The outbreak of COVID-19 revealed the vulnerability of commercially available face masks. Without having antibacterial/antiviral activities, the current masks act only as filtering materials of the aerosols containing microorganisms. Meanwhile, in surgical masks, the viral and bacterial filtration highly depends on the electrostatic charges of masks. These electrostatic charges disappear after 8 h, which leads to a significant decline in filtration efficiency. Therefore, to enhance the masks’ protection performance, fabrication of innovative masks with more advanced functions is in urgent demand. This review summarizes the various functionalizing agents which can endow four important functions in the masks including i) boosting the antimicrobial and self-disinfectant characteristics via incorporating metal nanoparticles or photosensitizers, ii) increasing the self-cleaning by inserting superhydrophobic materials such as graphenes and alkyl silanes, iii) creating photo/electrothermal properties by forming graphene and metal thin films within the masks, and iv) incorporating triboelectric nanogenerators among the friction layers of masks to stabilize the electrostatic charges and facilitating the recharging of masks. The strategies for creating these properties toward the functionalized masks are discussed in detail. The effectiveness and limitation of each method in generating the desired properties are well-explained along with addressing the prospects for the future development of masks.

1. Introduction

The enormous impact of COVID-19 pandemic on the global economy and health has stimulated extensive researches including material-related ones to address the urgent issues associated with this highly transmittable disease. The origin of this new pandemic is a new type of coronavirus named as severe acute respiratory syndrome coronavirus 2 (SARS-CoV-2), which raises significant threat to human beings.[1,2] The high transmission rate of this virus and its strong resistance against various types of antiviral and disinfecting agents has led to a new dilemma worldwide.[3,4] In less than one year, almost all counties around the world have been infected by SARS-CoV-2. Some tough measures such as travel restrictions,[5] shutting down of schools and business and even the lockdown of the entire city[6] were introduced at the initial wave to prevent more spreading of this deadly virus; whereas the consequences remain as one of the largest disasters in human history.[7,8]

While several vaccines have been announced to be effective in preventing of this virus,[9–11] vaccination of the entire population worldwide requires a prolonged period of time or could be even impossible. Meanwhile, SARS-CoV-2 has constantly changed through mutation, thus creating new variants which are highly infectious with worse fatality rates and also potentially lowering the effectiveness of vaccination.[12] Multiple variants of coronavirus have been reported in several countries over the past months during this pandemic.[13] Therefore, protection of the respiratory system is the simplest and the most convenient strategy to avoid infection and to minimize viral spreading. New studies have shown that surgical face masks can effectively inhibit the transferring of infecting agents, bacteria, and viruses from the environment to the human body.[14,15] However, there are several significant limitations related to the common face masks such as nonreusability and lack of antibacterial and antiviral activities. Therefore, it is necessary to replace the mask with a new one after use for a short period particularly in high risk regions, which leads to the generation of an enormous amount of waste masks. On the one hand, the discarded masks may contain a high number of microorganisms and viruses that could be coronavirus hazards and increase the high risk of the secondary transmission of disease,[16] thereby raising the high demand for the safe disposal of the used masks. On the other hand, the worldwide consumption of face masks is over 200 million pieces per day,[17] which creates a huge amount
of plastic waste since the majority of face masks is based on nonwoven fabrics from non-biodegradable polypropylene (PP). Currently, most countries use incineration as a key method for the disposing of discarded masks, which, however, produces a high amount of toxic gases and increases the greenhouse effect due to the substantial amount of CO₂ released.[18,19] Therefore, it is in high demand to increase the efficiency, lifetime, and reusability of face masks for better protection and meanwhile minimizing the negative environmental impacts.

To reuse the commercially available surgical face masks, washing with detergents or decontamination with disinfectant agents has been attempted, which, however, can reduce the efficiencies of the mask. For instance, washing the N95 masks with ethanol can destroy the fibrous structure of the PP layer in the mask.[20] Decontamination of N95 masks using H₂O₂ vapor,[21] H₂O₂ plasma,[22] ozone,[23] heating at 85 °C under various humidity levels,[24,25] and dry heat pasteurization[26] have been proved as proper methods for mask disinfection. The remaining disinfectant agent even at a trace amount might cause toxic effects on the human body. Therefore, for long-term use, the disinfection of the masks using external agents is not a recommended method.[27] Furthermore, it has been reported that various decontamination methods can vanish the charge of the PP layer in face masks leading to a significant reduction in the filtration efficiencies. While recharging of the masks usually requires high-tech method, Hossein et al. reported a simple method by using 1 kV potential through a DC voltage generator for successfully recharging the decontaminated N95 masks.[28] However, all these methods for decontamination and recharging require special equipment and skills which limit their practical utilization, particularly in remote areas.

Based on what explained above, the functionalization and engineering of the face masks for improving their inherent efficiencies and reusability without external cleaning and disinfectant agents are crucial matter not only for urgent need currently but also for future pandemics. Functionalization of masks has been performed to endow the following properties in the mask: i) increasing the anti-microbial and self-disinfecting properties by incorporating well-known antimicrobial agents such as metal nanoparticles (Ag, CuO, ZnO, etc.) and photosensitizers, ii) improving the self-cleaning behavior of the masks by superhydrophobization of the mask surface via the incorporation of grapheines, alky silanes, and perfluorinated polymers, iii) increasing the photothermal and electrothermal property of the mask for generation of high local temperatures that can easily inactivate a broad spectrum of bacteria and viruses, and iv) increasing the long-term stability of the static charges of inner layer in the masks along with improving the rechargeability of masks by incorporating triboelectric nanogenerators (TENGs) between the friction layers of the masks.

In this review, we first provide a brief discussion about the interactions of SARS-CoV-2 with various surfaces and the lifetime of this virus on the different surfaces in response to various disinfectant agents. After introducing the common properties of the face masks commonly used nowadays, we provide a real-time and appropriate summary of research works related to face masks from both modification and application points of view. As far as we know, this is the first comprehensive review detailing and summarizing the functional modification of the masks, which addresses the urgent needs under the currently ongoing pandemic. The methods for the preparation of the functional masks have been explained in detail and various functions that affect the efficiencies of the modification method have been discussed. Furthermore, the impact of the functionalization method on the antiviral, antibacterial, self-cleaning, and self-sterilization of the masks have been discussed in detail. The findings summarized herein could provide guidance for the further exploration of the functionality of the face masks for a variety of applications.

2. Surface Stabilities and Decontamination of SARS-CoV-2

The SARS-CoV-2 is a spherical shape enveloped virus with the size of around 120 nm (Figure 1).[29] This virus is made of three main components: RNA genome, lipidbilayer membrane, and surface proteins. The surface proteins are including spike (S) glycoprotein, membrane (M) protein, and small envelope (E) protein. Better understanding about this virus and the role of each protein is beneficial to the selection of proper materials for inactivating the corresponding action. S protein is responsible for receptor binding and membrane fusion. The lipide membrane protects the RNA of the virus which then can be replicated after entering the cells. The most abundant surface protein is the M protein whose main role is to control the virus assembly.[30] Finally, E protein is the smallest surface protein that controls the virus assembly, envelope formation, and permeability of the membrane.[31]

It has been proved that the inanimate surface contact is one of the key routes of the indirect transmission of SARS-CoV-2.[32] The lifetime and stability of SARS-CoV-2 and other coronaviruses on different surfaces have been reviewed by several groups.[33,34] The stability of SARS-CoV-2 on surfaces is somehow similar to SARS-CoV-1.[35] Indeed, the SARS-CoV-2 remains viable on some surfaces such as plastic and stainless steel up to 72 h, whereas on the copper and cardboard surfaces no viable virus was detected after 4 and 24 h, respectively.[36,37] The surfaces were free of the virus for high-pressure laminate, rubber flooring, wood laminate floor, commercial carpet after 8 h, vinyl sheet after 12 h, acrylic surface and quartz surface after 30 h, and vinyl wall covering after 168 h.[37] The reason for the different lifetimes of viruses on various surfaces is related to the different interactions of each surface with the virus, leading to the different time periods for inactivation.

The possible mechanisms for inactivation of SARS-CoV-2 by antiviral drugs,[38] disinfectants,[39] and various surfaces[40,41] have been reviewed already. Alcohols (ethanol and isopropanol) kill and inactivate the coronavirus via dissolving the virus lipid membrane, damaging its RNA strain, and denaturation of its proteins probably through disrupting the intramolecular H-bondings.[39] Various oxidizing agents (peroxides, peracids, ozone, etc.) can deactivate the enveloped viruses via the oxidation of thiol groups in virus proteins and denaturation of proteins.[42–45] Similarly, iodophors can release iodine which can penetrate into the membrane and oxidize the proteins’ thiols.
and also damage the RNA of the virus. Therefore, tethering of the safe oxidizing agents on the surface of personal protection equipment (PPE) can be used as an appropriate approach for fabrication of antiviral PPEs. Various phenolic-based disinfectants (including essential oils) kill the viruses via damaging the membrane of the virus which leads to the leakage of the seepage of the intracellular components of the virus and denaturation of proteins. In general, detergents or surfactants are amphiphiles with similar structures to the lipid molecules in the lipid bilayer of the virus. Therefore, these surfactants can create strong interaction with lipids in the virus membrane and tear down the lipid membrane.\(^{[41,46]}\) Overall, all the surfaces have been categorized into three groups including natural surfaces, artificial surfaces, and biomimetic surfaces.\(^{[34,40,41]}\) Natural surfaces containing some natural herbs and natural extracts can damage the RNA of the virus, and also inhibit the construction of enzymes for virus replication. In the artificial surfaces, the inactivation mechanisms have been divided into three forms including direct disinfection, indirect disinfection, and receptor inactivation. Surfaces containing some materials such as silver and copper have direct antiviral properties by releasing low concentrations of Ag\(^+\), Cu\(^+\), and Cu\(^{2+}\) ions which can prevent the proliferation of the virus via inhibiting the activity of respiratory enzymes and obstructing the functions of virus’ RNA.\(^{[47]}\) For indirect inactivation, several mechanisms have been proposed. i) The surfaces producing heat, light, and free radicals by responding to an external trigger can inactivate the virus. For instance, nanoparticles of some metals such as Au, Cu, and Ag can generate the localized surface plasmon resonance upon visible illumination.\(^{[48]}\) ii) Some materials such as graphene\(^{[49]}\) and Au\(^{50}\) have photothermal properties which create high temperatures upon illumination with sunlight. The high temperature can inactivate various types of viruses including SARS-CoV-2.\(^{[51]}\) iii) The materials such as photosensitizers and semiconductors can produce free radicals which are the well-known agents for inactivating viruses and other microorganisms. iv) There is another group of antiviral nanomaterials (cerium oxide, tungsten oxide, etc.) that act by inducing the redox reactions between the surface with the virus.\(^{[52]}\) v) Some surfaces bear small molecules with the ability to capture the virus and passivation of its spikes receptors. Smith and Smith listed 77 small molecules with the ability to attach the S-protein of SARS-CoV-2 and inactivate it.\(^{[53]}\) Immobilization of these small molecules on the surface of masks can improve the antiviral properties of the masks.\(^{[54]}\) The biomimetic surfaces often play the role based on the self-cleaning strategy. Excellent progress has been reported on developing bioinspired superhydrophobic surfaces by mimicking nature.\(^{[55,56]}\)

As it is obvious from the above examples, nanotechnology can be utilized as a proper tool for fighting against SARS-CoV-2. Several review papers have been published on the possible roles of nanomaterials for combating the current pandemic.\(^{[57-59]}\) Indeed, the first vaccine that went to the clinical trials was an mRNA vaccine tethered on lipid nanoparticles.\(^{[60]}\) Improving the efficacy of PPE and fabrication of synergistic antiviral coatings and surfaces is still of critical importance in reducing the spreading of this virus. In the case of face masks, tethering of the above-mentioned disinfectants and nanomaterials on the surface of the masks can improve the antiviral properties of the surface and therefore, prevent the indirect spreading and transmitting of SARS-CoV-2.

### 3. Face Masks

Face masks are the simple protection tools for fighting pandemics by preventing the wide spreading of viruses and microorganisms, trapping them and in advanced cases inactivating the trapped viruses/bacteria. Various types of face masks that can be applied for protection against COVID-19 have been reviewed by several groups.\(^{[61-63]}\) Various types of commonly used face masks during the COVID-19 pandemic are depicted in Figure 2.

The compressed polyurethane (PU) foam mask generally has a 3D porous structure with the ability to block 99% of the pollen-sized particles, which is cost-effective and washable. However, it almost has no filtration effect against small-size microorganisms including bacteria and viruses. Cloth face masks are a kind of simple homemade masks fabricated from a piece of household fabrics including cotton, woven, felted, knitted, and so on.\(^{[64,65]}\) These masks are usually washable and can be applied several times. The filtration efficiency of these masks depends on the type and structure of the fabrics and also the number of utilized cloth layers for the mask. However, they offer weak filtration efficiencies for viruses.
Surgical face masks made from polypropylene (PP) are the most popular ones world-wide. The masks generally consist of a PP meltblown nonwoven sandwiched between two regular PP nonwoven fabrics. The central layer is the main layer for filtration and the role of the inner and outer layers are, respectively, for absorbing moisture and repelling the water. While a surgical mask is very effective in filtration of aerosols and large particles (>5 µm), it does not offer good filtration for very small particles including viruses. Additionally, these non-biodegradable PP masks are the main reason for plastic pollution during the current pandemic. Filtering facepiece respirators (FFRs) are a group of face masks with the ability to filter very small particles even as small as 20 nm in some cases. Various types of FFRs including N95, N99, KN95, P100, FFP2, and FFP3 are available and named according to different standards of different countries. The number usually shows the filtration efficiencies. For instance, N95 and N99 can filter, respectively, 95% and 99% of airborne particles. The N95 respirator, the most famous FFR during the COVID-19 pandemic, is known as an electret filter because it bears an electrocharged layer with the ability to trap microaerosol droplets, virions, and various microorganisms with sizes larger than 100 nm. The KN95 respirator is made of four layers including the outer/inner layers, a filter layer, and a cotton layer. While the efficiencies of N95 and KN95 have been reported to be somehow similar, but the filter layer of KN95 is around 8 times thinner than N95. The filtration effectiveness of 0.3 µm particles by FFP1, FFP2, and FFP3 are around 80%, 94%, and 99%, respectively. Practically, the filtration efficiency of FFP2 and FFP3 is almost equal to N95 and N99, respectively.

It is noteworthy to mention that the efficiency of the masks with the same name but fabricated by different companies could be different. Therefore, the performances and filtration efficiencies aforementioned should be considered as approximate values.

4. Modification of Masks

The various strategies that have been explored for the functionalization of masks are summarized in Table 1, in which the active effect is classified by the species along with modification methods. The goals of these strategies are to improve the reusability, lifetime, antimicrobial activity, and self-decontamination of the masks. In the following sections the descriptions regarding each strategy in detail are presented in terms of the type of the active species incorporated into the masks.

4.1. Metals and Salts

Various metals and salts, especially in their nanostates, have been reported as strong antimicrobial agents. The most well-developed antimicrobial metals for biomedical applications include silver, copper, and zinc. These nanomaterials are surface engineered by using specific nanoparticles (NPs) and nanowires (NWs) coated onto cotton fabrics, CuO-impregnated woven and non-woven fabrics, and Ag/ZnO-embedded cotton/polyester blend fabrics. Especially, there are new reports about the efficiency of metal nanoparticles for inactivating SARS-CoV-2 such as Ag NPs, copper, and zinc ions. Accordingly, these metals in various forms have been embedded in the structures of respiratory face masks to endow the masks with boosted antimicrobial/antiviral activity.

In the simplest strategy, the PP middle layer of surgical masks was coated with various types of salts (including NaCl, K2SO4, and KCl) in the presence of surfactants to provide antiviral activity. This coating enhanced the hydrophobicity of the PP layer which is helpful in the adsorption of viral aerosols. While bare PP filter showed no resistance against the penetration of H1N1 virus-containing aerosol (2.5–4 µm), coating with NaCl enhanced the filtration efficiency up to 85% with increasing the NaCl content (Figure 3b). The adsorbed viruses could be deactivated in a two-step process: i) adsorption of the viral aerosol on PP surface along with dissolving the salt in the aerosols, ii) gradual evaporation of water which induces supersaturation and then recrystallization of salt. Consequently, the walls of the cell hosting virus are damaged by increasing the osmotic pressure of the outside medium during the drying process of the aerosol. The hemagglutinin activity (HA), a criteria for in vitro virus stability, showed a reduction of around 8% for bare PP filter; whereas it was reduced by almost 100% for NaCl-coated PP filter (Figure 3c). Also, TEM images revealed morphological destruction of influenza virus by NaCl-coated PP, leading to a nonspherical shape. Similarly, the PP layers coated with NaCl, K2SO4, or KCl could inactivate both Gram-positive and Gram-negative bacterial aerosols in vitro upon salt recrystallization.

Silver as a strong antimicrobial agent was used in 2006 by Li et al. for the fabrication of antibacterial masks. In this report, the most hydrophobic outer surface of surgical masks was coated with composite nanoparticles composed of Al2O3, TiO2, and Ag(I). Incubation of the NPs-coated masks in bacterial medium for 48 h showed 100% inhibition in viable Escherichia coli and Staphylococcus aureus whereas for the pristine mask no inhibition was reported. Instead, around 25% and 50% increases in the viable counts were reported for E. coli and S. aureus, respectively. Additionally, the as-modified mask showed no skin inflammation, itchiness, and allergy on 20 volunteers who wore the mask. Similarly, simple soaking of entire face masks in a dispersion of starch-capped Ag NPs yielded functional face masks with strong antimicrobial efficiency. The size control of Ag NPs is critical to maintain the strong antibacterial efficiency. This is mainly due to the fact that the size must be sufficiently small to allow nanomaterials to cross the cell wall of bacteria, thereby inducing destructive effects on the cell wall and DNA. The OH groups of starch cover the cell wall of bacteria, thereby inducing destructive effects. The OH groups of starch cover the cell wall of bacteria, thereby inducing destructive effects.

The zone inhibition diameters for the modified mask after soaking in 50 and 100 ppm of Ag NPs were increased around 1.5 and 2.1 times for S. aureus and around 2.0 and 4.3 times for E. coli. However, since the Ag NPs are covered in the whole structure of this mask, evaluation of the cytotoxicity of the mask should be an important issue which, unfortunately, was ignored by the corresponding researchers.
Table 1. Strategies for the fabrication of functionalized masks with improved performance.

| Mask’s modification method | Active effect | Remarks of the modified mask | Ref. |
|----------------------------|---------------|-------------------------------|------|
| **Metals and salts**       |               |                               |      |
| Coating the PP layer with various types of salts (NaCl, K₂SO₄, and KCl) | Increasing effect of the salts on the osmotic pressure of aerosols of viruses | 1) Increasing the filtration efficiency 2) Inactivating Gram-positive and Gram-negative bacteria | [71, 72] |
| Coating the outermost hydrophobic surface of surgical masks with Al₂O₃/TiO₂/Ag(I) NPs | Biocidal effect of Ag(I) | 1) 100% inhibition of E. coli and S. aureus in 48 h 2) No skin inflammation, itchiness, and allergy on 20 volunteers | [73] |
| Dip coating the whole face mask by starch capped Ag NPs | Biocidal effect of Ag(I) | Increasing the zone inhibition diameters up to 2.1 and 4.3 times for S. aureus and E. coli, respectively | [74] |
| Developing new mask using PAN/Ag nanofibers composite membrane | Biocidal effect of Ag(I) | 1) High stability of Ag on the fabrics 2) Inactivation of Pseudomonas and Staphylococcus bacteria | [75] |
| Developing new mask using CuO-loaded PAN nanofibers | Biocidal effect of CuO | 1) High antibacterial activity against E. coli and B. subtilis 2) At high contents of CuO, showed cytotoxicity | [76] |
| Coating the surface of PP layer with shellac/CuNPs nanocomposite | 1) Photoactive and hydrophobic effect of shellac 2) Biocidal effect of Cu NPs 3) Plasmonic effect of Cu NPs | 1) Increase the WCA of the PP to 143° 2) Increase the T of mask to >70 °C under sun irradiation 3) Inactivation of E. coli (>99.99%) under sun irradiation | [77] |
| Developing new mask composed of PA66 layer embedded with Zn(II) ions | 1) Capturing the virus by PA66 2) Killing the virus by Zn(II) | 1) Higher washability than cotton 2) Higher virus capturing than PP 3) Around 2-log reduction in IAV and SARS-CoV-2 titers in 1 h | [78] |
| Dip coating of PP in Cu@ZIF-8 NWs dispersion | Biocidal effect of Cu(II) and Zn(II) | Keep the hydrophobicity of PP Improved filtration efficiency Highly biocompatible (cell viability >99% in 48 h) Inhibition of E. coli (>90%), S. mutans (>85%) and SARS-CoV-2 (55%) | [79] |
| **Photosensitizers**       |               |                               |      |
| Proposing utilizing photoactive conjugated polymers and oligomers in masks structure | Release of biocidal ROS | 100% inactivating of SARS-CoV-2 near-UV light irradiation | [80] |
| Grafting the cationic poly(DEAE) onto the cotton fibers following by tethering with anionic photosensitizers | Release of biocidal ROS | Kill >99.99% E. coli and L. innocua and inactivating of T7 bacteriophage virus under light exposure | [81] |
| Developing new masks using photocatalytic TiO₂ based filters | Release of biocidal ROS | Kill all E. coli in 1 min under UV light (365 nm) Applied for the fabrication of light sterilizable masks | [82] |
| **Graphenes**              |               |                               |      |
| Embedding GO-crosslinked by TAIC into the cotton fabrics | | Inhibition (>99%) against E. coli and B. subtilis No irritation to rabbit skin Complete inhibition against SARS-CoV-2 viral | [83, 84] |
| Embedding a layer of PVDF/GO on the PP layer | 1) Superhydrophobicity of PVDF 2) TENG rule of GO NPs | 1) Increase the hydrophobicity of the PP 2) Increased the charge on PP to 2.0 nC cm⁻² 3) Long-term charge retention (5 days) 4) Recovery electrostatic charges of mask by simple thumb pressing | [85] |
| Incorporation of rGO into the melt-blown nonwoven fabrics | High electrothermal effect of rGO | 1) Rise local T to 80 °C in 4 min at voltage 3 V 2) Rise local T to 72 °C under sunlight 3) Kill >99% E. coli in 15 min upon electrifying 4) No effect on air permeability and filtration efficiency | [86] |
| **Immobilization of LiG on the surface of surgical mask** | High hydrophobicity and photothermal activity of the laser-induced graphene | 1) Superhydrophobicity of the modified mask (WCA 140°) 2) 95% absorption of solar spectrum 3) Increasing the surface temperature of mask to 80 °C in 100 s | [87] |
| **Immobilization of LiG/Ag composite on the surface of N95 mask** | 1) Biocidal and plasmonic effect of Ag(I) 2) High hydrophobicity and photothermal activity of the laser-induced graphene | 1) Superhydrophobicity of the modified mask (WCA 140°) 2) 100% absorption of solar spectrum 3) Increasing the surface temperature of mask to 80 °C in 60 s | [88] |
| **Immobilization of LiG on the surface of surgical mask** | High hydrophobicity and photothermal activity of the laser-induced graphene | 1) Superhydrophobicity of the modified mask (WCA 150°) 2) Increasing the surface T of mask to 62 °C in 60 s in solar irradiation 3) Killing >99.99% of E. coli upon electrifying the mask upon solar irradiation | [89] |
By taking advantage of Ag NPs, Kharaghani et al. prepared polyacrylonitrile/silver (PAN/AgNPs) nanofibers composite membranes by dipping the PAN nanofibers in AgNO₃ solutions for developing washable antibacterial masks.[75] The silver was highly stabilized on the surface of PAN fibers due to the formation of very stable complexes with the chelating aromatic heterocycles generated in the PAN chain backbone. These chelating agents are produced upon PAN pyrolysis which can further be catalyzed by the presence of Ag ([Figure 4a]).[112] This chelation increased the stability of the Ag NPs on the fabrics so that the fabrics could be washed without reducing their efficiencies. The SEM and TEM showed the uniform distribution of Ag NPs (20 nm in diameter) on the surface of PAN nanofibers ([Figure 4b,c]). Increasing the number of cycles of the dip coating increased the Ag content and therefore, increased the antibacterial activity of the fabrics by releasing more silver into the medium. However, very high contents of Ag NPs could lead to the generation of some aggregates with less antibacterial efficiencies. On the other hand, the leaching-out of Ag NPs has always been the challenge for such modification. Nevertheless,
NPs could be slowly released from the nanofibers and gener-°cally with water contact angle (WCA) of 124° incorporated CuO NPs enhanced the hydrophilicity dramati-
two times higher than that of nanofiber mats of pure PAN. The
ability of nanofiber mats of PAN/CuO (1 wt%) were more than
thus facilitating the air flow among the fibers. The air perme-
increased the air permeability of the nanofiber mats due to
negligible effect on the elongation at break. The CuO NPs also
NPs improved the mechanical strength of the nanofibers with
addition of 0.25–1.0 wt% CuO NPs. The incorporated CuO
was around 141 nm which was increased to 161–197 nm by the
B. subtilis E. coli and Pseudomonas aeruginosa, proving the ant-
biotic activity against Sphingomonas and Staphylococcus bacteria.
Hashmi et al. prepared CuO-loaded PAN nanofibers by elec-
trospinning of a solution of PAN in DMF in the presence of
dispersed CuO NPs and applied for the fabrication of antimic-
robial breath masks.[86] The diameter of pure PAN nanofibers
was around 141 nm which was increased to 161–197 nm by the
addition of 0.25–1.0 wt% CuO NPs. The incorporated CuO
NPs improved the mechanical strength of the nanofibers with
negligible effect on the elongation at break. The CuO NPs also
increased the air permeability of the nanofiber mats due to
the increased porosity of dense PAN fibers caused by the NPs,
thus facilitating the air flow among the fibers. The air perme-
ability of nanofiber mats of PAN/CuO (1 wt%) were more than
two times higher than that of nanofiber mats of pure PAN. The
incorporated CuO NPs enhanced the hydrophilicity dramati-
cally with water contact angle (WCA) of 124° for pristine PAN
and zero degree for the PAN/CuO fibers. The incorporated CuO
NPs could be slowly released from the nanofibers and gener-
ated strong antibacterial activity against E. coli and B. subtilis.
However, high CuO content induced some toxicity in the masks. Indeed, NIH3T3 cell viability results showed the via-
bility of around 88%, 78%, 75%, 68%, and 59% for nanofiber
mats containing 0%, 0.25%, 0.5%, 0.75%, and 1.0 wt% CuO
NPs. In another report, coating a hybrid nanocomposite layer of
shellac/copper nanoparticles (CuNPs) on the surface of a non-
woven surgical mask using a microfluidic spray device affords
a photoactive antiviral mask (PAM) with high hydrophobicity,
self-cleaning, and reusable features (Figure 5a–d).[75] The simple
process for this modification is depicted in Figure 5b. Shellac
is a natural hydrophobic polyester with extensive application
in bioadhesive and biocompatible coating materials,[113,114] while
the nanosized copper particles are excellent antibacterial mate-
rals.[115] The SEM images (Figure 5e) clearly showed a homo-
genous coating on PP fibers by shellac/Cu nanoparticle layer.
The WCA of the pristine nonwoven fabrics in the mask was
around 111°, however, after 1 h the water droplet adsorbed into
the fabric. By contrast, for the modified mask the WCA increased
to 143° and the droplets did not adsorb onto the mask even after
1 h (Figure 5f). Shellac is also a well-known photoinitiator due
to its adsorbing ability toward UV–vis light; and in parallel,
CuNPs have robust interaction with light thanks to their surface
plasmon resonance excitation. Accordingly, solar illumination
increased the surface temperature of the PAM mask to around
70 °C (Figure 5g) and therefore, could inactivate the SARS-CoV-2
facilely. Additionally, this process is reproducible, implying the
reusability of the mask after simple self-cleaning and steriliza-
tion upon solar irradiation. Also, the coating by the nanocom-
posite layer showed a negligible effect on the filtration efficiency
of the mask. The modified photoactive mask showed strong
antibacterial activity (>99.99% for E. coli) upon solar irradiation.

Gopal et al. proposed the application of Zn-embedded poly-
amide 6.6 (PA66) for the fabrication of face masks with the
ability to capture and then inactivate SARS-CoV-2 and influen-
za A virus (IAV) H1N1.[79] Comparison of the amounts of the virus
captured by cotton, PP and PA66 after impregnation in the virus
medium showed that liquid retention and virus retention on PP
has the lowest amount due to its hydrophobicity. On contrary,
the retention on cotton and PA66 was higher due to the hydro-
phobicity of these fabrics. However, washing the textiles with
between-80 (without inactivating the virus) showed that around
90% and 60% of the virus could be removed from the PA66
and cotton, respectively. This clearly indicated the higher washability
of PA66 than cotton for the remaining antiviral effect. Since
Zn(II) salts can inactivate viruses,[116] after capturing the viruses
by PA66 mask, viral deactivation can be induced by Zn(II). One
of the significant advantages of Zn(II) over Cu(II) is the less tox-
icity of Zn(II) against normal cells. Incubation of the PA66 fab-
rics bearing Zn(II) ions with IAV and SARS-CoV-2 led to around
2-log of reduction of viruses in titer tests for 1 h.

Kumar et al. tried to combine the advantages of both Zn(II)
and Cu(II) and incorporate them simultaneously into the PP-
based MERV15 filter material (three-layer) to provide reusable
antimicrobial masks.[9] Specifically, thin copper@ZIF-8 core–
shell nanowires (Cu@ZIF-8 NWs) with average diameter 80 nm
(Figure 6a,b) were fabricated using biocompatible pluronics F-127
copolymer as a stabilizing agent and adhered to the PP layer of
face mask (Figure 6c).[9] Immobilization of the Cu@ZIF-8 NWs
onto the PP layer was performed by simple dip-coating of the
PP layer in dispersions of NWs in ethanol. This modification
did not change the hydrophobic character of PP. However, it
improved the filtration efficiency of the mask (Figure 6d). On
contrary, treating PP with pure ethanol declined the filtration
efficiency dramatically, which was probably due to the loss of

![Figure 4](www.advancedsciencenews.com)

**Figure 4.** a) Pyrolysis of PAN fibers in the presence of Ag, which leads to the generation of chelating agents in the PAN structure. Reproduced with permission.[112] Copyright 2003, American Chemical Society. b) SEM and c) TEM images of hybrid PAN/Ag nanofibers. Reproduced with permission.[75] Copyright 2018, MDPI.
surface charges of the PP layer, as reported by others as well.\[117\] Coating the Cu NWs with a ZIF layer improved the biocompatibility and reduce the cytotoxicity of copper due to the slower release rate of Cu ions. Additionally, the antibacterial activity of hybrid Cu@ZIF-8 NWs was much stronger than that of Cu NWs or ZIF-8 alone against \textit{E. coli} and \textit{S. mutans} (Figure 6e). The reason was related to the slow degradation of the NWs and co-release of Zn(II) and Cu(II) ions which can kill the bacteria. Furthermore, the antiviral activity against SARS-CoV-2 using virus-infected Vero E6 cells showed around 55% inhibition of virus replication in 48 h with cell viability of 99% (Figure 6f,g).

In summary, the incorporation of selected metal-based NPs and water-soluble salts can endow the masks with high antimicrobial activity. However, there are some challenges that need to take into consideration for practical applications. i) The water-soluble salts can easily be washed away from the mask and thereby the efficiency of the mask reduce dramatically. ii) Leaching out of metal NPs can endow allergy or other side effects on the human body. Therefore, a wide-range evaluation of the toxicity of the active components embedded in the masks is essential. Additionally, there are some other types of antimicrobial metal-based NPs reported, such as Fe,\[118\] Au,\[119\] Mg,\[120\] and the feasibility of those NPs for rendering the masks antimicrobial and antiviral should be investigated. Moreover, it is worthwhile identifying proper carriers for metal NP, like micro- or mesoporous materials, to minimize the leaching effect.

4.2. Photosensitizers

Photosensitizers are groups of organic/inorganic compounds that can capture the energy of the light and transfer it to the
surrounding oxygen to generate extremely reactive oxygen species (ROS).[121,122] The produced ROS can kill all microorganisms in a short time.[123] Therefore, ROS-generating materials have been incorporated into textiles and fabrics for improving the antimicrobial properties of these materials. For instance, conjugation of 3,3′,4,4′-benzophenone tetracarboxylic acid photosensitizer to cotton fabrics enabled 99.99% inhibition of *E. coli* and *S. aureus* under UV light exposure.[124] Similarly, grafting of photoactive anthraquinone-2-carboxylic acid onto the silk fibroin/cellulose acetate blend nanofibrous membranes showed 99.9999% contact-killing of *E. coli* under UVA irradiation.[125]

There are several reports about the incorporation of ROS generators in the face masks to capture and inactivate the bacteria and viruses during breathing, thereby preventing lung infection. Monge et al. also incorporated the photoactive conjugated polymers and oligomers into the masks and other PPEs as strong materials for the inactivation of SARS-CoV-2.[80] Accordingly, three oligomeric phenylene ethynlenes and two conjugated polymers (see Figure 7) were examined. By incubation of oligomers and polymers with SARS-CoV-2 and exposing the medium to near UV (300–400 nm) or vis (420 nm) light, the infection of SARS-CoV-2 on Vero cells was reduced quickly and effectively (Figure 7). Hydrophobic and electrostatic interactions between ionic conjugated polymers and oligomers with SARS-CoV-2 spike protein were the main reason for antiviral activities. Indeed, these interactions bind the virus to the material which then upon light irradiation generates ROS, leading to the rapid degradation of the virus. Oligomers 1 and 3 and polymer 5 showed the most powerful antiviral activity with complete inhibition in ≈20,10, and 60 min, respectively. It is worth mentioning here that despite the strong inherent antibacterial activity of polymeric quaternary ammonium 4[126] it showed no activity against SARS-CoV-2 on dark condition. Therefore, using conventional quaternary antibacterial materials for deactivating SARS-CoV-2 is unlikely appropriate.

Tang et al. immobilized the anionic photosensitizers onto the cationic cotton cloth to fabricate a daylight-induced antibacterial and antiviral cloth as a face mask.[81] The cationic cotton

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**Figure 6.** TEM images of a) Cu NWs and b) Cu@ZIF-8 NWs. c) SEM image of fibers of face mask coated by dip coating in 1 mg mL⁻¹ dispersion of Cu@ZIF-8 NWs. d) Filtration efficiency of the face masks before and after functionalization with Cu@ZIF-8 NWs. e) The antibacterial performance of Cu NWs, ZIF-8, and Cu@ZIF-8 NWs. f) Toxicity of Cu@ZIF-8 NWs and Remdesivir against Vero E6 cells, and g) antiviral efficiency of Cu@ZIF-8 NWs and Remdesivir at 24 and 48 h postinfection. Reproduced with permission.[79] Copyright 2020, Wiley.
fabrics were prepared by surface grafting of cotton fabrics with 2-diehtylaminoethyl chloride (DEAE-Cl) in alkaline condition. The resulting cationic fabric was postfunctionalized via electrostatic interactions with anionic photosensitizers (Figure 8a) which can release ROS under light exposure. Functionalization of cotton fabrics by polyDEAE along with photosensitizers (Rose Bengal, RB & sodium 2-anthraquinone, 2-AQS), without having any impact on the morphology of the fabrics (Figure 8b–e), improved the antibacterial efficiency dramatically. While pristine cotton fabrics showed no biocidal activity, the inhibition rate against *E. coli* and *L. innocua* for cotton@polyDEAE were around 98% and 86%, respectively, in 30 min; and further increased to >99.99% (under light exposure) for both bacteria after incorporation of photosensitizers. However, the biocidal activity was severely reduced to almost 0% in dark condition. Furthermore, the antiviral evaluation against T7 bacteriophage (a model virus with even higher ROS resistance than coronavirus) showed no activity for pristine cotton and cotton@polyDEAE whereas the photosensitizers-bearing fabrics showed strong ability in inactivating T7 bacteriophage (Figure 8g). Importantly, the modified fabrics were washable and after three times washing and 7 days exposing to light only negligible reduction in the biocidal performance was observed. The findings from the work above demonstrated that simply cationic modification of fabrics, via grafting quaternary ammonium groups, is not sufficient to render the fabric antiviral. Further modification of such conventional disinfectant is essential for enhancing the performance.

**TiO**₂ is well-known for its photoactive properties via releasing ROS upon UV irradiation[127,128] with a strong ability to inactivate various viruses including SARS-CoV-2 as reported very recently.[129,130] Horváth et al. prepared photocatalytic **TiO**₂ nanowires (**TiO**₂NWs)-based filters for the construction of cost-effective and reusable masks with antimicrobial properties (Figure 9).[82] **TiO**₂NWs have high processability and can produce freestanding and flexible films (Figure 9c) without leaching nanowires under normal flow conditions.[131] The obtained textile showed strong antibacterial activity against
E. coli under UV light (365 nm) and almost all the bacteria were inactivated in 1 min whereas the control using Teflon filter under the same UV irradiation showed weak antibacterial properties (Figure 9d). This textile could be applied for the fabrication of light sterilizable face masks (Figure 9e,f) with the ability to reuse more than 1000 times.

Overall, while photosensitizers are shown to be effective agents for endowing the masks with antimicrobial and self-sterilizing properties, they lose their efficacies in the absence of light. Therefore, in cloudy weather, during the daytime with less sun illumination, and in the areas with less sun irradiation, the effectiveness of the masks containing photosensitizers will be lowered substantially or even lost completely at extreme conditions. Therefore, incorporating compounds such as endoperoxides and phenalenone-based photosensitizers that can release ROS even under dark conditions can be considered as a proper solution to tackle this problem. On the other hand, the results on the antiviral performance of those photosensitizers are rather limited. Particular attention should be paid to the antiviral activities against coronavirus in future research.

4.3. Graphenes

Graphene-based materials have been used extensively in biomedical applications. Especially after the outbreak of the SARS-CoV-2 pandemic there have many reports on utilizing graphene-based materials for fighting against this virus.
including some related to the use of graphenes in face masks. The key and unique properties that graphenes can endow in the masks include i) superhydrophobicity of graphenes increases the wetting resistance of the mask by aerosols containing viruses and bacteria and enhances the self-cleaning of the masks, ii) excellent electrothermal behavior of graphenes can create local high temperatures which can easily inactivate the microorganisms, and iii) inherent antimicrobial properties of the graphene-based nanomaterials.

Inserting the graphenes into the mask structures is often performed via the following strategies. i) Fabrication of some paste or inks of graphenes, which are then spread on the layer of mask. The properties of the layer can be tuned by adjusting the composition of the paste/ink mixture. The addition of other components to the paste has been attempted to create hybrid materials. ii) In situ generation of graphenes on the surface of masks by well-established techniques such as laser-induced forward transfer (LIFT).

Zhao et al. immobilized graphene oxide (GO) onto the cotton fabrics by three different methods to render the fabrics antibacterial and antiviral for fabrication of face masks.\[83,84\] The 1st method involves the filtration of aqueous GO suspension through the cotton fabrics. Therefore, GO particles are adhered to the fabrics by strong van der Waals and H-bonding interactions. For the other two methods, the fabrics were first soaked in an ethanol solution of triallyl isocyanurate (TAIC, a radical crosslinker) and then applied for the filtration of GO suspension. Subsequent crosslinking polymerization of TAIC by γ-irradiation (the 2nd method) or thermal polymerization (3rd method) improved the stability of GO on the fabrics. All the GO-modified fabrics showed antibacterial inhibitions >99\% against *E. coli* and *B. subtilis*. However, washing the fabrics removed the GO from the fabric made by the 3rd method; whereas the GO remained adhered to fabrics over the 1st and 2nd methods. Indeed, the incorporation of low polar TAIC reduces the interaction between GO with fabrics. However, γ-irradiation can generate radicals on all components including GO and cotton by breaking the σ linkages. The coupling of generated radicals can stabilize the GO on the surface of fabrics. Furthermore, the animal tests showed no irritation to rabbit skin after 3 days.\[83\] Later, evaluation of the antiviral efficiencies showed nearly complete inhibition against SARS-CoV-2 viral.\[84\]

The N95 masks are multilayers in which the middle layer of PP, prepared usually via melt-blown extrusion, has electrostatic charges that attract the viruses and help to improve the filtration efficiencies over 95\%. However, these electrostatic charges

**Figure 9.** a) SEM image titanate nanowires as the precursors for TiO₂ NWs. b) The scale up production of titanate nanowires. c) A fabricated filter paper from TiO₂ NWs after spreading of titanate nanowires and calcination thermal treatment. d) Comparison of the bacterial inhibition performance of TiO₂NWs filter with the control Teflon filter. e) Construction of a mask prototype by connecting the TiO₂NWs filter paper to a 3D-printed plastic frame. f) Decontamination of the mask by UV irradiation. Reproduced with permission.\[82\] Copyright 2020, Wiley.
often disappear after around 8 h exposure to the environmental conditions, which, therefore, reduce the efficiencies of N95 masks remarkably. Incorporation of hydrophobic TENGs into the membranes, films, and fabrics have been proposed as a reliable method for increasing the lifetime of the electrostatic charges. For instance, Lv et al. prepared a single-electrode TENG using a hydrophobic ionic liquid gel which was stable under different environmental conditions for 3 months with humidity up to 80%. Figerez et al. embedded the GO NPs in the friction layers of masks which acted as a TENG with high electrostatic charge retention capacity and excellent rechargeability even at humid medium. Specifically, the PP layer in the N95 mask was simply coated by an ink paste composed of polyvinylidene fluoride (PVDF) and GO in isopropanol to improve the triboelectric voltage and charge of the PP layer. The high hydrophobicity of PVDF in the casting ink increased the WCA from 103° for pristine PP to 133° for the modified PP. Applying the pressure with the thumb pressing generated the voltages of around 7 and 17 V and the charges of 1.5 and 2.0 nC cm⁻² on the pristine and modified PP monolayers, respectively, with the charge retention periods up to 2 and 5 days. The modified PP layer was sandwiched between cotton and nylon fabrics to assemble a three-layer N95 mask. This trilayer mask can be readily recharged by simple mechanical movements such as hand-bending or sliding one over the other. Accordingly, the effective lifetime of the N95 mask by this strategy could be enhanced significantly. In another report, graphene was used as a local heat generator for disinfection to provide reusable self-sterilization masks. The simple process of fabricating electrothermal graphene filters and embedding them into the mask structure is depicted in Figure 10a–c. In the first step, a patterned flexible conductive cloth tape, as interdigital electrodes, was attached to the surface of a filter layer composed of melt-blown nonwoven fabrics (MNF). Then, the graphene-modified MNF (mod-MNF) was produced by coating a graphene layer (graphene ink = reduced GO + silicone modified acrylic resin + amino resin + polyvinylpyrrolidone + water) with high electrical and thermal conductivity onto the MNF. The electrothermal/photothermal behavior of the mod-MNF is depicted in Figure 10d. By increasing the applied voltage to the electrodes, the temperature was raised to 80 °C at 3 V in 4 min. Also, irradiation by the simulated sunlight increased the temperature to around 72 °C. The elevated temperature could kill the E. coli bacterium with the efficiencies of 95% and 99.8% by electrifying for 5 and 15 min, respectively, indicating strong self-sterilization (Figure 10e). Furthermore, the graphene-modified masks showed the air permeability and filtration efficiency similar to the unmodified masks. The performance of the mask remained unchanged after folding/unfolding 200 times, implying the high durability of the masks. Using laser to convert and pattern carbon precursors (e.g., polyimide, SPEEK, and Bakelite) directly into graphene (called laser-induced graphene, LIG) has proved as a scalable and cost-effective method for fabricating functional graphene.
Figure 11. a) The fourth-generation dual-mode LIFT to continues-LIFT transfer of graphene onto a second polyimide followed by a then pulse-LIFT transfer of graphene onto the mask surface. b) Description for the simple scale up of this strategy via roll-to-roll production of a graphene-coated mask. SEM image of c) pristine nonwoven fibers and d) graphene-coated nonwoven fibers. e) Optical absorption behavior of pristine and graphene-coated masks. f) The temperature of the surface of pristine and graphene-coated masks in response to solar illumination. Reproduced with permission. Copyright 2020, American Chemical Society.
By adjusting the processing conditions, a superhydrophobic graphene can be obtained.\textsuperscript{[141]} Additionally, the LIFT graphene has a strong photothermal activity which makes it a powerful antibacterial agent.\textsuperscript{[144]} Accordingly, a dual-mode LIFT process was reported by Zhong et al. for tethering a graphene layer on the surface of commercial surgical masks to provide superhydrophobic and photothermal porous layers.\textsuperscript{[183]} The schematic process for the modification is presented in Figure 11a,b. The SEM images (Figure 11c,d) clearly showed the smooth microfibers for the pristine mask and the appearance of nanostructured flakes attached to the microfibers. The modified mask with a black appearance was superhydrophobic (CA 140°) so that the water droplet could move freely on the graphene-coated surfaces of mask without wetting the mask surface. Study on the photothermal performance of the mask showed that the pristine mask weakly absorbed the solar spectrum whereas the graphene-coated masks adsorbed over 95% of the solar spectrum in the range of 300–2500 nm (Figure 11e). Accordingly, the solar light irradiation of the masks increased the temperature of the pristine mask to 45 °C in 5 min whereas the temperature of the modified one was increased to 70 °C in 50 s and further increased to 80 °C after 100 s (Figure 11f).

In the extension of the previous work, Zhong et al. deposited Ag NPs along with graphene onto N95 masks by LIFT strategy to provide a plasmonic photothermal and superhydrophobic layer on the mask with highly improved antimicrobial protection.\textsuperscript{[186]} The methods for this immobilization are depicted in Figure 12a,b. The first method (M1) involves the depositing of only Ag NPs whereas in the second method (M2) a layer of Ag NPs and graphene are simultaneously deposited on the N95 surface. Ag NPs create the plasmonic effect and antimicrobial effect whereas the incorporated graphene further improves the photothermal property and hydrophobicity of the modified mask. The plasmonic effects of M1 and M2 (Figure 12c) were much higher than pristine surfaces. Also, the WCA for the pristine mask was 68° whereas co-immobilization with graphene endows strong hydrophobicity to the surface (140°). Visible light irradiation showed that after 5 min the temperature of the surface of pristine and M1 increased slightly to less than 40 °C whereas for M2 temperature increased to 60 °C in 10 s and further reached to 80 °C in 1 min (Figure 12e). Both elevated temperature and superhydrophobicity are foreseen in the modified mask with specifically designed unique features, such as high superhydrophobicity, high photothermal activity, and biocompatibility.

Moreover, for the commercial N95 masks,\textsuperscript{[145]} the photothermal performance of the mask showed that the mask temperature increased to 80 °C after 100 s. While no antiviral study was performed using LIG mask, however, high temperature generated upon solar irradiation has been proved promising for inactivating the SARS-CoV-2 virus.\textsuperscript{[89]}

4.4. Miscellaneous Other Methods

Several other methods have also been explored or adopted by researchers for endowing some especial properties in the mask structure such as coating the surface of the mask with alkylsilane groups to improve the hydrophobicity of the polyurethane masks,\textsuperscript{[90]} by biocide agents to increase the antimicrobial activity,\textsuperscript{[92,93]} or by boron nitride\textsuperscript{[94]} and copper metal\textsuperscript{[95]} as excellent thermal conductive materials.

Ray et al. improved the hydrophobicity of the masks by coating a monolayer of highly hydrophobic hexadecyltrimethoxysilane (HDTMS) on the surface of masks.\textsuperscript{[91]} The face mask made from compressed-polyurethane typically has a microporous structure with the ability to block 99% of the particles of pollen size and can be reused easily after washing. However, its high hydrophilicity reduces its efficiency significantly after it becomes wet. To address this problem, the hydrophobization of its surface was conducted via a two-step silylation, i.e., first by the hydrolysis of tetraethyl orthosilicate (TEOS) on its surface, followed by coating with a monolayer of HDTMS.\textsuperscript{[91]} The WCA of the pristine mask was 85° which, however, became zero after 15 min when the water droplet was completely absorbed by the mask. On the other hand, the WCA for the modified mask was increased to 132° which remained unchanged after 15 min, indicating stable hydrophobicity of the surface. Soaking the modified mask in water and squeezing the mask samples showed almost no decrease in the Si content indicating the strong connection of the Si layer to the mask surface with guarantee its reusability after washing. Martí et al. modified the surface of nonwoven face mask filter
by dip coating in an ethanol solution of 0.1% benzalkonium chloride (BAK) to create antibacterial property in the mask surface along with capability for the inactivation of SARS-CoV-2. This coating did not induce a detrimental effect on the porous morphology of the fibrous nonwoven mask. Also, the modified mask showed strong antiviral activity with almost 100% viral inhibition in 1 min against phage ph 6 (a viral model of SARS-CoV-2). On the other hand, the untreated mask and the mask treated only with ethanol showed no antiviral activity. Furthermore, the BAK-modified mask showed strong inhibition activity against methicillin-resistant S. aureus (MRSA) and S. epidermidis (MRSE) bacteria. Despite this strategy appears to be facile, without the results on biocompatibility, it is still doubtful whether this modified mask is feasible for practical applications since the BAK can be readily leached out of the surface of the mask by moisture, potentially leading to skin and lung contamination upon contacting with face and breathing.

In another safer approach, the extracts of licorice roots as bio-based antiviral agents were embedded into the mask structure, while the extracts already demonstrated powerful antiviral activities against various viruses including RSV, HIV, and SARS-CoV. Practically, electrospinning of an aqueous solution of polyvinyl alcohol (PVA) containing licorice roots extracts was used to prepare nanofibrous membrane as the active layers of the mask. Air permeability and breathability of the masks could easily be controlled by tuning the size of the nanofibers. Although this method appears to be very safe and effective for the fabrication of bio-based antiviral masks, no antimicrobial studies were reported by the authors.

The weak heat diffusion efficiency of the PP layer in masks creates an unpleasant sweltering sense while wearing. Accordingly, Xiong et al. developed hexagonal boron nitride (h-BN)/PP nanocomposite fibrous membranes to fabricate face masks with high comfortability and antibacterial activity. The fabrication
included i) plasmas bombardment of h-BN NPs to create OH groups on the NPs' surface followed by functionalization with quaternary ammonium salts (QAC) through reaction with 3-(trimethoxysilyl)-propyl dimethyloctadecyl ammonium chloride, ii) the stabilization of the obtained QAC@h-BN NPs by mixing with an aqueous solution of sodium alginate, and iii) soaking the homemade PP ultrafine fiber nonwovens (diameter 1–4 \( \mu \text{m} \)) in the stabilized QAC@h-BN NPs dispersion and post-crosslinking by Ca(II) ions. The QAC@h-BN-modified PP layer was then sandwiched between an internal layer (a hydrophilic nonwoven) and an external layer (hydrophobic PP nonwoven) to assemble the mask (Figure 15a). The content of the immobilized NPs layer could be easily controlled by changing the concentration of the suspension mixture. The filtration efficiency for commercial PP (diameter 4–10 \( \mu \text{m} \)) were around 92% which was increased to 94% for the homemade PP ultrafine fiber nonwovens and further increased to >99% after treating with QAC@h-BN NPs. At the same time, the thermal conductivity of PP was 0.12 W m\(^{-1}\) K\(^{-1}\) which by coating with QAC@h-BN NPs increased to 0.88 W m\(^{-1}\) K\(^{-1}\) with almost no change during five

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**Figure 13.** a) Immobilization GNEC film on the Si substrate using cyclotron resonance (ECR) sputtering system. b) Embedding of the GNEC into the mask structure i) vertically deposited graphene nanosheets with thickness 70 nm, ii) exfoliating the GNEC film with high-frequency vibration, iii) ultrasonic-extrusion (40 kHz and 600 W) for homogeneous distribution of GNEC thin layer between the melt-blown fibers, and iv) the fabricated GNEC mask. c) Photothermal activity of pristine and GNEC mask for 200 s solar irradiation. Reproduced with permission.[90] Copyright 2020, Springer.
times recycling (Figure 15b). The SEM images clearly showed the connection of the fibers by the NPs pastes (Figure 15c). While the unmodified PP layer showed almost no antibacterial activity, the QAC@h-BN/PP layer could kill >99% *E. coli* and 96% *S. aureus* (Figure 15d).

In another advanced strategy, a hybrid and reusable Cu/PAN-based filter composed of three layers was developed for potential application in face masks.[95] The three layers are shown in Figure 16b,c: i) the air filtration layer, made by the electrospinning of PAN solution in DMF, for the removal of airborne pollutants and particulate matter (PM), bacteria, or viruses from breathing stream, ii) the heating layer, made by electroplating of Cu on the PAN nanofiber mat, responsible for the production of high heat for deactivation of bacterial and virus particles, and iii) the thermal insulation layer made of polytetrafluoroethylene for preventing the heat from transferring to the other side of the filter and avoiding the burning of the human skin. This three-layer filter could be simply embedded into the structure of face masks to generate high local temperatures in response to weak voltages to kill the microorganisms (Figure 16d). The temperature increment responding to the voltage was directly related to the copper content which could be adjusted by the electroplating time. Exposing the 2 V voltage to the heating layer for 60 s, the temperatures were increased to 52, 100, and 133 °C for the samples with electroplating times 15, 30, and 60 s, respectively. Also, as depicted in Figure 16e,f increasing the applied voltage increased the temperature. The generated heat by the Cu microfiber mat could kill all the *E. coli* bacteria. Furthermore, the temperature and time required for deactivation of some viruses such as mouse hepatitis virus,[149] porcine epidemic diarrhea virus,[150] and SARS-CoV were below 60 °C and <30 min, suggesting the effectiveness of this filter under relatively moderate conditions.

Wang et al. prepared a rechargeable PVA-based mask with durable charge-retention even under high humid conditions.[96] The final mask was self-assembled by sandwiching the PVA fibers as the inner layer between two PP on the outer layers. The entire system acts as a TENG. Indeed, the PVA layer spontaneously forms H-bonding with H2O molecules exhaled by the human body and fixes the water molecules which, therefore, increases the triboelectricity. This mask easily is rechargeable by hand touching. Additionally, friction between PVA and PP layer during breathing process can generate contact-charge and therefore, the fixed water molecules on PVA contribute to triboelectrification due to its high electropositivity. The overall result is the increase in the charge quantity of the medical mask. Compared to the PP-based TENG system, the performance of PVA-based TENG could be further enhanced by increasing the medium humidity. By increasing the humidity from 15% to 95%, the short-circuit current ($I_{sc}$) and open-circuit voltage ($V_{oc}$) were increased from...
14.4 µA and 220 V to 46.6 µA and 800 V, respectively, i.e., ≈26 times higher than those for PP TENG at 95% humidity. Therefore, despite the lack of antiviral results, this unique mask made from commodity polymers has good potential to prevent viral infection even in high-humidity environments.

5. Conclusion and Outlook

The fragility of the current face masks against COVID-19 highlighted the urgent demand for developing advanced and functionalized masks in the current or even postpandemics. The conventional masks only act as filtrating materials or barriers without deactivating viruses and bacteria. Consequently, the masks might become the sources for spreading viruses or microorganisms after disposal. Therefore, safe discarding methods are required to eliminate the spreading of this contaminated source. The most reliable method for discarding these masks is incineration. However, due to the production of over 250 000 tons of mask waste per day,[62] incineration generates a massive amount of toxic gases and CO₂, which raises pressing environmental concerns including the increase of greenhouse gases in the atmosphere. Accordingly, fabrication and development of functionalized masks with reusability, self-sterilization, self-cleaning, antiviral, and antibacterial properties is in high demand to not only provide better protection against the pandemic diseases but also benefit the environment by reducing the excessive consumption of mask.

The addition of inherently antimicrobial agents such as metals (Ag, Cu, and Zn) and some types of essential oils has been proved as a versatile tool to boost the antiviral and antibacterial properties of the masks. The antimicrobial agents based on metal nanoparticles or ions rely on their steady and prolonged release from substrates (e.g., masks), followed by diffusing into the microorganism and destroying its DNA structure for deactivation. However, some types of metal ions such as Cu(II) and Zn(II) can create high cytotoxicity in high content upon contact with skin. Therefore, adjusting the content of metal ions at appropriate levels and proper fixation onto the mask to avoid the burst release is essential to reduce the side effects. On the other hand, the compounds releasing ROS as powerful antimicrobial agents can be fixed on the surface of mask layers by either covalent bonding or multi-electrostatic interactions. The release of ROS is often triggered by light irradiations. While these masks are highly efficient in daylight conditions, maintaining their effectiveness in dark environment is still challenging due to the failure or inability to release ROS. Therefore, further research on the incorporation of dark-active...
ROS releasing compounds into the structure of the masks is required to provide a proper solution for this issue. Many of the microorganisms can be deactivated upon heating. Indeed, the SARS-CoV-2 can be deactivated at 56 °C in 15 min.\textsuperscript{[151,152]} Therefore, the addition of various agents to the masks that can create high local temperatures was introduced by several researchers. Among them, graphene is one of the best candidates since it not only possesses high electrothermal and photothermal properties but also can endow the masks with self-cleaning function due to its superhydrophobicity. The emerging technologies such as laser-induced forward transfer have been adopted for scaling-up the surface coating of the masks with thin graphene layers. Upon applying low voltages (<3 V) or sun illumination the temperature of the graphene layer can increase rapidly even to over 100 °C, which is far beyond the level required for inactivating various microorganisms or viruses including SARS-CoV-2. Furthermore, a combination of other agents such as Ag or PVDF can further improve the antibacterial behavior and hydrophobicity of graphene-incorporated layers. However, Canada healthcare in a preliminary assessment has found that graphene nanoparticles can be inhaled by the mask wearers and therefore, create serious health risks, especially on lung.\textsuperscript{[153]}

Another aspect that affects the performance of the surgical and N95 masks especially regarding the microorganism filtrations is the electrostatic charge that can adsorb or capture the microbes, thus inhibiting their transmittance to our breathing system. Incorporating TENGs between the friction layers of the masks has been utilized as a promising strategy to enhance the lifetime of electrostatic charges and endow the rechargeability of the masks upon simple friction movements of the masks such as by hand tapping or inhalation/exhalation breathing.

Figure 16. a) The overall illustration of the common face masks that are exposing to PMs, bacteria and viruses from the saliva and sweat of humans. b) Photograph and a cross-section SEM image of the hybrid three-layer filter. c) Simple description of the rule of each later. d) Embedding this three-layer filter in a commercial facemask and recording the infrared image after applying a voltage of 3 V. e) Step for the filtration experiments and determination of the heating and insulation effectiveness of each layer in a layer in the hybrid filter. f) The heating and insulation performance of the hybrid layer. Reproduced with permission.\textsuperscript{[95]} Copyright 2021, American Chemical Society.
Despite significant advances that have been reported during last year in the fabrication of advanced face masks, by precise examining of the methods and strategies mentioned above, there are some challenges in practical applications of these as-fabricated face masks. i) Most of the developed methods require an external stimulus (such as light, voltage, and pressure) to trigger the functions of the incorporated active components, which practically limits the applications to some extent. For instance, those requiring light will not be useful in dark environments; whereas the functional agents requiring voltage to activate often rely on a battery carried by users, thus creating complication or inconvenient applications. ii) Instability or poor retention of the water-soluble modifying agents (such as inorganic salts, essential oils, and quaternary ammonium compounds) can be considered as the second significant issue. Therefore, fixation of such modifiers via various approaches for the controlled release of modifiers or the elimination of leaching-out of active components needs to be further explored. iii) While techniques based on the incorporation of nanomaterials into the structure of masks have been proved as promising for improving the antiviral activity of the masks, however, the possible inhaling of nanoparticles and therefore, generating toxicity is a great concern that needs to be addressed. iv) The majority of the modifications have been performed so far on PP-based nonwoven fabric which is non-biodegradable and has already created enormous environmental concerns after disposal; hence, the biodegradable fabrics possessing functions similar to PP are in high demand.

Overall, there are still plenty of rooms to further improve the properties and functions of the masks. On the one hand, replacing the PP nonwoven with cotton or cellulose-based nonwoven fabrics can reduce the environmental impact remarkably though the inherent features of PP nonwoven should be well maintained. On the other hand, the high hydrophilicity of the cotton or cellulose-based fabrics might reduce the self-cleaning properties of the masks. Therefore, the tailor-modification of those biodegradable fabrics is required. Accordingly, in our view, achieving an antiviral mask without creating health risks and environmental pollution is possible by fabrication of a multilayer mask based on the functionalized cotton or cellulose-based nonwovens: i) the outer and inner layers of the mask can be made by hydrophobization of the cellulose-based nonwoven grafted with hydrophobic chains or segments to improve the self-cleanliness of the mask; ii) the middle layer can be tailored by covalently grafting well-known biocompatible antiviral agents or polymers (such as aminoglycosides, polysaccharides, peptides, branched polymers and dendrimers etc.). The covalent grafting prevents the potential leaching of the ingredient via inhalation. Additionally, these masks tend to be washable and reusable easily. However, the feasibility of incorporating those polymers into the masks needs to be further assessed.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

antimicrobial efficiency, antiviral agents, functionalized masks, SARS-CoV-2, self-sterilization

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