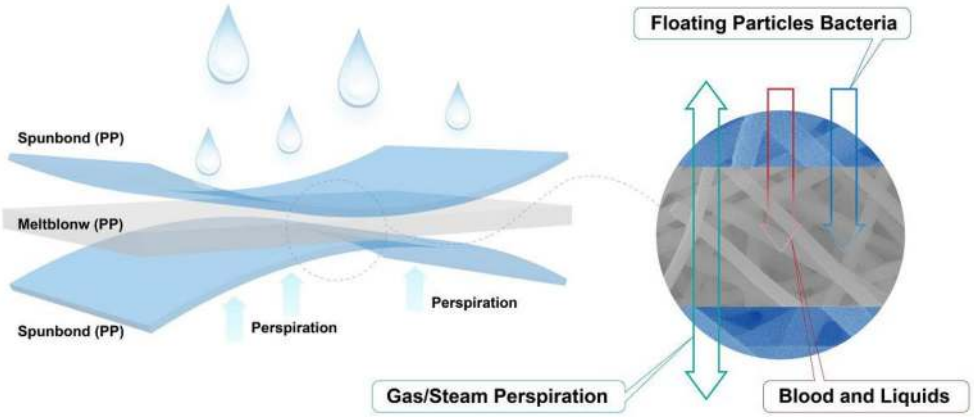

Fig. 2 Schematic of structure and protection mechanism of current ordinary face masks

diameter, fiber charge) and particle characteristics (diameter, density, and velocity) [9]. If the surface of the protective mask is contaminated with droplets during the practical applications, the virus could penetrate into the protective layer along with the droplets. Besides, the hands of medical staff or users could get contaminated when mask is removed. Generally, the effectiveness of these masks depends on their proper usage and handling. Improper usage and touch could dramatically increase the risk of pathogens transmission [10], as is the case with the current COVID-19 epidemic. Furthermore, it is necessary to functionalize the filtration systems by addition of nanomaterials, and producing the reusable virus inactivating devices. Such a functional enhancement mitigates the risk of being infected by direct or secondary vectors [11].

Current advancements in nanotechnology provide a platform for minimizing the risk of transmission of infectious agents from contaminated protective equipment such as masks. A possible pathway to this perspective is to equip the personal protective devices with antiviral elements. Such an essential upgrading can be obtained by embedding the antiviral nanomaterials in the fibers or non-woven fabrics which are typically used as face protective materials. For this purpose, both inorganic and organic materials and composites can be used as the functional elements. Nevertheless, different materials with different physical and chemical natures, stabilities and degrees of anti-mirobial functions should require different applications and manufacturing processes.

Metal-Based Nanomaterials as Antiviral Materials

Metal-based nanoparticles have unique physicochemical properties due to their small size and high specific surface area, which enable them to interact with viruses and other micro-organisms. A variety of metal and metal oxide nanoparticles (such as silver, copper, titanium, gold, and zinc) have been introduced as antiviral agents [12]. Table 1 summarizes and compares the typical metal-based nanoparticles antiviral materials. Infection of the host cells by viruses mainly occurs via four mechanisms: attachment, penetration, replication, and budding. On the other hand, antiviral function of metal-based nanoparticles contains three interacting stages, (1) Linking of connecting to the virus and inhibiting the virus attachment penetration into the cell; (2) generation

Table 1 Comparison of the typical metal-based nanoparticles antiviral materials

Types	Preparation	Size (nm)	Performance	References
Ag NPs	Electrochemical	7.1	Infected cells cultured in 100 ppm Ag NPs for 48 h, the cell survival rate reach 98%	[14]
Ag@OTV	Surface modifier	3	The cell survival rate remains 90%	[18]
Ag_2S NPs	Chemical reduction	< 5	Inhibited PEDV more than 99%	[22]
Au NPs	Chemical reduction	10	Reduce viral infections (a reduction of 92% after 6 h interaction)	[31]
CuO NPs	Surface modifier	< 100	Improve five orders of magnitude in virus-killing than the control N95	[42]
Cu_2O NPs	Chemical reduction	50	Reduce viral infections (a reduction of 90% at concentration of 4 μg/mL)	[43]
TiO_2	Sonochemical	8	Excellent antiviral performance against NDV at the concentration of 6.25 μg/mL	[51]

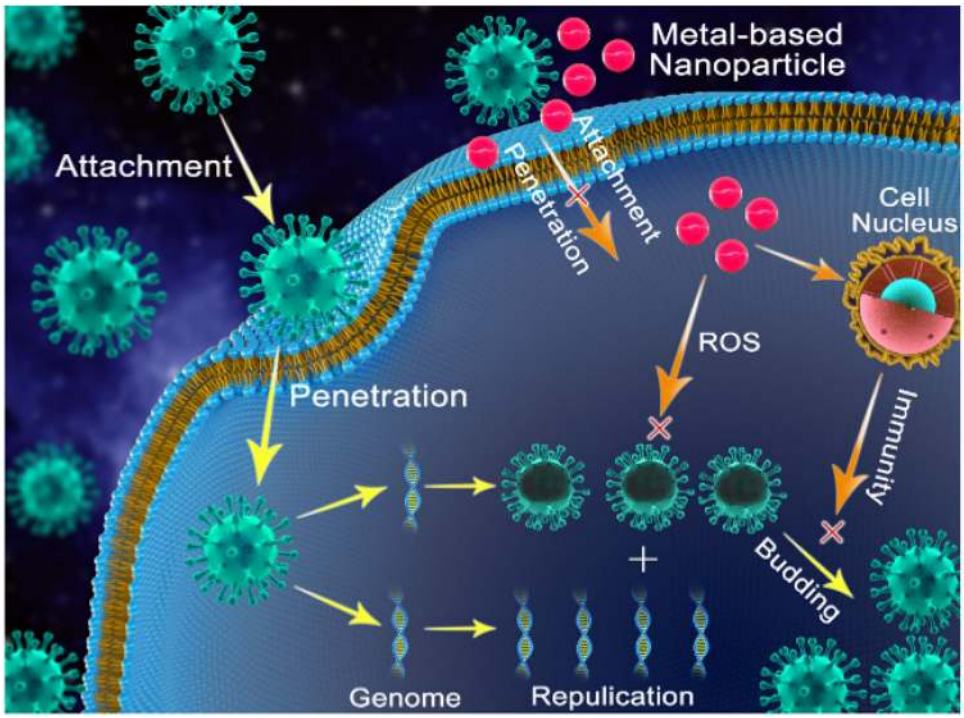

Fig. 3 Schematic presentation of antiviral mechanism of metal-based nanoparticles

of highly active oxygen and other ions and radicals which adhere to the wall (spkies or membrane) and destroy the structure and function of viral proteins and nucleic acids; (3) simulating the nucleus to increase the immune response of the host cell, and inhibiting the budding and spreading of the virus (Fig. 3).

Silver-Based Antiviral Nanoparticles

Silver and it's derivatives are known a classic anti-microbial compounds, and are still in high-demand for their impressive anti-pathogen performance. Silver nanoparticles (Ag NPs) can simply interact with the outer layers of the virus and prevent their attachement on and penetration into the host cells. The average particle size of Ag NPs is an important factor that affects its antiviral ability. For example, Krzyzowska et al. [13] report the synthesis of Ag NPs with an average particle size of 33 nm, prepared by chemical reduction method, using tannic acid as surface ligands. This Ag NPs couls effectively control the herpes simplex virus type 2 (HSV-2) infection in mice by inhibiting the adhesion of the virus to host cells. Interestingly, this process produced no toxic and pro-inflammatory incidences (Fig. 4a). To obtain Ag NPs with smaller particle sizes, Huy et al. [14] suggested a simple electrochemical method, and obtained a Ag NP sample with an average size of 7.1 nm. In a 48-hours cultural test with 100 ppm Ag NPs, the cell survival rate was determined to be as high as 98%, whereas the cell viability was only 2% in control samples (without Ag NPs). The antiviral function is related to this fact that the Ag NPs can easily contact with polioviruses (25–30 nm), and destroy their proteins molecules, so that prevent them to bind with the host cells. Addition of surfactants to the synthesis method can control the average size of Ag nanoparticles. Many types of surfactants (such as PVP [15], citric acid [16] and plant polyphenol [17]) have been suggested for this application, as their influence on average particles size could substantially improve the anti-infection function of Ag NPs.

To improve the antiviral activity, some therapeutic agents can be used as the surface ligands for Ag NPs. For example, Oseltamivir (OTV) is a therapeutic agent for antiviral applications. Zhu et al. [18] used OTV as the surface modifier and synthesized Ag@OTV NPs with average size of 3 nm. When Ag@OTV solution was used to culture the cells infected with influenza virus (H1N1), the cell survival rate remained as high as 90%, which is obviously highed than that of bare AG MPs (65%). This enhancement resulted from the synergistic anti-infection effects of Ag NPs and OTV ligands. Ag@OTV could effectively inhibit H1N1 influenza, creating virus-induced apoptosis of host cells. This could mainly occur through ROS-mediated p53 and AKT signaling pathways (Fig. 4b). Similarly, other therapeutic agents (such as amantadine [19], zanamivir [20], and aminoadamantane [21]) have also been coupled with Ag NPs, and the resulting NPs exhibited boosted antiviral activity.

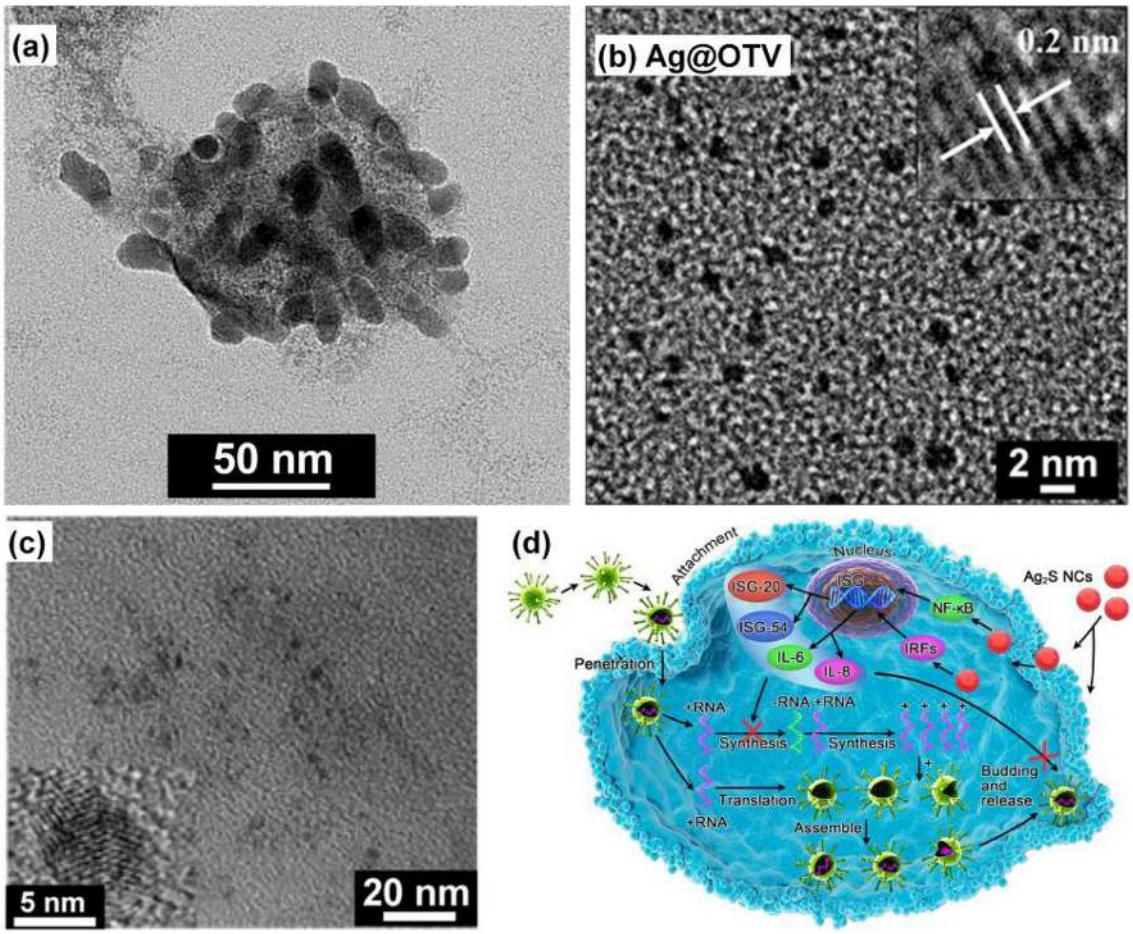

Fig. 4 Silver-based antiviral nanoparticles. **a** HSV-2 covered with silver nanoparticles (Ag NPs). **a** Reproduced with permission from Ref. [13]. Copyright 2018 MDPI. **b** SEM image of of Ag@OTV particles. Lattice orientation obtained from transmission electron microscopy (TEM), is depicted on inset. **b** Reproduced with permission from Ref. [18]; Copyright 2016 American Chemical Society. **c** TEM image of Ag_2S NCs. Lattice orientation obtained from TEM, is depicted on inset. **d** Mechanisms of the antiviral activity of Ag_2S NCs. **c**, **d** Reproduced with permission from Ref. [22]; Copyright 2018 American Chemical Society

Beyond silver nanoparticles, other silver compounds are also considered as effective antiviral materials. Han et al. [22] prepared Ag_2S nanoparticles (Ag_2S NCs) with average size of less than 5 nm by using glutathione as a capping reagent (Fig. 4c). Ag_2S NCs inhibited the porcine epidemic diarrhea virus (PEDV, a positive-strand RNA virus) more than 99%, and demonestrated an acceptable biological safety. In addition, Ag_2S NCs can affect on some other types of RNA viruses (PRRSV), as well. The antiviral activity of Ag_2S NCs is mainly ruled out by inhibiting RNA synthesis and viral budding. It was also argude that, the activation of ISG proteins and pro-inflammatory cytokines might be an important factor in this case (Fig. 4d). Similarly, other silver compounds (such as silver bis(citrato)germinate [23] $AgNO_3$ [24] and silver acesulfame [25]) have been known as the excellent anti-virus substances.

The above mentioned studies have proved that silver and its derivative compounds are of strong virus killers. However, there is still a serious challange in combination of silver (or silver-derivative) NPs with fibers, when they are going to be applied in personal protection equipment. Surface coating is a facile technology for this application. Wang et al. [26] used surface coating for deposition of Ag NP on silk at the supporting materials. Ag NPs induced a powerful pathogen killing ability, which could be visually indicated by color changes, due to the plasmon resonance effect of Ag NPs. When Ag NPs-decorated silk fibers were used to contact pathogens, more than 99% of E. coli specimen was destroyed. This process can be completed in a short course of time, at room temperature, and is associated with low energy consumption and environmental protection. Other fiber materials (such as polyester [27], cotton [28], and chitosan [29]) can also prominently contribute to the antibacterial activities when are coated by Ag NPs. However, there are, so far, few results and evidences on the antiviral

properties of Ag NPs-decorated fiber, which atill need to be addressed in wider field.

Gold-Based Antiviral Nanoparticles

Gold nanoparticles (Au NPs) possess excellent biocompatibility, stability, and ability to bind with biological ligands (bioconjugation), which has great relevance for applications in the field of antiviral materials [30]. The mechanism of viral inhibition by Au NPs has been realized to be based on blocking the viral particles to be binded to the cell, thereby inhibiting virus attachment/entry and controlling the cell-to-cell spread of the virus. For instance, Laura et al. [31] prepared Au NPs with particle the average size of 10 nm via chemical reduction method using the plant extracts as the reducing agent (Fig. 5a). This Au NPs could significantly reduce the viral infections (a reduction of 92% after 6 h interaction). The virucide effect of Au NPs was perhaps due to the interaction of the Au NPs with the viral receptors, inhibiting the virus attachment to the host cells and avoiding viral infection (Fig. 5b). In order to further explore the effect of the average size of Au NPs on antiviral efficacy was considered. Haag et al. [32] used sialic acid-terminated glycerol dendrite as ligand, to obtain two different sizes of Au NPs (2 nm and 14 nm). The particles average size was shown to be substantially determinant in antiviral ability. When a dispersion of 14 nm Au NPs was applied in a culture medium, containg the cells infected by influenza virus (Fig. 5c), the

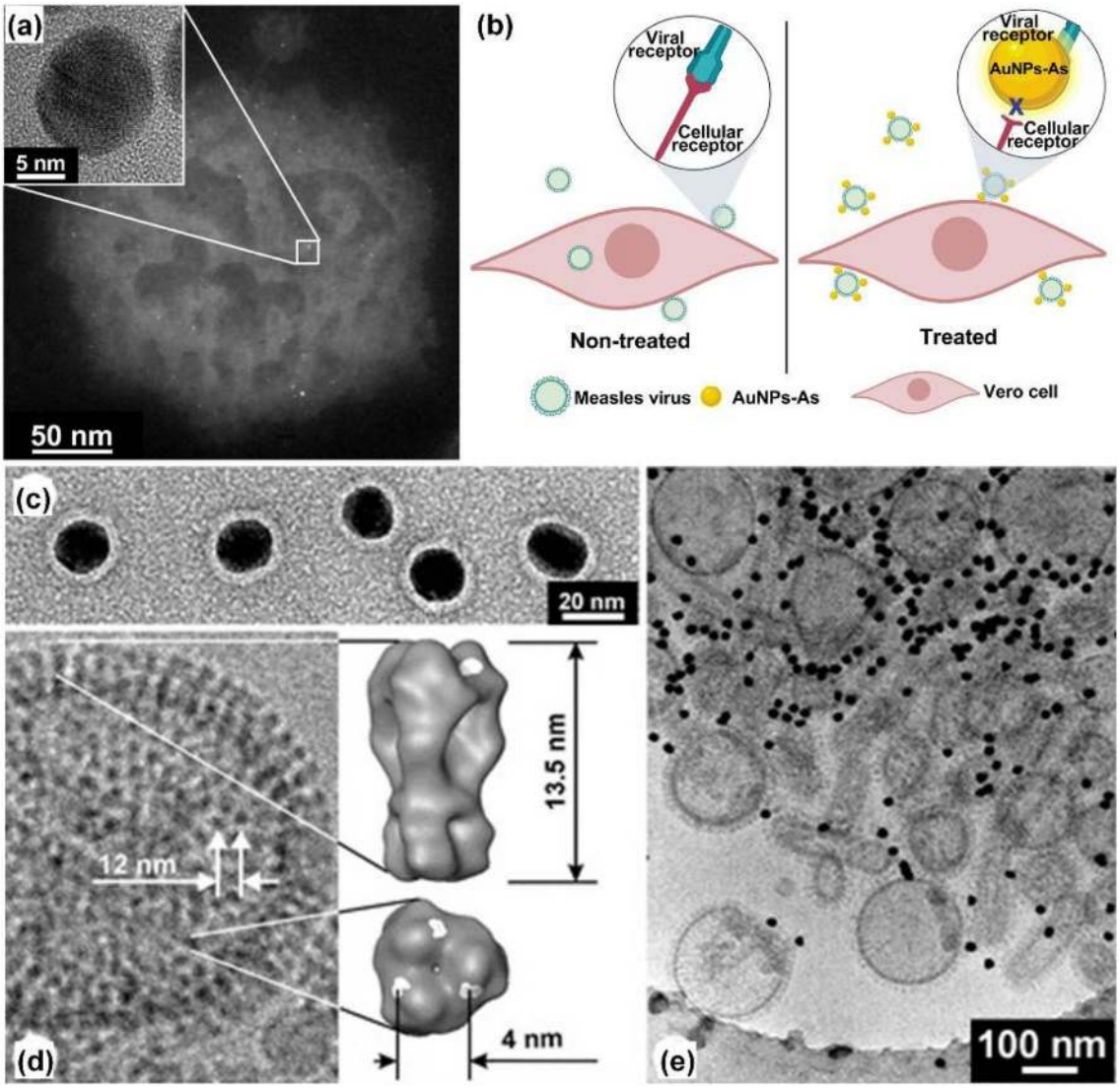

Fig. 5 Gold-based antiviral nanoparticles. **a** Measles virus exposed to Au NPs. **b** Schematic representation of the virucidal effect of Au NPs. **a**, **b** Reproduced with permission from Ref. [31]. Copyright 2019 MDPI. **c** Amphiphiles functionalized Au NPs. **d** Influenza AX31 virion showing the individual trimeric fusion protein HA sticking out of the viral membrane. Receptor binding sites. **e** Au nanoparticles binded to virus. **c**–**e** Reproduced with permission from Ref. [32]; Copyright 2010 Wiley

cell survival rate remains as high as 60%. The same test with 2 nm Au NPs could only save 5% of the cells population. Such a notable difference was attributed to the multivalent effect, which cause the larger Au NPs make a stronger binding forces with the protein molecules on the surface of virus (Fig. 5d, e). As a size controlling factor, various types of surfactants (such as *N*-acetylneuraminic acid [33], peptide [34], and nucleic acid [35]) were tested in synthesis madia, and the issuing Au NPs were compared bsed on their size-dependent antiviral potentials activities.

In order to improve the specificity of Au-based antiviral materials, Huang et al. [36] fabricated a gold nanoparticle BNA conjugated network (DNA-Au NPs). The DNA-Au NPs network exhibited a fascinating antiviral ability against the respiratory syncytial virus (RSV). When the DNA-Au NPs network, RSV virus, and cells were cultured together, the cell survival rate exceeded 90%. This DNA-Au NPs networks formed a protective layer on cell membranes that inhibited viral infections, thereby preventing virus attachment and entry, virus budding and intercellular spreading. Different morphologies of Au NPs have different antiviral properties and mechanisms. Shree et al. [37] presented the antiviral mechanisms of gold nanorods (45 nm × 10 nm) against RSV. The survival rate of cells infected with RSV was 82% in 2.5 μg/mL content of gold nanorods. Gold nanorods inhibited viral infections mainly by inducing a cellular immune response. Cytotoxicity is an important aspect that need to be considered when nanoparticles act on biological systems. However an excessive cytotoxicity will also affect the cell itself. In order to reduce the toxicity of Au NPs and improve its properties, Gabriela et al. [38] constructed micro-nano hybrid materials (Au NPs/LDHs) by assembling the gold nanoparticles (3.5 nm) on a large scale double hydroxides layer (LDHs, 150 nm). Au NPs/LDHs showed excellent antiviral abilities at extremely low concentrations, and the cell survival rate after hepatitis B virus (HBV) infection was over 90%. The gold released from the Au NPs/LDHs composites interacts directly with the virus particles, and simply trap the viruses in the cell and prevent their transmission from cell to cell. However, the high price of gold nanoparticles limits their scale of use in personal protective equipment.

Copper-Based Antiviral Nanoparticles

Copper oxide nanoparticles are widely used in antibacterial materials due to their low price, great stability, and broad antibacterial properties [39, 40]. Few researchers have studied the antiviral properties and mechanisms of copper oxide-based nanoparticles (CuO NPs). This metal oxide and specially it's nanoparticles can destroy the integrity of the virus and the degradation of its genome. Ahmad et al. [41] proved that CuO NPs have an outstanding anti-HSV-1 virus efficacy, as the cell survival rate reached 83.3% when CuO NPs were co-cultured with HSV-1 infected cells, at the highest non-toxic concentration of CuO NPs (100 μg/mL). The copper ions released from CuO NPs catalize the production of reactive oxygen species (ROS), which can colapse the HSV capsid integrity and degrade the whole genome. In order to explore the application of CuO NPs in respiratory protective equipment, Gadi et al. [42] reported the preparation of antiviral respiratory protective face mask by impregnation of CuO NPs into an N95 mask. The antiviral respirator was composed of four layers. The outer and inner layers (A, B) have different fiber fineness, and CuO NPs were evenly distributed on the surface of the fiber, as shown on Fig. 6a, b. The presence of CuO NPs in the masks acts as the killer of the virions which were remained in the mask without altering its physical barrier properties. With this procedure, the antiviral function of N95 masks were improved by five orders of magnitude.

Cuprous oxide nanoparticles (Cu_2O NPs) are of other metal-oxides for antiviral purposes. Hang et al. [43] investigated the antiviral efficacy of Cu_2O NPs against hepatitis C virus (HCV), in vitro. When the HCV virus was treated with Cu_2O NPs at a concentration of 4 μg/mL, its infection rate against the cells was reduced by 90%. Antiviral mechanism of Cu_2O NPs was thought to interfere with the attachment and entry of HCV virions into host cells. Larger Cu_2O NPs (~ 50 nm) inhibited HCV viruses (~ 30 nm) to be attached to the cells, through the multivalent binding of virions, thereby blocking the entry of the virus into the cell. In order to elucidate the antiviral activity of copper compounds with different valences, Mazurkow et al. [44] synthesized multi-phases Cu_xO_y (CuO and Cu_2O) hybrid by calcinating at different atmospheres (Fig. 6c). They concluded that Cu_2O has a relatively better antiviral ability (Fig. 6d). The difference in antiviral activity between CuO and Cu_2O was certified by zeta-potential measurements. Cu_2O was found to have a higher isoelectric point of 11.0, which makes it more prepared to interact with viruses (Fig. 6e). A similar observation was reported by Kayano [45].

Other Cu-based compounds have also been studied as competitive antiviral materials. Yoshie et al. [46] investigated the antiviral activity of nanosized copper (I) iodide (CuI) particles with average size of 160 nm. CuI particles exhibited a prominent antiviral reaction against influenza A viruses (HIN1), at a concentration of 17 μg/mL. Moreover, it was indicated that CuI generates hydroxyl radicals in aqueous solution, which inactivates the virus by oxidizing the surfacial lipid groups. Other cuprous compounds such as Cu_2S and CuCl have also been verified as potential anti-infections [47].

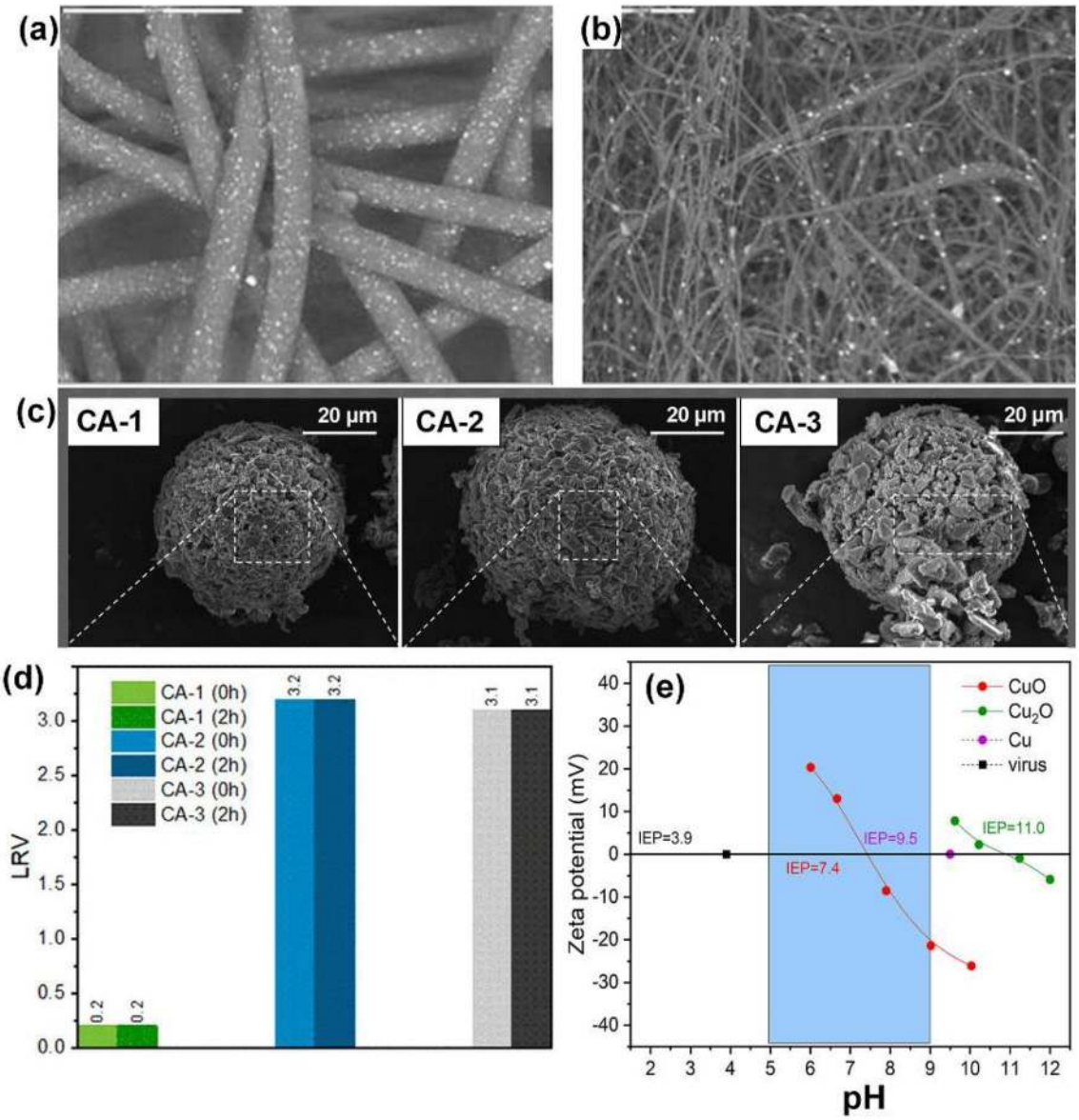

Fig. 6 Copper-based antiviral nanoparticles. **a** External layer of mask containing CuO NPs. **b** Internal layer of mask containing CuO NPs. **a**, **b** Reproduced with permission from Ref. [42]. Copyright 2010 PLoS. **c** The surface morphology of copper-based hybrids materials. **d** Antiviral properties of copper-based hybrids materials. **e** Comparison of zeta potential profile of virus, CuO, Cu_2O, and Cu. **c**–**e** Reproduced with permission from Ref. [44]; Copyright 2020 American Chemical Society

Other Metal Oxides as Antiviral Nanoparticles

In addition to the above mentioned materials, the antiviral abilities of the other types of metal nanomaterials have equally been of interest to researchers. Zinc oxide and titanium oxide have been successful in micro-biological assessments, but so far attracted less attentions. Yogendra et al. [48] proved that a negatively charged ZnO NP sample can simply trapped the herpes virus, and inhibit its attachment to the host cells. When ZnO was co-cultured with viruses and cells, the cell survival rate increased by over 50%. Sun et al. [49] and Seyed et al. [50] separately studied the inhibitory trait of the ZnO NPs on HSV-1. Sara et al. [51] synthesized a TiO_2 NPs sample, with tetragonal lattice orientaion, and an average particle size of 8 nm, by a simple sonochemical procedure. This TiO_2 NPs sample showed an exceptional antiviral performance, versus newcastle virus (NDV), when it's concentration in culture medium was set at 6.25 μg/mL. The inhibiting mechanism was defined to be based on destruction of the lipid membrane and blocking the virus attachment. Beyond the mentioned items, there are some other metlas and metal-oxdes anti-viruses, such as tin oxide

(SnO_2) [52], gallium [53] and iron oxide [54], which are potential candidates for being embeded into the personal protective fabrics, for daily useage.

Nonmetal Nanomaterials as Antiviral Materials

Carbon-Based Antiviral Materials

Carbon atoms can link to each other, in different ways and differenr binding energies, therefore make various allotropes, such as 0D carbon dots (CDs), 1D carbon nanotubes (CNTs), and 2D graphene oxide (GO). Different carbon allotrpes have been examined in term of their anti-microbial effects, which are originating from their unique physical and chemical properties. One of the most important dominating factors is the geometry of the carbon materials, which has shown to be profoundly determinant in their anti-infection perfromance. A brief description of carbon-based nanomaterials with different physicochemical characteristics and antiviral activity is brought in the following section: Han et al. [55] investigated the effect of CDs against viruses by using pseudorabies virus (PRV) and porcine reproductive and respiratory syndrome virus (PRRSV) as the models of DNA and RNA viruses, respectively (Fig. 7a). After CDs treatment, the infection of cells by PRV and PRRSV was reduced to more than 80%, compared with untreated controls (Fig. 7b). They demonstrated that the cells treated with CDs can stop the multiplication of PRV and PRRSV by production of interferon-a (IFN-a) and IFN-stimulating genes (ISGs). The surface properties of CDs affect its safety and biocompatibility. In this context, Huang et al. [56] prepared a core–shell CDs sample, by dry heat treatment of curcumin, and investigated the antiviral activity of this sample against enterovirus 71 (EV71), as preceived an excellent antiviral capability, together with a compelling biocompatibility. When the CDs solution with 5 μg/mL concentration, was applied on the culture cells, infected by EV71 virus, the inhibition rate against virus-infection exceeded 99%. This level of performance could be gained when concentration of curcumin in culture medium was set at 200 μg/mL. In vivo experiments of CDs can outstandingly improve the survival rate of a mice speimen, infected with EV71 virus. Carbon nanotubes [57] have been also looked as anti- virus, but their high cytotoxicity makes their application prospects unclear.

As a two-dimenstional carbon allotrope, graphene oxide has found to be an intresting anti-pathogen. Han et al. [58] reported the broad-spectrum antiviral activity of GO (Fig. 7c) against pseudorabies virus [PRV, a DNA virus (Fig. 7d)] and porcine epidemic diarrhea virus [PEDV, an RNA virus (Fig. 7e)]. Both GO, and rGO exhibited fascinating antiviral behaviours, arising from their unique single-layer structure and surfacial negative charges. It was inferred that the cell infection by PRV and PEDV can be controlled to two-orders of magnitude, when the concentration of GO, in medium, is set at 6 μg/mL. The negatively charged GO showed a higher potential to electrostatically interact with the viruse before entring into the cell, ending to destruction of it's single-layer structure and sharp edges (Fig. 7f). However, the mechanism of antiviral activity in GO remains controversial. Ronit [59] reported that GO inhibits herpes simplex virus type-1(HSV-1) infections. They believe that blocking of viral attachment can be the primary antiviral mechanism. Furthermore, combination of carbon-based anti-pathogens with fibers, in application for the face masks, without affecting the physical and chemical properties of carbon molecules, is still challenging and needs to be solved.

Other Inorganic Antiviral Nanoparticles

Li et al. [60] developed a selenium-adamantine hybrid (Se@AM) NP, and studied its antiviral properties against the H1N1 influenza virus. In term of morphology, these hybrid NPs featured a uniformly distributed sepherical form, with an average size of 100 nm (Fig. 8a). In a functional point of view, in presence of this sample, the infection rate of the virus could be controlled by 79% reduction. Compared with the bare Se NPs with 58% reduction, the performance of SeNPs was reckoned to be obviously better. This evaluation was carried out based on based on H1N1 influenza virus (Fig. 8b, c). Mateus et al. [61] investigated the biocompatibility and antiviral activity of silica nanoparticles (SiO_2), with distinct surface properties. Experiments disclosed the antiviral ability of SiO_2 NPs against enveloped viruses, which was rule out by attachment inhibition, and suppression of their viral transduction ability.

In addition to the aforementioned inorganic anti-viruses, salt has also a long history in killing microorganisms. Ilaria et al. [62] introduced a reusable virus deactivation system, by functionalization of the center part of the fibrous filtration element of surgical mask, using sodium chloride salt (Fig. 8d). 100% survival rate was certified, when this system was applied for the virus- infected mices (Fig. 8e). Such an excellence was attributed to the role of PP filtration coating, in adhesion and entrapment of the viral aerosols (Fig. 8f). Destruction mechanism was assigned to the mechanical stresses, from recrystalization of salts, when aerosols loose their liquid phase.

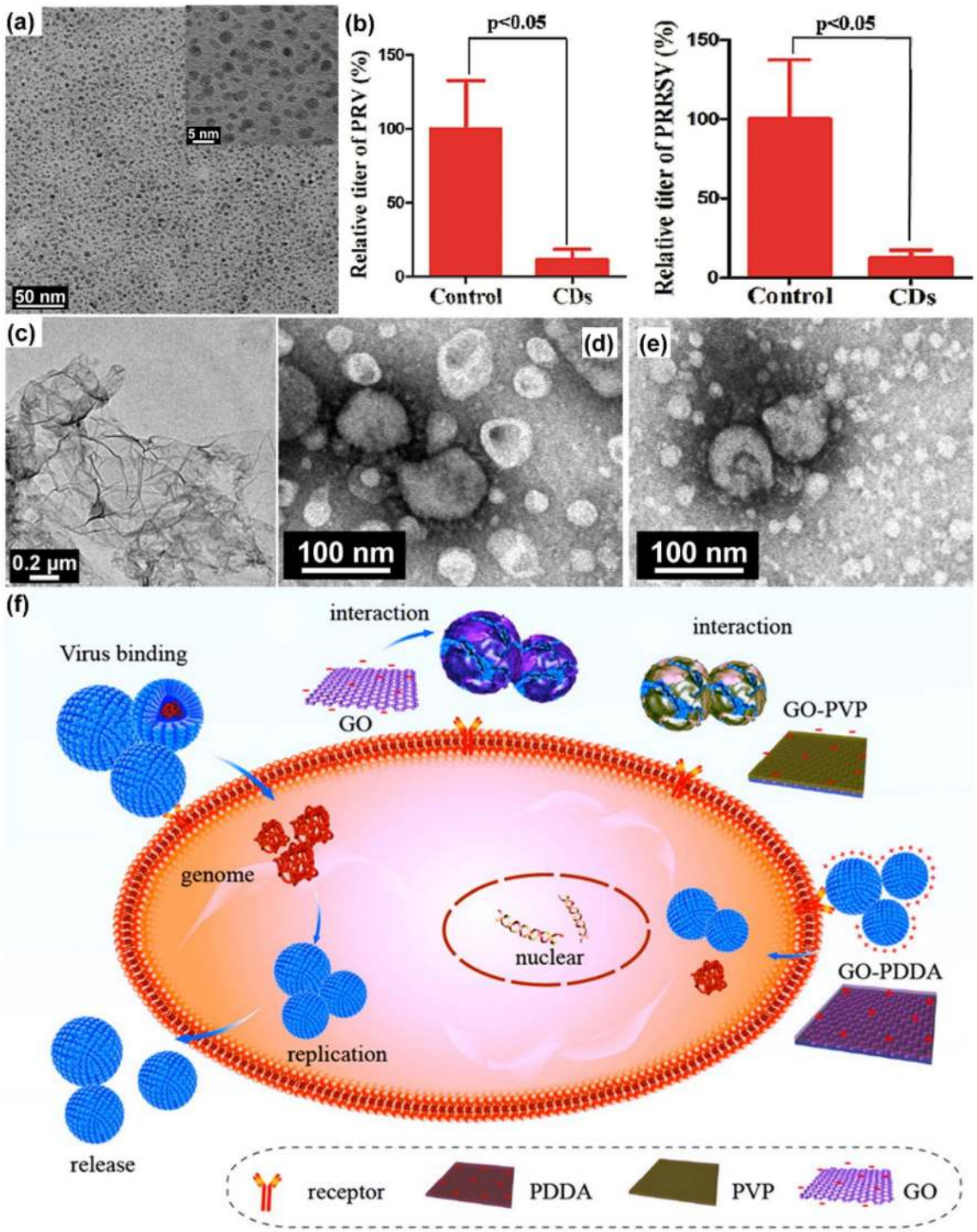

Fig. 7 Carbon-based antiviral materials. **a** SEM and TEM (inset) images of carbon dots. **b** Antiviral ability of CDs against PRRSV and PRV. **a**, **b** Reproduced with permission from Ref. [55]. Copyright 2016 Elsevier. **c** Morphology of GO. **d** Morphology of PRV treated with GO, for 1 h. **e** The morphology of PEDV incubated with GO, for 1 h. **f** Mechanisms of antiviral activity of GO. **c**–**f** Reproduced with permission from Ref. [58]; Copyright 2015 American Chemical Society

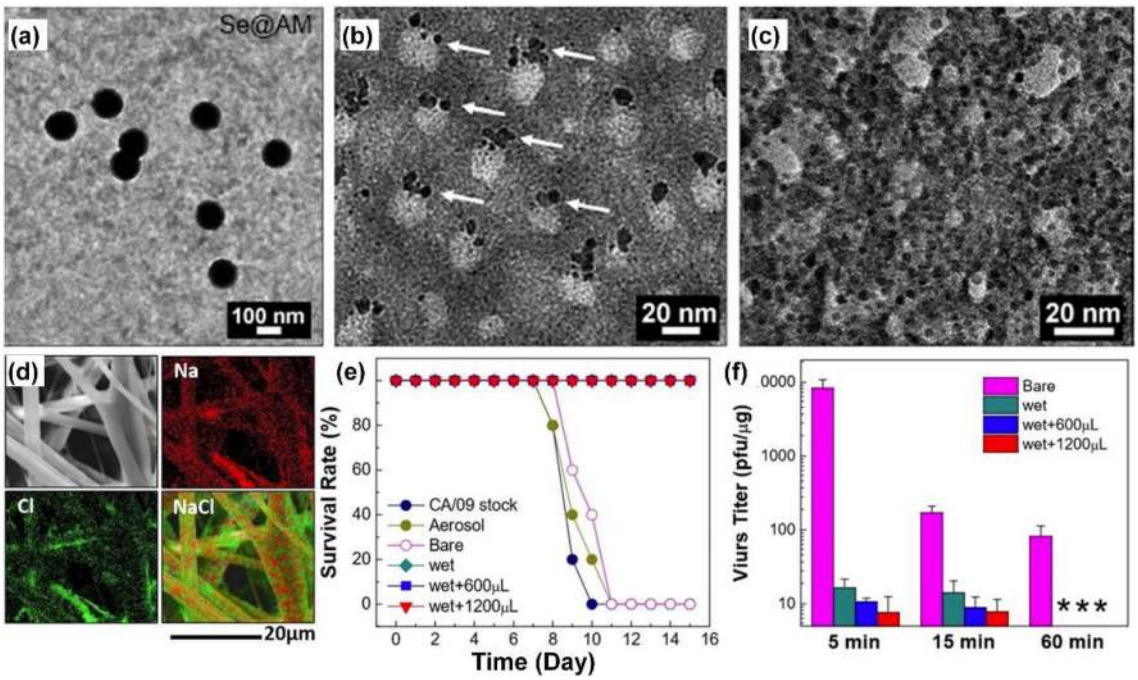

Fig. 8 Inorganic antiviral nanoparticles. **a** SEM image of Se@AM. **b** Morphology of Se@AM attached to H1N1. **c** Morphologic abnormalities in Se@AM-treated H1N1. **a**–**c** Reproduced with permission from Ref. [60]. Copyright 2018 Taylor and Francis. **d** Morphology and elemental distribution pattern of filter containing NaCl. **e** Inhibition of virus activity. **f** Influence of incubation status on the the active life-time of viruses. **d**–**f** Reproduced with permission from Ref. [62]; Copyright 2017 Springer Nature

Table 2 Comparison of the organic antiviral materials

Types	Performance	Mechanism of antiviral	References
N-halamine	Contact with 0.5% *N*-halamine for 30 min, the infection rate reduce seven orders of magnitude	Interrupt RNA specific sites	[63]
N,*N*-dodecyl methylpolyethylenimines (PEIs)	Kill the influenza virus with essentially 100% efficiency within minutes	Damage lipid membrane	[64]
Chitosan	At concentration of 1 g/L inhibited the infection of NCV	Stimulation of immune response	[66]
Zinc-tetra(4-*N*-methylpyridyl)porphine ($ZnTMPyP^{4+}$)	After exposure to light for 60 min, inactivating bacterial and viruses at least 99.89% and 99.95%	Production of ROS	[71]
Sunlight active nanofiber membranes	Killing rate of bacteria and viruses higher than 99%	Production of ROS	[73]

Organic Antiviral Materials

Organic antiviral materials kill pathogens by the reaction on the surface proteins or nucleic acids, or destroy the morphology or proliferation of pathogens, via generation of reactive oxygen species (ROS), under external stimulation. Based on their anti-microbial function, the organic antiviral materials can be divided to antiviral and photodynamic antiviral materials. Table 2 summarizes and compares the different types of the organic antiviral systems.

Intrinsic Antiviral Materials

Intrinsic antiviral material can lead to virus inactivation due to their chemical structure. As shown in Fig. 9a, many synthetic and natural compounds have intrinsic antiviral properties. *N*-halamine is an effective organic synthetic antibacterial material, which is widely used for antibacterial

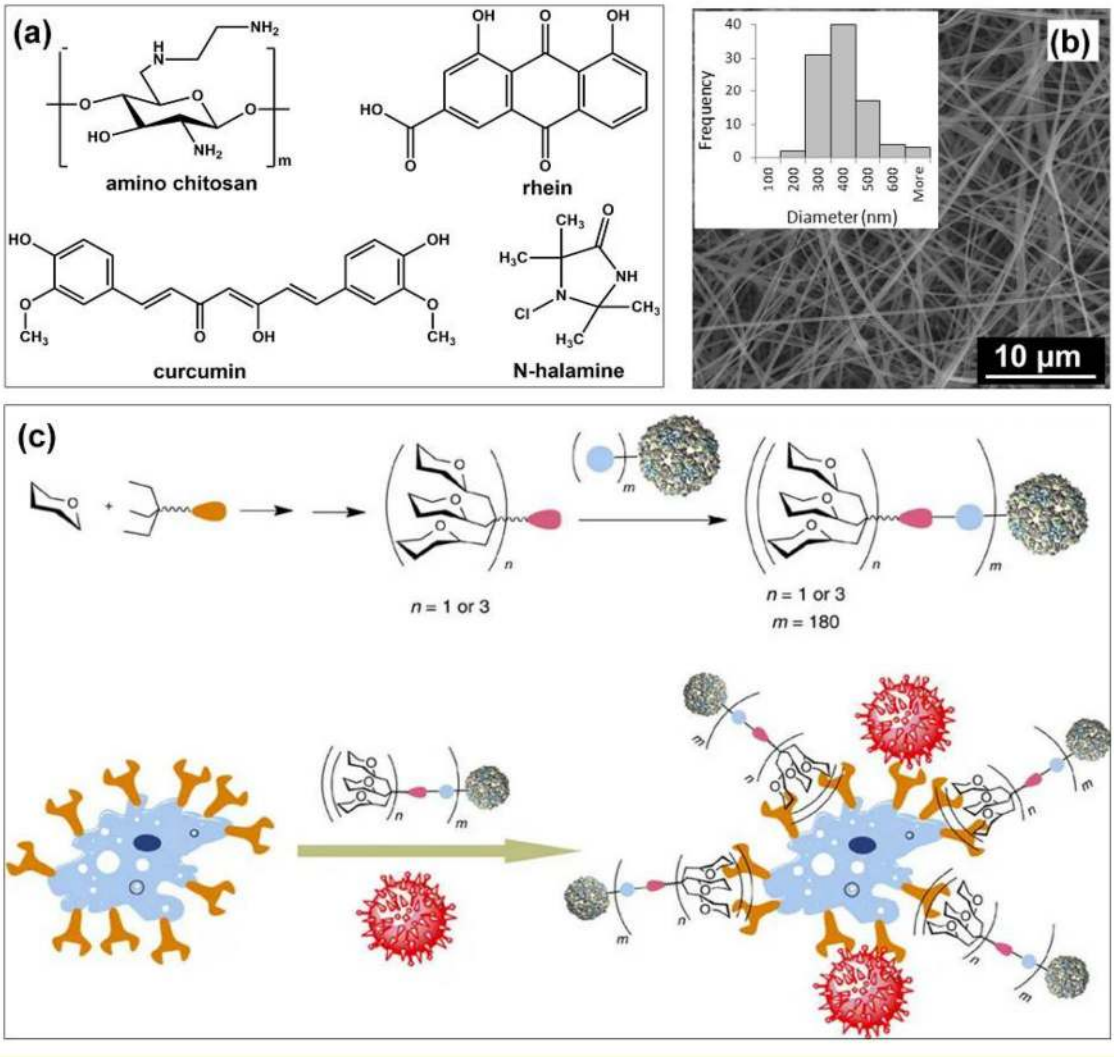

Fig. 9 Intrinsic antiviral materials. **a** Chemical structures of intrinsic antiviral substances. **b** Morphology of chitosan nanofibrous mats. Inset is distribution of fiber diameter. **a**, **b** Reproduced with permission from Ref. [67]. Copyright 2019 Elsevier. **c** Schematic virus-like glycodendrinanoparticles and their function. **c** Reproduced with permission from Ref. [65]; Copyright 2012 Springer Nature

modification of fibers, but its antiviral properties have been rarely studied. Ren et al. [63] propose *N*-halamine coating on the surface of non-woven fabrics to obtain fabric materials with antibacterial and antiviral activity. They remark that the deposited *N*-halamine was stable, non-volatile, and caused an efficient antiviral activity. After being exposed to 0.5% *N*-halamine for 30 min, the infection rate of the virus was reduced to seven orders of magnitude. *N*-halamine could kill the AI viruses in a short matter of time, with disrupting its genetic and replication capabilities. This function was managed by destruction of the specific active sites on the viral RAN. The hydrophilicity of the surface is also a crucial factor of antiviral ability. Organic materials are often used to change the hydrophilicity of the surface of various protective materials. In order to obtain a hydrophobic surface, Jayanta et al. [64] synthesized the branched or linear hydrophobic N, *N*-dodecyl methylpolyethylenimines (PEIs) and verified their antiviral activity against influenza virus. The hydrophobic PEIS could kill the influenza virus, as well as E. coli and S. aureus, with 100% efficiency, in few minutes. Hydrophobic PEIS can damage the lipid membrane of the virus by erecting fragments of the polycationic chains (''tentacles''). On the other hand, the organic materials are used for assembling the virus-mimic which can effectively interact with receptors and inhibit the invasion of viruses to the host cells. Renato et al. [65] reported a virus-like glycodendric nanoparticles

assembled with highly valent glycodendrimeric, condtructed via nested layers of multivalency. The surface of glycodendrinanoparticles is highly glycosylated and up to 32 nm in diameter, mimicking the size and surface of a pathogen. The glycodendrimeri-nanoparticles sample which could prevent infection of T-lymphocytes and human dendritic cells by the Ebola virus (inhibition rate > 80%), through competitive blockage of the DC-SIGN (dendritic cell-specific intercellular adhesion molecule-3-grabbing nonintegrin, one of the most important pathogen recognition receptor) (Fig. 9c).

In addition to the above synthetic compounds or specific compound structures, there are still many natural compounds with prominent antiviral activity. He et al. [66] studied the antiviral properties of chitosan materials. They synthesized 6-deoxy-6-bromo-*N*-phthaloyl chitosan and tested its antiviral activity. Additionally, they indicated that chitosan derivatives showed excellent antiviral activity. At a chitosan derivative concentration of 1 g/L, the infection of NCV was completely inhibited through the stimulation of an immune response. In order to study the application of chitosan in biomedical engineering, Khorasani [67] fabricated chitosan nanofibrous mats using the electrospinning method and investigated the ability to kill pathogens (Fig. 9b). The results showed that the nanofiber mats had a broad-spectrum antibacterial effect, but the related antiviral ability was not mentioned. Other natural compounds such as R. tanguticum nanoparticles [68], catechins [69], and curcumin [70] had also been shown to have excellent killing abilities against various viruses.

Photodynamic Antiviral Materials

Photodynamic antiviral materials are usually driven by light, to produce reactive oxygen species (ROS), which can selectively kill the pathogens. Photodynamic antiviral materials can achieve efficient, broad-spectrum and long-acting killing of pathogens, and are safe for the environment. Therefore, they have a great potential in preparation of biological protection materials. Richard et al. [71] explored the anti-infective efficacy of films containing zinc-tetra(4-*N*-methylpyridyl)porphine ($ZnTMPyP^{4+}$, photoactive substance). After exposure to the light for 60 min, this photodynamic polymer was capable of inactivating both bacteria and viruses, with the rates of 99.89% and 99.95%, respectively. Production of ROS is the main mechanism for the efficient killing of microorganisms, in this system. When photodynamic materials are used in fibers, their compatibility with fibers, the life-time of photosensitizer and the diffusion range of reactive oxygen species will affect their antiviral properties. Encapsulation of photosensitizer can effectively improve the compatibility and prolong the life-time of the photosensitizer. Mosinger et al. [72] prepared a stable photoactive nanoparticle sample by covering of photosensitizer with polyethylene. The polyethylene nanofiber membrane was prepared by electrostatic spinning and used to encapsulate the photosensitizer. The nanofiber membrane inhibited the function of both bacteria and viruses, by more than 99%, after a short exposure to visible light.

Also, the solely photo-driven biocidal character of photo antiviral materials leads to the instantaneous biocidal function of fast decaying or quenching under dim light and dark conditions. Thus, it is necessary to solve the decrease of killing efficiency in a dyssophotic environment. Sun et al. [73] prepared nanofiber membranes driven by daylight with high antiviral activity, via electrostatic spinning (Fig. 10a, b). The nanofiber membranes yielded 99% killing rate on both virus and bacteria, based on ROS production (Fig. 10c). The nanofiber membrane could also generate and retain it's biological activity in sunlight. They additionally, considered the application of this antiviral nanofiber membrane in bioprotective equipment, and studied the ability of the issuing equipment, for interception effect on aerosols, and killing the trapped pathogens (Fig. 10d). Results showed that the filtration performance of the nanofiber membrane values with current commercialized filtration materials, as could kill 100% of the trapped pathogens.

Conclusions and Perspectives

Currently, antiviral personal protective devices, especially the face masks, have received considerable attentions, in both academic and industrial fields of research. Most of the commercial masks are unable to suffciently filter the tiny aerogels containing the viruses. On the other hand, viruses which are attached to the filtering materials can penetrate through the moist mask, and in this way increase the risk of infection. This mini-review looks into the most recent advances in antiviral agents, and the methods which are used for preparation of protective materials. Improving the antiviral capability of the face masks, can reduce the risk of cross-infection or secondary infection during the useage or handling. Recent progresses in this field indicate that nanotechnology can foumdamentally evolves the structure and effcetiveness of the current respiratory protection devices.

To date, thousands of nanomaterials and nanotechnology-related procedures serve the trend of this progression, as discussed here. Different potential anti-microbial systems, which are integrable into the face masks are introduced in this work. Also, various anti-infection mechanisms, including attachment blocking, reproduction inhibitory action and deformation of

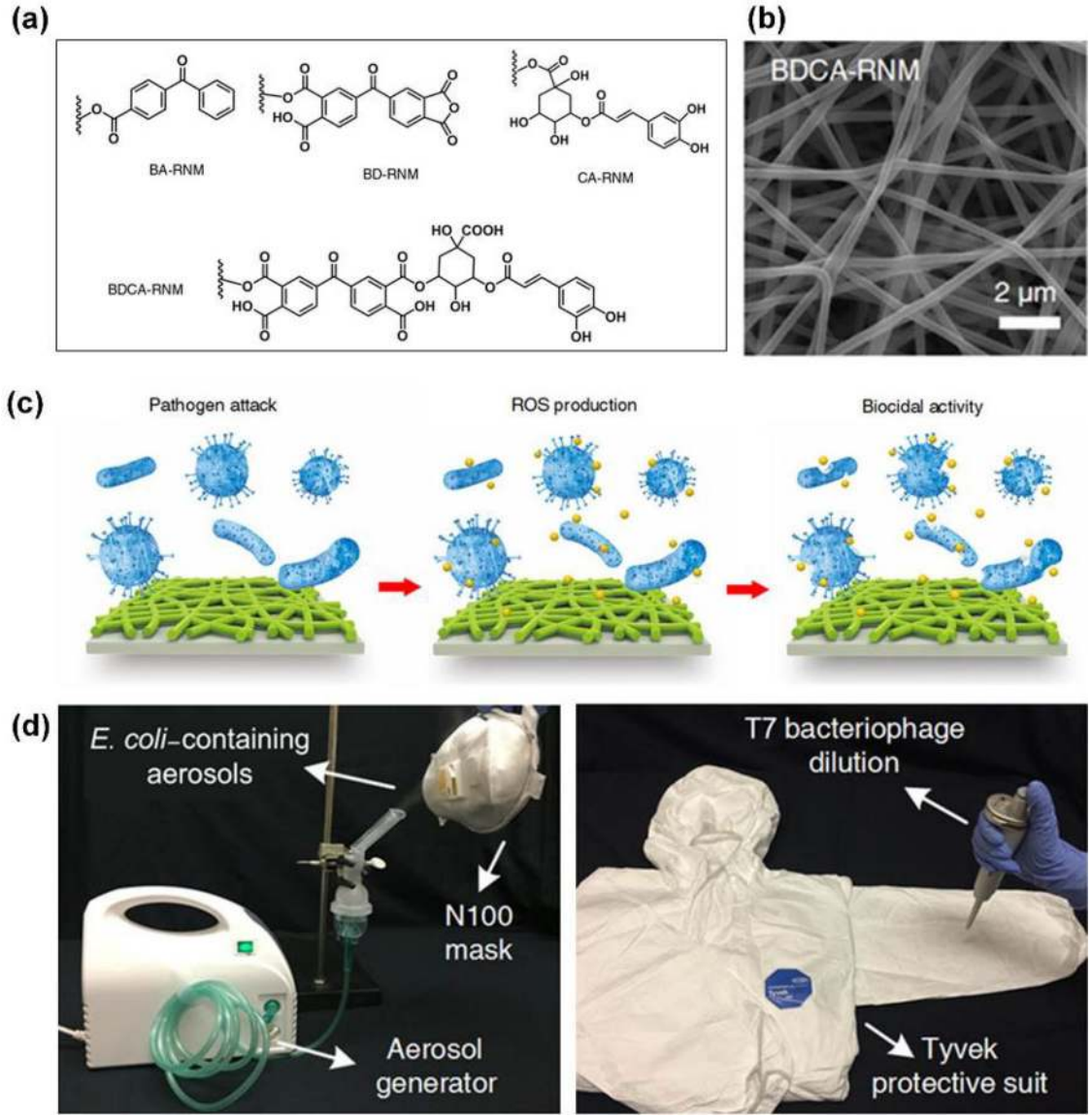

Fig. 10 Photodynamic antiviral materials. **a**, **b** Chemical structure and SEM image of photo-active nanofiber membranes. **c** Schematic demonstration of biocidal function of nanofiber membrane. **d** Application of antiviral fibers in mask and protective suit. Panels in this figure reproduced with permission from Ref. [73]. Copyright 2018 AAAS

the virial wall and membrane are highlighted. As a closing point, this review shed a light to the current shortcomings in personal protective facilities, which are lack of enough comfort, high efficiency, safety and intelligence (Fig. 11). These serious setbacks can solve by (1) product engineering, to be adapted with human face, skin and body, and to controlling the, unwanted affcets such as accumulation of heat and moisture during usage; (2) to improve the filtering efficiency and breathing, without risks, by tuning of the structural factors, such as diameter of the fibers size of the holes, and thickness of the filtering materials; (3) to apply the nanotechnology-related procedures in order to augment the entrapting potential, antiviral capabilities and intelligence of protective equipment. Finally, the functional integration and engineering of protective devices are currently unsystematic, and further research and study are required.

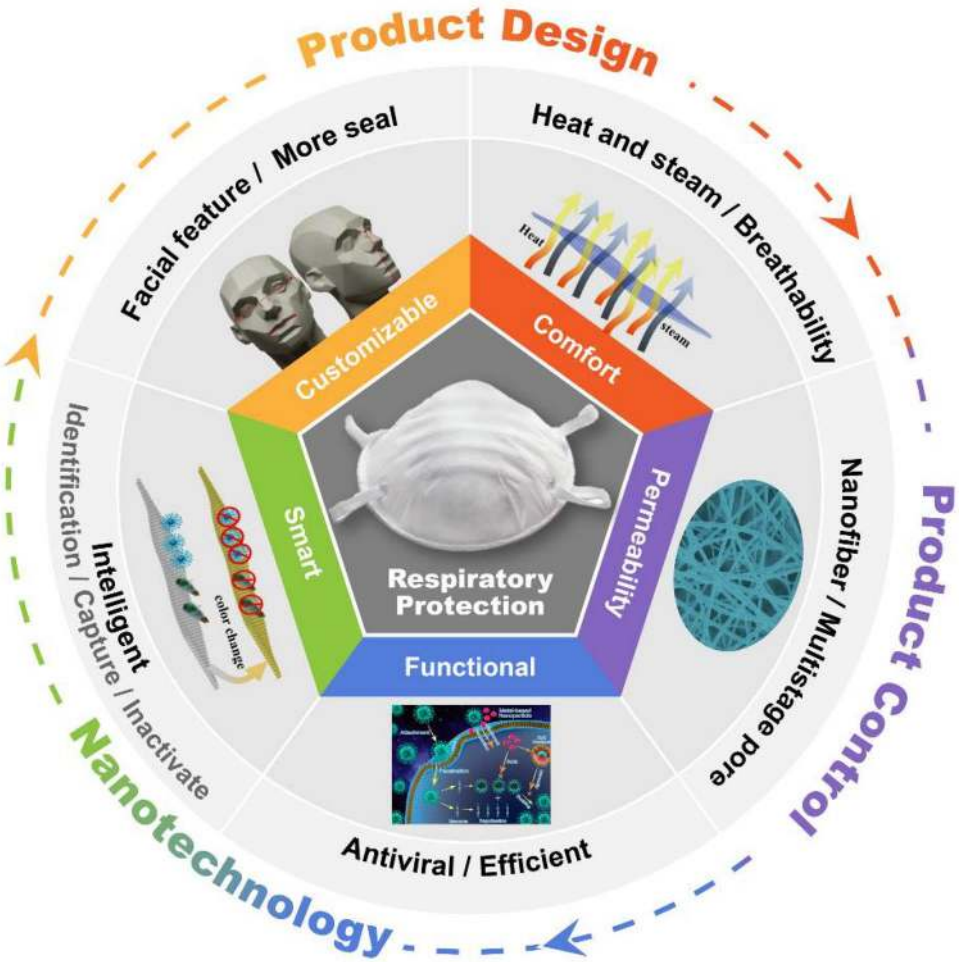

Fig. 11 Graphical expression of future development prospect of respiratory protection devices

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Compliance with Ethical Standards

Conflict of interest The authors declare that there is no financial and non-financial competing interest.

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