Nanoparticles-Based Face Masks and Respirators for Preventing COVID-19 Transmission: Breathability Versus Biocidal Activities

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Abstract

Use of face masks and respirators are significant in preventing the transmission of coronavirus disease 2019 (COVID-19) via respiratory droplets or aerosols. The development of face masks and respirators have been focused on the modification using nanoparticles (NPs) to obtain biocidal activities. The incorporation of NPs can also increase the hydrophobicity of the material that assists the repelling of virus carrying droplets or aerosols. Nevertheless, the common cost of gaining those benefits is breathability. Previous studies have reported on the discomforts of wearing a face mask or respirator, one of which is stems from breathing difficulty. At the time of pandemic, maintaining the comfort wearing of face masks or respirators is even more crucial. Thus, this review article is important to keep the breathability aspect gaining a spotlight in the development of NPs-modified face masks or respirators. Herein, we discuss the relationship between the addition of NPs with breathability of the material. In the beginning of discussion, types of protective respiratory equipments, and biocidal activities of the modified fabrics are discussed. Strategies in maintaining the air permeability for long duration use and self-cleansing feature are also discussed.

Keywords: *Nanoparticle, Face mask, Respirator, Breathability, Antibacterial, Antiviral*

Introduction

The on-going coronavirus disease 2019 (COVID-19) pandemic has caused the cumulative death of more than 2.3 million worldwide, with more than 100 million confirmed cases as of February 14th, 2021.[1] Currently, COVID-19 has been recognized to be transmitted via viral-containing respiratory droplets or aerosols, close contact, and fomite routes.[2, 3] Responding the increase of COVID-19 cases, several restrictions have been in place differently in each country. US Centers for Disease Control and Prevention (CDC) released a recommendation for general public to wear face masks or mouth covering fabrics as a preventive measure against COVID-19 in public settings, even when six feet-distancing has been done.[4] Several other countries even legally mandate their citizens to wear face mask

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in public.[5-7] For healthcare workers, the use of surgical mask and respirators are a must to provide protection against transmission in a high-risk environment.[8]

Advancement in improving the performance of face masks or respirators has been significant in the field of nanotechnology during the pandemic. Nanoparticles (NPs) have received significant attention from scientific communities due to their biocidal activities, which can provide extra protection against COVID-19. Furthermore, microbial coinfection in patients with COVID-19 has been observed to add more complexity in the diagnosis and treatment.[9] To prevent the microbial coinfection, some research groups have showcased that fabric modification utilizing NPs could provide antibacterial properties.[10-31] Recently, the antiviral activities of NPs-modified fabrics have also been investigated.[32, 33] Hence, this future technology may contribute to more effective prevention of COVID-19 transmission or other respiratory viruses.

However, breathing comfortability of the face masks or respirators affected by the NPs-based modification has been scarcely discussed. Discomforts of using face masks and respirators have been underlined in several works.[34-36] It was reported that healthcare workers suffer headaches ascribed to the use of respirators.[37] Not to mention, various adverse skin reactions can be caused by wearing face masks or respirators.[38-40] Indeed, those reports[34-37] suggested that the burden is rather psychological than physiological. However, it is important to avoid a modification that can cause extra discomforts, especially in regard of breathing process. Hence, we will discuss how the beneficial biocidal properties of the modified respiratory equipment are intertwined with its breathability.

Transmission of COVID-19

COVID-19 is a respiratory disease caused by SARS-CoV-2, one of the five human coronaviruses, genus betacoronavirus. This spherical lipid-based enveloped virus is surrounded by spike proteins and has a diameter of around 100 nm.[41] While the etiology and pathogenesis of SARS-CoV-2 are not fully known, it has been reported that host cell entry is mediated by angiotensin-converting enzyme 2 (ACE-2),[42] a protein expressed in the epithelium of the human airway[43] as well as the lung parenchyma.[44] Comparatively with SARS-CoV, SARS-CoV-2 has higher affinity to ACE-2[45] and has faster infection rate.[46] Therefore, it is biologically plausible that the transmission of COVID-19 is mainly facilitated by respiratory droplets or aerosols.[47, 48]

There have been extensive works on how COVID-19 is transmitted via respiratory droplets which cover the investigation on the droplet sizes and environment settings. A study on the mechanistic movement of the droplets in a calm indoor setting revealed that aerosols are maintained longer in the air than droplets.[49] Droplets and aerosols can have longer transport in the air when they are generated by sneezing and coughing.[50, 51] As a physiological defence mechanism, coughing releases around 3,000 droplet particles, and more droplets are released during sneezing (40,000).[52] The diameter of droplets is varied (1 – 2,000 μm), but 95% of them are within the range of 2 to 100 μm. Droplet size of less than 100 μm in diameter can be transported up to 4 – 7 meter away by sneezing or coughing suggesting the physical distancing may not be effective to avoid the respiratory transmission.[53] Hence, the role of using face masks and respirators is one of the most significant preventive efforts for COVID-19 transmission.

Protective Respiratory Gears

Medical face masks

Originally, a simple single layer of gauze was used as a medical face mask, aiming to protect the patients from the contamination from the surgeons during operative procedures.[54] Later, it was developed with the overall design comprising three layers; hydrophilic layer (inner part), filter (middle part), hydrophobic layer (outer part). Hydrophilic layer has a function to govern the humidity by absorbing the aerosol from the wearer. Filter acts to selectively regulate the exchange of particles from both sides of the face masks through size exclusion. Hydrophobic layer provides protective repelling mechanism against the aerosols and droplets entering the side of the user. Medical face masks are regulated under Food and Drug Administration (FDA) jurisdiction as medical gears with loosely fitted and disposable characteristics. Though the masks may not tightly-fitted to the face, a study has reported its effective filtration against respiratory droplets (> 5 μm) and aerosols (≤ 5 μm) containing coronaviruses.[55]

Respirators

On contrast to loosely-fitting medical face mask, respirators have much tighter facepiece void with the ability of repelling particles whose size is less than 5 µm. These devices have different nomenclatures depending on the country. The National Institute for Occupational Safety and Health (NIOSH) of the USA classifies the respirators based on their filtration efficiency with N-, R-, and P- groups for non-oil resistant, moderate oil resistant, and strong oil resistant, respectively. The initials are followed by the indication of their filtration efficiencies; for instance, N95 for N-respirator with 95% filtration efficiency, R95 for R-respirator with 95% filtration efficiency, and soon.[56, 57] Nonetheless, the efficiency may fall lower than that stated at high flow rate of inhalation.[58] In particular, N95 has four fundamental layers from the outer layer, filter layer, support layer, and up to the inner layer. Its outer layer can be decorated with ventilator fan for easier respiration.[59] NIOSH has released the test standards for respirators, namely inhalation/exhalation tests, NaCl aerosol challenge, valve leak, and dioctyl phthalate (DOP) test for verification (NIOSH Procedure No. RC-APR-STP-0057, 0058 and 0059).

Homemade face masks

During the pandemic, scarcity in personal protective equipment, including face mask is expected. In such condition, non-medical homemade face masks can be the alternative. A previous study found a significant decrease in the amount of excreted droplet when a simple cloth face mask was in use.[60] Regulation on the mandatory use of face mask has been proven to yield significant reduction in daily COVID-19 cases in the USA.[61] As recommended by WHO, the homemade cloth face masks should be used with at least three layers of fabric.[56] Homemade face masks have been manufactured using various materials such as cotton, air-jet down-proof fabric, satin, polyurethane, polyester, linen, silk, nylon, and cellulose.[62-65] The filtration efficiency of these fabrics depends on their threads per inch (TPI), which is determined by the total number of threads in an inch counted on the length of a fastener. The filtration efficiency of 80% can be achieved by fabrics with >300 TPI.[66] However, for common polyester-, cotton-, silk, and nylon-based fabrics, their efficiencies only reach 5-25%.[63] Note that the use of these homemade cloth face masks is not recommended for high-risk environment.[67]

Nano Particles Embedment

NPs can be incorporated onto the surface of fabric materials through a variety of methods that affect the characteristics (including air permeability) as well as the stability of the immobilized-NPs. NPs embedment via electrospinning is conducted by simply homogenizing fiber materials and priorly prepared NPs.[15, 17, 33, 68] It is worth to mention that the NPs may have high conductivity which results smaller fiber diameter concomitant to the generation of high charge density on the surface of the ejected jet.[17] *In situ* NPs impregnations using green route with plant broths as reducing agent have been reported.[16, 21, 22, 24, 28] Simple adsorption technique, followed by metal ion reduction using UV irradiation, has also been applied.[27] However, coating or nanocoating via immersion and spraying is the most common method for NPs embedment onto fabrics.

Advantages and Disadventages of Nano Particles Embedment

Biocidal activities of nano particles

Incorporation of metal NPs onto fabric materials have shown the biocidal activities against various microorganism. Gram-negative *Escherichia coli* and gram-positive *Staphylococcus aureus* are among the most widely used bacteria in the reported studies, to test the antibacterial activities of NPs-based fabrics.[11, 13, 17, 19, 20, 22-29, 32] Others have tested the biocidal activities against *Candida albicans, C. parapsilosis, Xanthomonas aconopodis, Enterococcus faecalis, Proteus vulgaris, Klebsiella pneumoniae, Pseudomonas aeruginosa, S. epidermidis, Bacillus subtilis,* and *Bacillus cereus*.[15, 19, 23, 24, 27, 28, 69] Based on those studies, the employment of various NPs could effectively kill the bacteria, including multidrug-resistant *S. epidermidis* and *S. aureus*.[70, 71]

Inhibition mechanism of the bacteria depends on the type of NPs. For instance, Ag NPs could cause bacterial cell death by interfering the cell respiratory system, interfering ATP production and DNA replication, increasing cell membrane permeability, and generating bacterial cell-derived reactive oxygen species (ROS).[72, 73] Metal oxide NPs (such as ZnO, MgO, CaO, CuO,

TiO_2 and so on) have biocidal activities attributed to the production of ROS from electrons and holes reaction under UV/Vis radiation.[31, 32] In particular, TiO_2 NPs show promising self-cleansing properties which can photodegrade the remnant of microorganism from the fabric surface.[19, 20, 31, 32]

A challenging factor for the metal oxide NPs is the need of light exposure to induce the photocatalytic activities. To overcome, some researches incorporate Ag NPs to provide biocidal effects even without the presence of light.[20, 23, 33] Despite the fact that Ag could have antioxidant activities,[16] the synergism between Ag and photocatalyst or active compound in promoting ROS-induced cell death has been observed.[17, 20] As another alternative, the fabric can be modified with 3,3′,4,4′-benzophenone tetracarboxylic acid to provide photo-induced active metastable structure which can still produce ROS during dark condition.[14, 17, 74]

Recently, NPs-based face masks have been investigated for its ability to inactivate viruses. ZnO nanorods and Ag NPs, incorporated in electrospun nanofibers-based face mask, has inhibitory activities against coronaviruses and influenza viruses.[33] Another study reported Cu NPs-decorated pristine face mask was effective in inactivating virus-like particle (VLP) of SARS-CoV-2.[32] The mechanism of the antiviral activities was attributed to the degradation of viral structure due to photocatalytic and photothermal effects. Another study reported that viral genetic encoding protein could be degraded after exposed with ROS promoted in photocatalytic activities of TiO_2.[75] In addition, it has been reported that NPs have antiviral properties against a wide variety of viruses.[76]

Droplets and aerosols rejection

Physical mechanism of antiviral protection on respiratory equipment relies on the filtration and repelling of virus containing droplets and aerosols. To repel the virus carriers, NPs can be added to enhance the surface hydrophobicity of the face masks or respirator's filter membrane.[32, 77] Hydrophobicity of the face masks can be measured by contact and roll-off angles.[30, 32] In particular, a study has achieved super hydrophobicity for various fabric material coated with SiO_2 NPs mixture.[30] Furthermore, a hydrophobic layer may repel humidity increasing the comfortability.

Moreover, the rejection of droplets, aerosols, and viral particles can be facilitated by size exclusion that depends on the pore size of the material. Filtration efficiency of Cu NPs-coated pristine mask was pretty similar to that of untreated face mask.[32] Filtration of NaCl particles by Ag NPs-based polyvinyl alcohol membrane revealed to be more efficient than that of N95, at a cost of increased pressure drop.[17] The study did not perform an investigation on the effect of Ag NPs addition, but the higher pressure drop means lower breathability and, as a consequence, lower comfortability.

Breathability

Prolonged use of surgical masks and N95 respirator has been recognized to lead the users to feel headaches, light-headedness, and suffocation.[35, 78] During COVID-19 pandemic, significant number of healthcare workers experienced headaches caused by wearing masks.[79] Factors responsible for the headache cases among healthcare workers include the design and psychological stress.[79] Difficulties in breathing and speaking as well as increases in temperature and humidity are responsible for such discomfort of wearing protective respiratory gear.[80]

Physiologically, wearing face masks or N95 respirators have been proven to yield no clinical relevance on the respiration and O_2 delivery.[35, 81, 82] However, there has been an observation on the significantly higher CO_2 level in N95 wearers in comparison with surgical face mask wearers.[35] Moreover, significant decrease in O_2 and increase in CO_2 was observed after the N95 wearers finished 1 h treadmill walking session.[81] Although that study concluded the effects are minor, the changes of O_2 and CO_2 levels can potentially lead to hypoxemia[82] and hypercarbia.[83] A previous study revealed increased nasal airflow resistance of more than 100% as a result of wearing N95 respirator.[84] The same study also revealed that N95 respirator may reduce air exchange volume as much as 37%. It is ascribed to only partial amount of air volume can pass through the pores of the respirator's layers (**Figure 1a**). Modification with nanoparticles may further decrease this air exchange volume due to smaller size of pore diameter as a consequence of fiber diameter expansion by binding agents, active agents, or NPs agglomeration (**Figure 1b**). Therefore, it is important to investigate the effect of NPs embedment with the breathability of the material.

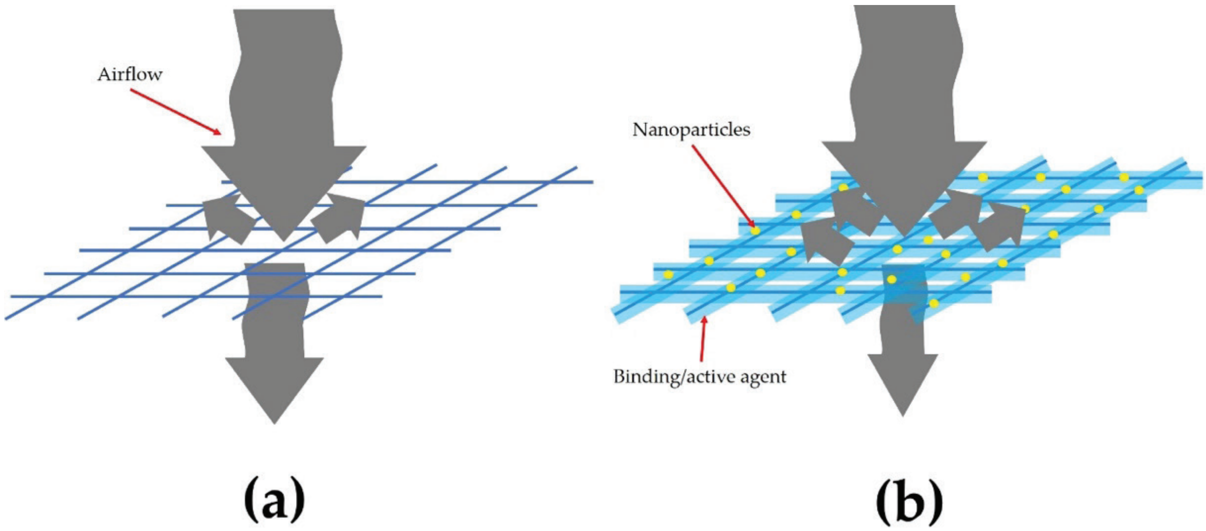

Figure 1. Representation of airflow passing through (a) unmodified fabric and (b) NPs modified fabric of face masks or respirators

Breathability is a parameter determining the comfortability of a face mask, since it has a correlation with moisture movement and thermo-regulation of the fabric.[85] NPs incorporation to the face masks have effects on the breathability. In one study, the coating of nanofibers onto commercial surgical face mask yielded lower air permeability leading to poorer breathability of the fabric.[68] The employment of mesoporous nano silica NPs with polydimethylsiloxane binder, however, did not change the original breathability of the spray-coated textile.[30] On another report, Cu NPs nanocoating results in similar pressure drop with uncoated mask at low air velocity.[32] Yet, increase in pressure drop is experienced by the Cu NPs-coated mask as the air velocity increased, indicating poorer breathability.[32] Lower breathability of the Ag NPs-based respirator membrane filtration, in comparison with that of N95, is associated with the dense properties of the matrix (polyvinyl alcohol).[17]

Observation of porous structure using scanning electron microscope (SEM) images can also suggest the breathability of the NPs-modified fabric. Insignificant changes in the SEM images have been observed in samples with spray-coatings of SiO_2,[77] TiO_2,[31, 86] and Cu NPs.[32] On contrary, significant changes in the pore structure and fiber diameter have been found in SEM images from SiO_2-TiO_2-Ag-embedded cellulosic membrane[20] and Ag NPs-based electrospun fiber,[17] respectively. Based on the explanation above, to optimize the breathability of the face mask, the selection of NPs attachment methods and textile material is important.

Self-cleansing

One of the recent advancements in the development of NPs-embedded protective respiratory equipment is photo-induced self-cleansing properties. Excellent self-cleansing was performed by bacterial cellulose (BC)/SiO_2/TiO_2 composite against deposited crystal violet dye under UV irradiation for 50 minutes.[20] Similarly, effective self-cleaning was observed in the photobleaching of crystal violet dye (reaching 97% in 10h irradiation) by Mn:TiO_2-embedded textile.[31] Removal of microbial cells has been achieved by the NP-s modified materials, which can prevent bio-fouling and, further, maintain the breathability.[20, 32] Additionally, self-cleansing or self-sterilization can ease the disinfection process by simply light-irradiating the fabric and remove the risk of contamination or transmission during discarding process. The role of NPs technology prevention of COVID-19 transmission and its advantages and disadvantages are summarized in **Figure 2**.

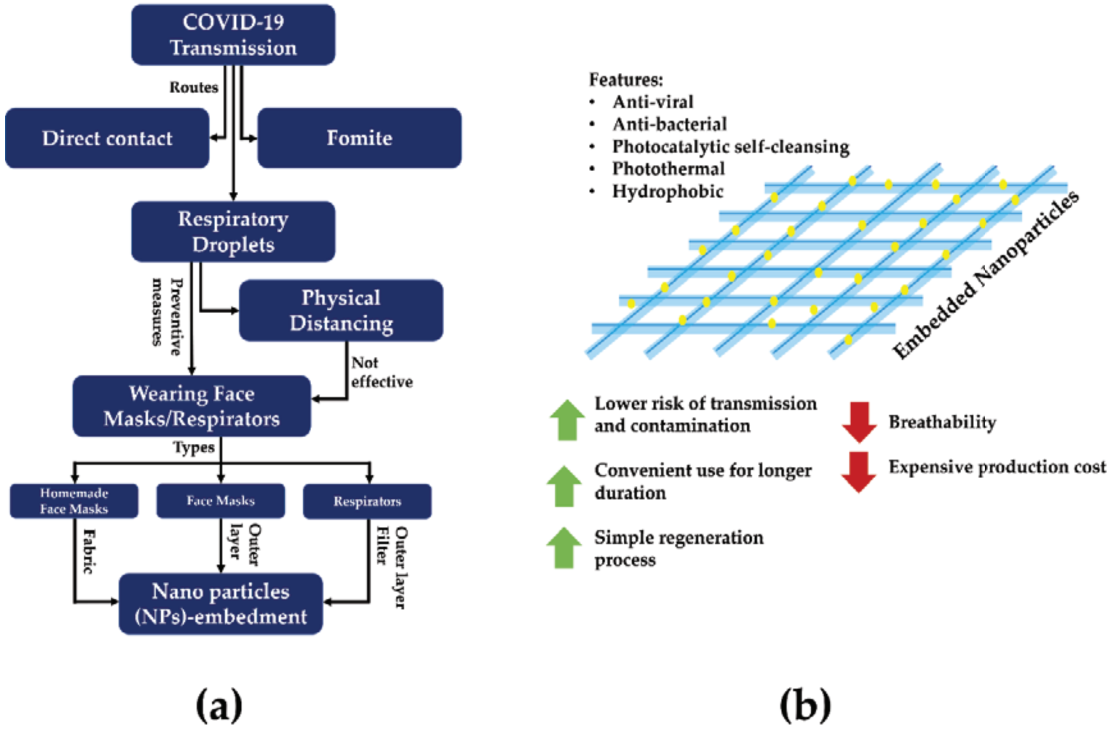

Figure 2. (a) Schematic diagram of the prevention of COVID-19 transmission through nanoparticle technology. (b) Features, strengths (green arrow), and weaknesses (red arrow) of NPs-based face masks or respirators.

Conclusion

Modification of face masks and respirator by employing NPs are found to have effective biocidal activities, where current researches have focused on developing antiviral fabrics. The antimicrobial activities can be attributed to the chemical and physical mechanisms. Despite their excellence in term of biocidal activities, the modification effects on breathing comfortability are rather problematic since several works reported poorer breathability. Spray-coated fabric, so far, has the least changed breathability. Additionally, self-cleansing feature from TiO_2 embedment may contribute in sustaining the breathability during long hour use by preventing microbial cells-induced biofouling. Studies regarding the effect of NPs incorporation on the breathability of the materials are still scarce and rather non-uniform. Thus, we recommend further researches to include the investigation of breathability of the material after the NPs embedment.

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