Improvement of performance and function in respiratory protection equipment using nanomaterials

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Abstract Nanotechnology has become one of key areas for the current development and research. Nanotechnology focuses on matter at the nanoscale and is capable of using different approaches to produce nanomaterials, structures, devices, and systems. One of the concerns that have to be addressed is the adverse effects of exposure to pathogens and pollutants in different workplaces and environments. Respiratory protective equipment (RPE) is one of the personal protective equipment (PPE) utilized to reduce the risk of exposure to environmental or occupational respiratory hazards. Thus, various studies have been conducted for improving the functional properties of sorbents or filters in different kinds of RPE. Different categories of nanomaterials have been reported as effective agents for achieving this goal. The application of these nanomaterials in mask layers or respirators’ cartridge could significantly increase the filtration efficiency, breathing comfort, and antibacterial/antiviral properties of the masks and respirators. The present study aimed to comprehensively review the nanomaterials used in different types of face RPE with emphasis on various properties of the utilized nanomaterials. The study also aimed to show an applied perspective for future research on this important subject.

Keywords Nanoparticles · Nanofabrication · Filtration · Mask · Respiratory protective equipment · Health and environmental effects

Introduction

The field of nanotechnology is one of the most popular and hot-topic areas for research and development, which has attracted a lot of attention in the recent years. Nanotechnology aims at the creation of nanomaterials, nanostructures, nano-devices, and nano systems with new features and functions (Hulla et al. 2015; Zhu et al. 2004; Nikaeen et al. 2020a). Nanotechnology is widely applied in various fields including medicine, agriculture, and industry due to the unique properties of nanomaterials (Singh 2017; Nikaeen et al. 2020b). Nanomaterials are classified into nanoparticles (NPs), nanofibers, nanotubes, nanowires, nanohelices, nanozigzags, nanopillars, nanobelts, nanospheres, nanopyramids, and nanotubes based on their morphologies. Besides, based on the chemical composition, nanomaterials are divided into single constituent NPs, nanocomposites, nanogels, quantum dots, branched dendrimers, and metallic, polymeric, ceramic, semiconductor, and
core–shell nanomaterials (Saleh 2020). Nanomaterials are used to protect humans against harmful physical, chemical, and biological agents. For example, they are used in various cases including protective clothing (Thilagavathi et al. 2008), electromagnetic radiation protection shields (Verma et al. 2017), noise and vibration reducers (Jia et al. 2020), air and water purifier filters (Gao et al. 2018a; Li et al. 2008), and respiratory protective equipment (RPE) (O’Dowd et al. 2020).

Air contaminants in industrial and medical workplaces can increase the risk of exposure to chemicals, viruses, bacteria, mycobacteria, non-tuberculous mycobacteria, and other environmental contaminants that have adverse effects on human health (Makri and Stilianakis 2008; Zhou et al. 2018). If it is impossible to take engineering control measures to prevent or reduce the inhalation of air contaminants, it is necessary to wear RPE such as facial masks including medical/surgical masks and respirators. The inherent capability of masks to resist the penetration of contaminants is directly related to their effectiveness in removing pathogens and contaminants (Zhou et al. 2018). Therefore, researchers have been looking for new ways to improve the features and effectiveness of RPE. In this context, respiratory comfort and thermal comfort as well as the antibacterial/antiviral properties of RPE can be enhanced by using various modifications including coating the nanomaterials on the layers of face masks and increasing the filtration efficiency.

In this study, a community review has been conducted regarding the nanomaterials used in various kinds of mask with emphasis on their sizes, types, and compounds to remove and filter contaminants. A brief review on the application of nanomaterials was published in 2018 by discussing nine papers (Abbasi-nia et al. 2018). However, this is the first systematic review with comprehensive details and an update for covering almost all related publications and reports on the subject as well as a snapshot on the benefits of nanomaterials for increasing the protection ability of RPE against air pollutants.

**Methods**

A comprehensive literature search was conducted in various databases in English such as Web of Science, Scopus, and PubMed. Google scholar was also searched to cover missing documents in the first 15 pages. Although some patents available from Google Pant were related to the current study, they were excluded from this review to perform the study only on research articles. No language filter was considered for papers with English abstracts. The following keywords were used as the search list to find the related articles:

“Nano” OR “nano fiber” OR “nanofiber” OR “nano particle” OR “nanoparticle” OR “nanoparticles” OR “NPs” OR “metal NPs” OR “metal oxide NPs” OR “nano composite” OR “nano clay” OR “nano material” OR “nano compound” OR “nano structure” OR “nano wire” OR “nano tube” OR “nanotube” OR “nano cluster” OR “nano sheet” OR “narrow” OR “nanorod” OR “carbon nanotube” OR “CNT” OR “carbon nano tube” OR “SWCNT” OR “SWCNTs” OR “MWCNT” OR “MWCNTs” OR “Graphene” OR “Graphene Oxide” OR “GO” OR “reduced graphene oxide” OR “rGO” OR “carbon dot” OR “quantum dot” AND

“mask” OR “respirator” OR “Respiratory protection device” OR “personal respiratory protection” OR “respiratory protective equipment” OR “RPE” OR “respiratory cartridge” OR “half mask” OR “surgical mask” OR “N95 mask.”

The abovementioned keywords were searched in titles, abstracts, and keywords. Subsequently, all the articles were entered into the MENDLEY software, and duplicated articles were removed from the obtained library. In the next step, two researchers independently reviewed and evaluated the articles to exclude the irrelevant studies. Then, the abstracts of the remaining articles were scanned and reviewed to keep the relevant studies. For ambiguous articles, full-texts were checked to ensure meeting the inclusion criteria. Finally, the full texts of the collected publications were evaluated to extract the required information to ensure meeting the inclusion criteria and relevance to the study objectives. The current search was completed on May 1, 2021.
Results and discussion

Polymeric nanofiber

Nanofibers refer to fibers less than one micron in diameter (Grafe and Graham 2003). Polymeric nanofibers are one of the compounds that have been used extensively for the preparation of face masks in the recent decades (Yun et al. 2010). Generally, polymers can be categorized in two groups, i.e., natural and synthetic. Some examples of natural polymers are cellulose (Sehaqui et al. 2016), gelatin (Zhang et al. 2005), collagen (Matthews et al. 2002), chitosan (Haider and Park 2009), and silk fibroin (Vasita and Katti 2006), while some examples of synthetic polymers are polyvinylidene difluoride (PVDF) (Han et al. 2019), polyurethane (PU) (Lee et al. 2007), and polybenzimidazole (PBI) (Ogunlaja et al. 2014). Polymers can be involved in the fabrication of nanofibers using electrospinning, phase separation, template synthesis, and self-assembly techniques, with the electrospinning technique being the most common one (Dahlin et al. 2011; Zhu et al. 2017). This technique has been widely used due to its very simple setup, versatility, and capability of producing nanofibers with various diameters and compositions (Li and Xia 2004).

Up to now, some studies and inventions have been conducted on the use of polymeric nanofibers in face masks, particularly surgical masks and respirators, to increase their effectiveness. What follows includes a review of these studies. Additionally, the characteristics of these masks and respirators have been summarized in Table 1.

Akduman used a polymeric nanofiber layer in the N95 respirator based on cellulose acetate (CA) and PVDF. In that study, PVDF and CA nanofibers were fabricated by the electrospinning technique. The mentioned nanofiber layers showed a higher mechanical filtration performance in comparison to conventional face mask layers (Akduman 2021). Skaria et al. also reported that surgical masks including nanofiber filters had higher air permeability compared to conventional surgical masks, which resulted in a greater breathing comfort and a higher filtration efficiency (Skaria and Smaldone 2014).

Due to the global prevalence of SARS-CoV-2 during the COVID-19 pandemic, use of highly effective RPE has significant impacts on human health (Bartoszko et al. 2020). The SARS-CoV-2 has a variety of diameters from 60 to 140 nm, with an average diameter of 100 nm (Zhu et al. 2020). Meanwhile, standard N100, N99, and N95 respirators have been certified at the 300 nm size (most penetrating particle size (MPPS)) by the US National Institute for Occupational Safety and Health (NIOSH). Until now, no standard filter has been developed for capturing airborne viruses and 100-nm nano-aerosols. Recently, Leung and Sun developed a novel charged PVDF nanofiber filter technology for the effective filtration of SARS-CoV-2 and nano-aerosols. The goal of that study was to achieve at least 90% efficiency in the filtration function for nano-aerosols (NaCl aerosol) with the size of 100 nm and a pressure drop of less than 30 Pa. The single-layer and multi-layer PVDF nanofiber filters were investigated with four different diameters, i.e., 525, 349, 191, and 84 nm. In the single-layer mode, the efficiency of the nanofiber filters with 84, 191, 349, and 525 nm diameters for capturing 100 nm aerosols were 61.9%, 51.8%, 45.3%, and 39.6%, respectively. Consequently, the single-layer nanofiber filters did not reach the required filtration efficiency. Moreover, the results related to the multilayer nanofiber filters indicated that increasing the layers and base weight increased the filtration efficiency, consequently increasing the pressure drop. Moreover, two filters, i.e., 3L (84 nm fiber, 0.191 gsm) with the total 0.57 gsm and 8L (349 nm fiber, 0.096 gsm) with the total 0.77 gsm, provided a 90% efficiency with a pressure drop of less than 30 Pa (Leung and Sun 2020a).

In another study, Leung and Sun investigated the effect of multilayer nanofiber filters on respirators against airborne SARS-CoV-2. In that study, charged and uncharged nanofiber filters were compared in terms of aerosol capture efficiency, and the results demonstrated that the charged nanofiber had a higher efficiency. Among the charged multilayer nanofiber filters, 6-layer charged PVDF provided better protection against airborne SARS-CoV-2 and nano-aerosols. The filtration efficiencies of 6-layer charged PVDF nanofiber filters were 88%, 88%, and 99% for 55, 100, and 300 nm ambient aerosols, respectively, with a pressure drop of 26 Pa. It was quite close to the targeted value (filtration efficiency of 90%) for 100 nm aerosols. Additionally, it was at least 10 times more breathable compared to the conventional N95 respirator (Leung and Sun 2020b).
### Table 1: Application of different nanofibers in the production of various types of masks and respirators

| No | Nanomaterial type                        | Chemical composition                                      | RPE type   | Size of Nanomaterial | target pollutant           | Pollutant size | Efficiency | Ref                        |
|----|-----------------------------------------|-----------------------------------------------------------|------------|----------------------|-----------------------------|----------------|------------|---------------------------|
| 1  | Polymeric nanofiber                     | Cellulose acetate (CA) and polyvinylidene fluoride (PVDF) | N95 FFRs   | D = CA (319.02–264.02 nm) & PVDF (236.50 to 142.59 nm) | Particle                      | NR            | 95%        | Akduman 2021)             |
| 2  | Polymeric nanofiber                     | 6-layer PVDF                                               | N95 respirator | D = 525 + _191 nm   | COVID-19 virus               | 55 nm 100 nm 300 nm | 88% 88% 96% | Leung and Sun 2020b)      |
| 3  | Polymeric nanofiber                     | Polysulfone                                               | regular gauze masks | Bead diameter = 168 nm string diameter = 49 nm thickness = 165 µm | PM<sub>2.5</sub> particle     | <2.5 µm       | >90%       | Li and Gong 2015)         |
| 4  | Polymeric nanofiber                     | Polyacrylonitrile (PAN)                                   | FFP2 respirator | D = 150 nm          | Coronavirus and nano-aerosols | 100 nm        | 97%        | Kadam et al. 2019)        |
| 5  | Polymeric nanofiber                     | 4-layer PVDF                                               | Face mask   | D = 84 nm           | Bacteria and viruses         | 80 – 160 nm    | 98%        | Leung and Sun 2020a)      |
| 6  | Polymeric nanofibers                    | Polyvinylidene difluoride (PVDF)                          | Face mask   | D = 50–100 nm       | Particulate matters (PMs)    | >2.5 µm        | 98.50%     | Ullah et al. 2020)        |
| 7  | Polymeric nanofibers                    | Polybenzimidazole (PBI)                                   | Dust proof mask (respirator) | D = 150 nm          | Dust                           | NR            | NR         | Lee et al. 2019)          |
| 8  | Polymeric Nanofiber                     | Spun and other kind of polymers                           | Air purification type mask (filter) | D = 25–120 nm       | Aerosol particles            | 300 nm        | 99.99%     | Han 2017)                 |
| 9  | Polymeric nanofibers binary             | Nylon6 – polyacrylonitrile nanofibre-nets binary          | Not applicable (just test on material for possible use in mask) | D = 265 nm          | Aerosol particles            | 300 nm        | 99.99%     | Wang et al. 2015)         |
| 10 | Polymeric nanofiber/nanoporous polymeric| Nylon6 nanofiber/nanoporous polyethylene                  | Face mask   | D = 50–1000 nm (nanoPE) & D = < 100 nm (nylon6)         | Particulate matter (PM)     | <2.5 µm       | 99.60%     | Yang et al. 2017)         |
| 11 | Nanofiber                               | NR                                                        | N95 respirator | NR                   | Bacteria                      | NR            | 99.90%     | Suen et al. 2020)         |
| No | Nanomaterial type                                                                 | Chemical composition                                                                 | RPE type          | Size of Nanomaterial | target pollutant         | Pollutant size | Efficiency | Ref                                                                            |
|----|---------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|------------------|----------------------|--------------------------|----------------|------------|--------------------------------------------------------------------------------|
| 12 | Nanofibrous material (polymeric nanofiber/metal oxide/carbon nanomaterial)       | Matrix of polylactic acid and cellulose acetate containing copper oxide nanoparticles and graphene oxide nanosheets (CuONPs/GO@PLA and CuONPs/GO@CA nanofibers) | FFR respirator   | NR                   | Microbe and virus        | NR             | NR         | Ahmed et al. 2020                                                                |
| 13 | Polymeric nanofiber                                                              | NR                                                                                  | Surgical mask    | NR                   | Aerosols                | <2 μm          | NR         | Skaria and Smaldone 2014                                                          |
| 14 | Polymeric/metallic nanoparticles composite nanofiber                             | Polyvinyl alcohol / silver nanoparticles composite nanofiber(PVA/AgNPs)            | FFR respirator   | D = 207 nm           | …                        | NR             | 92.60%     | Xianhua et al. 2020                                                               |
| 15 | Polymeric nanofiber/metallic nanoparticle                                        | Nylon6 nanofiber/silver nanoparticle                                                | Surgical mask    | N6 (D = 150–250 nm/Th = 2 mm) AgNPs (D = 16 nm) | Bacteria (Escherichia coli) nanoparticle | NR             | NR         | Khamis Aloufy and Abdel-Moneim El-Messiry 2013                                   |
| 16 | Polymeric nanofiber/metallic nanoparticle                                        | Polyacrylonitrile(PAN) Nanofiber/silver nanoparticle                                | Surgical mask    | PAN (D = 257 nm) AgNPs (D = 40–50 nm) Nanocomposite = 125 nm | Bacteria (S aureus and E. coli) | NR             | 99%        | Selvam and Nallathambi 2015                                                       |
| 17 | Polymeric nanofiber + metal oxide nanoparticle                                   | 99% polyacrylonitrile (PAN) nanofiber + 1.00% copper oxide nanoparticle (PAN/CuO) | Medical mask     | D = 197 nm PS = 17.54 Å | 20 nmm–0.2 μm            | NR             | NR         | Hashmi et al. 2019                                                               |
The feasibility of the extended use and reuse of the masks and respirators is of great value and interest, especially during the COVID-19 pandemic. Ullah et al. compared the reusability of melt-blown and nanofiber filters in face masks. To do so, all parameters affecting the performance of the two filters were evaluated before and after the cleaning treatments including air permeability, pressure drop, breathability, cytocompatibility, and filtration efficiency. Besides, two stages were adopted for cleaning treatments including (1) dipping of the filters in 75% ethanol and (2) spraying 75% ethanol on the filters. Based on the results, air permeability and pressure drop were better in melt-blown filters compared to nanofiber filters. However, breathability was better in nanofiber filters due to their uniform pore diameter distribution. Among the investigated parameters, filtration efficiency was of higher importance. The efficiency of melt-blown filters had a sharp drop to 64% after the treatments, while the nanofiber filtration efficiency remained almost constant at 97–99%. Additionally, the nanofiber filters did not exhibit any cytotoxicity on tested human cells. Overall, the results indicated that the use of nanofiber filters in face masks provided the reusability option. In other words, the face mask could be reused several times after simple cleaning with ethanol (Ullah et al. 2020). The schematic presentation of the evaluation process and comparison of some performance parameters of melt-blown and nanofiber filters in face masks have been depicted in Fig. 1 (Ullah et al. 2020).

A novel nanofibrous facial mask was designed by Ahmad et al. This newly designed facial mask consisted of two main parts: a fixed piece and a disposable filter piece. The fixed part was made of molten polylactic acid (PLA), while the disposable part consisted of a multilayer of PLA and CA nanofiber doped with graphene oxide (GO) and CuO NPs. The

![Fig. 1 Schematic presentation of the treatment of face mask filters with spraying and dipping using 75% ethanol and evaluation of reusability (a) (comparison of melt blown and nanofiber before and after treatment), air permeability (b), surface area (c), and porosity percentage (d) (Ullah et al. 2020) (Adapted with permission from ACS Appl. Nano Mater. 2020, 3, 7, 7231–7241. This article is made available via the ACS COVID-19 subset for unrestricted RESEARCH re-use and analyses in any form or by any means with acknowledgement of the original source. These permissions are granted for the duration of the World Health Organization (WHO) declaration of COVID-19 as a global pandemic.)](image-url)
polymeric nanofiber network played the role of stopping the airborne particles while escaping or moving. Additionally, the GO and CuO NPs were considered to have antiviral and antibacterial properties, which prevented the transmission and activation of viruses and bacteria on the filter surface. On the other hand, the modification of polymeric nanofiber networks by NPs in this design could provide a filter with dual mechanical and biological functions, which was very effective in protecting healthcare workers (HCWs) during the COVID-19 pandemic (Ahmed et al. 2020).

Particulate matter (PM) is one of the environmental pollutants that has caused serious concerns due to its adverse effects on human health (Harrison and Yin 2000). Facial masks, as a kind of RPE, are widely used to filter pollutants. Conventional filters are not effective in filtering the PMs less than 2.5 microns in diameter. In the recent years, studies have explored the effects of nanofiber filters on the capture efficiency of PM$_{2.5}$. For instance, Wang et al. fabricated nylon6 polycrylonitrile (PAN) nanofiber membrane with two-dimensional nano-nets. The membrane had a high efficiency in capturing PMs with a diameter of 300 nm due to its small pore size, high porosity, and average diameter of 265 nm (Wang et al. 2015). Xingzhou Li also applied a nanofiber polysulfone filter as a mask filtration material due to the health hazards regarding the PM$_{2.5}$ in haze pollution in most Chinese cities as well as the lack of efficient gauze masks in filtering these particles. The filter was synthesized by electrospinning technique at three different times (15, 30, and 60 min) on the surface of a non-woven polypropylene on grounded aluminum foil. All of these filters showed over 90% rejection efficiency against PM particles and acceptable air permeability. However, the 15-min nanofiber mask had the lowest pressure drop and the highest comfort breathability, while the 60-min nanofiber mask had the highest efficiency along with lower breathing comfort. Because of the importance of both features, the 15-min nanofiber mask was found to be a better choice (Li and Gong 2015).

Lee et al. conducted a study in 2019 and used polybenzimidazole (PBI) nanofiber membrane filters in respiratory dust-proof masks to evaluate their performance compared to commercial masks. The results confirmed that the use of the PBI membrane filters with a low pressure drop (130 Pa) had more than 98% efficiency for removing PMs. Due to the reduction of pressure drop, it led to a high breathability and higher performance. Thus, its quality factor was three times higher than that of commercial masks. Other advantages of the PBI filters were reusability after cleaning and mechanical, chemical, and thermal stability, which made it suitable for various applications. Moreover, nanofiber filters increased the PMs’ capture efficiency due to their electric dipole moments. Furthermore, the capture efficiency of the polymer increased with increasing dipole moments. Meanwhile, this could greatly increase the binding of the PM to the polymer surface due to the creation of a dipole–dipole or induced-dipole force (Lee et al. 2019).

Using a face mask and respirator in adverse environmental conditions such as extreme temperature and humidity could increase the heat stress, sweating, and discomfort and even lead to the growth of microorganisms. Thus, in addition to high removal efficiency and comfortable breathing, the concept of thermal comfort is also important for face masks. In conventional face masks, thermal properties are adjusted by changing the thickness of the fibers, but this can negatively affect the particle removal efficiency and air permeability. Hence, thermal management in face masks has been introduced for the application of masks in both indoor and outdoor spaces in severe environmental conditions. This concept was first introduced in the research carried out by Ankun Yang et al. (Yang et al. 2017). In that study, two systems with cooling and heating effects were designed. One system included nanofiber on nanoporous polyethylene (fiber/nanoPE) and the other involved nanofiber on nanoPE modified with a silver layer (fiber/Ag/nanoPE) with cooling and heating effects. The results revealed a removal efficiency of over 99% as well as good air permeability. Therefore, nanoPE was used as a supporting layer with transparency characteristics against mid-infrared radiation emitted from human body and nanoPE modified by a thin layer of Ag to increase the radiation reflection of human body. Additionally, nylon-6 nanofibers had a higher efficiency in removing PMs due to their small fiber diameters and high dipole moments compared to the polypropylene used in conventional masks (Yang et al. 2017). The optical properties and thermal imaging of the discussed face masks have been presented in Fig. 2, which has been adapted from the original research (Yang et al. 2017).
Kadam et al. assessed the effects of bilayer nanofiber membranes on reducing the filter pressure drop and bulkiness in 2019. In that study, the bilayer beaded nanofiber membranes were used to make light and efficient respiratory filters against particles sizing 0.3–5 µm. The bilayer nanofiber membrane with bead structure was divided into two types, i.e., beads on the top (BT) and beads at the bottom (BB). The results demonstrated that the BB (99%) had higher filtration efficiency compared to the BT (88%) due to its greater thickness (220 vs. 165 µm) and smaller pore size. Before the interception of the aerosols with smaller pores (0.42 µm) in the lower half of the electrospun nanofiber membrane (ENM), diffusion through the top layer was also improved through the large pores (2.93 µm) of BB (Kadam et al. 2019).

Han et al. designed and analyzed a new structure for fine dust masks using nanofiber filters instead of non-woven fabrics in 2017. In this proposed design, the diameter of the mask filter was reduced from 25 µm in non-woven fabrics to 25–120 nm in nanofibers, thereby increasing the mechanical adsorption of fine particles on the surface. The new design could also be attached more closely to the face to prevent the entry of fine dusts into the gap between the face and the mask (Han 2017).

In a previous study, Suen et al. compared traditional and nanofiber N95 filtering facepiece respirators (FFRs) among 104 nursing students. The FFRs were evaluated in terms of mask fit and usability before and after nursing procedures. Usability was assessed by eight parameters, namely facial heat, breathability, facial pressure, speech intelligibility, itchiness, difficulty of maintaining the mask in place, and comfort level. Based on the results, the nanofiber N95 had a higher fit factor compared to the 3 M N95 FFRs during various body movements. In fact, 66.3% and 78.8% of the participants obtained a fit factor above 100 from the 3 M N95 and nanofiber N95 after nursing procedures, respectively. Besides, the results

![Fig. 2](image_url) Thermal imaging and optical properties of the investigated face masks. a Total FTIR transmittance of nanoPE, fiber/nanoPE, and two commercial face masks. The shaded area is the human body radiation. b Thermal imaging of bare faces and faces covered with the sample (fiber/nanoPE) and two commercial face masks. The rectangular box that appears to be cold was from the tape which has been used to transfer the fibers onto nanoPE. (Yang et al. 2017) (Adapted with permission from Nano Lett. 2017, 17, 6, 3506–3510. Copyright 2017 American Chemical Society)
of usability evaluation indicated that the nanofiber N95 FFRs had higher compatibility and usability in comparison to the 3 M N95 FFRs. Additionally, coating of nanomaterials on the surface of the respirator resulted in an increase in water repellency and bacterial filtration efficiency compared to the respirator without nano-coating (Suen et al. 2020).

In conclusion, application of polymeric nanomaterials, especially in fiber forms, were the most promising issue in increasing the protection potential of masks and respirators. CA, PVDF, nylon, polyacrylonitrile, polysulfone, and PBI nanofibers as well as nanofibers on nanoporous surfaces such as polyethylene were the most common materials that were mostly fabricated in nano size using electrospinning. However, the arrangement of polymeric nanomaterials could be an important factor in the filtration efficiency. For example, different filtration efficiencies were reported in a bilayer nanofiber membrane with different locations of the bead structure on the nanofiber (beads at the top and beads at the bottom) (Kadam et al. 2019). On the other hand, modification of polymeric nanofibers with other kinds of nanomaterial such as graphene oxide and metal oxide could enhance some properties of the utilized nanofibers, especially their biological activity, which will be reviewed and discussed in more details in the following parts of the article.

Metallic Nanoparticle

Metallic NPs that are made of pure metals such as gold, silver, zinc, and iron have unique properties due to their high specific surface area and high fractions of surface atoms. Among these NPs, the nano-silver has rapidly become a well-known product in manufacturing face masks due to its antimicrobial applications. In 2013, Kamis et al. designed an antibacterial medical face mask, in which nylon6 nanofiber was used as an adsorbent to capture bacteria/NPs and silver NPs as an antibacterial agent. In that study, nylon6 nanofibers and silver NPs were synthesized using electrospinning and chemical reduction methods, respectively. In this design, the antibacterial effects of silver NPs on thin (1 mm) and thick (2 mm) nanofibers were investigated. In the thin layer, silver NPs had no effects on reducing the bacterial growth. However, the bacterial growth significantly decreased in the thick layer. This could be due to the greater adsorption of silver NPs on the thicker nanofiber surface, which increased its antibacterial effect (Khamis Aloufy and Abdel-Moneim El-Messiry 2013). In other words, the dimensional ratio of silver NPs allowed them to interact with other particles and fill the gap between bulk materials and atomic or molecular structures, eventually increasing their antibacterial efficiency. Additionally, 1 gr of the NPs could give antibacterial properties to hundreds of square meters of the substrate (Thakkar et al. 2010).

Selvam and Nallathambi investigated a composite filter including electrospun PAN nanofibers with incorporated silver NPs in terms of bacterial filtration efficiency (BFE) and anti-bacterial activity against both gram-positive S. aureus and gram-negative E. coli bacteria. The synthesis of silver NPs is usually done by reducing soluble silver salts using a reducing agent such as dimethylformamide (DMF). In that study, dual-use DMF was used both as a solvent for PAN electrospinning and as an agent for the initial reduction of silver ions to silver NPs. The results indicated that pure nanofibers had no anti-bactericidal properties. In contrast, increasing the amount of silver NPs in nanofibers was accompanied by an increase in the antibacterial activity of the filter, which represented the strong antibacterial properties of silver NPs against gram-positive and gram-negative bacteria. In addition, the amount of silver NPs in the nanofibers along with the electrospinning time played an important role in improving BFE. According to the results, electrospinning time of 2–2.5 h and silver percentage of 12–12.5 could provide 99% filtration efficiency with good antibacterial properties (Selvam and Nallathambi 2015).

Xianhua et al. assessed filtration and air and moisture permeability in composite nanofiber mask materials in a recent study in 2020. The structure of this mask was composed of PVA nanofibers and silver NPs as well as non-woven activated carbon fabric as a substrate. In this structure, increasing the mass fraction of the silver NPs significantly increased the filtration efficiency (Xianhua et al. 2020).

Hiragond et al. also utilized silver NPs in dual concentrations to increase the antibacterial activity of conventional face masks in 2018. The results showed that a modified face mask with a solution of 100 ppm silver NPs with the average particle size of 10–15 nm had a higher antibacterial activity against...
highly resistant bacteria such as *E. coli* (Hiragond et al. 2018).

As shown in the previous studies, silver is an antimicrobial agent that can be highly toxic to resistant bacteria at low concentrations. Silver NPs are able to enter the bacterial cytoplasm by passing through the plasma membrane and lipid bilayer where they attack the DNA and eventually lead to the destruction and death of the bacteria (Hiragond et al. 2018; Palza 2015).

Nanomaterials can also be applied in the process of physical vapor deposition to form a gold catalyst containing a lattice of activated carbon coated with titanium oxide particles, in which gold nanoparticles are deposited. This catalyst is able to show high activity in different conditions (high and low temperatures and different humidity levels) as well as at high and low concentrations of carbon monoxide. In the study conducted by Croll et al. in 2010, this catalyst was employed to design and evaluate two personal protective breathing cartridges; one for escaping from carbon monoxide (CO) environments and the other for operational chemical, biological, radiological, and nuclear (CBRN) applications. The results indicated that nanogold CO oxidation catalyst was a suitable CO purification technology for respiratory protection cartridges (Croll et al. 2010).

To summarize this part, silver NPs are the most common and useful NPs in the design of masks and respirators. Thus, different chemical or green methods using plant or natural extracts can be applied to prepare silver NPs with different sizes of coating agents in future investigations. According to the review of the abovementioned works, metal NPs were useful due to their antimicrobial properties.

**Metal oxide and metal composite**

At present, metal oxide NPs have attracted the attention of many researchers due to their potential applications in various fields such as chemistry, medicine, biomedicine, and decomposition. Their various applications can be attributed to their abilities to change their specific size, which can alter their chemical, magnetic, conductive, and electronic properties (Chavali and Nikolova 2019; Samari et al. 2019). Metal oxide NPs can be used to improve the properties of face masks and respirators. In this context, their antimicrobial properties are often used.

A prior study was performed by Li et al. in 2006 to determine the antimicrobial activity of surgical masks with the simultaneous use of metal and metal oxide NPs. In that study, a mixture of silver metal NPs and titanium oxide was used to reduce the risk of emergence of silver-resistant microorganisms. The NPs were coated on one side of the mask fabric using a textile machine. The results revealed a 100% reduction of *E. coli* and *S. aureus* bacteria in the treated masks after 48 h of incubation. As a result, this mask did not cause any skin irritations for the users. However, there was no reduction in the non-treated masks. Surprisingly, the viable bacteria counts (cfu/g) increased by 25–50% after 24 h (Li et al. 2006a). In another study published by Li et al. in the same year, the protective performance of N95 respirators and surgical face masks was compared to that of their treated samples (Li et al. 2006b). The studied masks and respirators were coated according to the method described in Chinese patent number 03142467 (Li and Hu 2003). To reduce the risk of inhalation, the mixture of silver nitrate and titanium dioxide NPs was coated on the outer layer of the masks/respirators. The results revealed no statistically significant difference between the untreated and treated samples in terms of air permeability, water vapor, and breathability. Considering water repellency and antibacterial activity, however, there was a statistically significant difference between the coated and non-coated facemasks/respirators with NPs. Therefore, NP coating on facemasks/respirators could reduce the risk of infection transmission (Li et al. 2006b).

Sha et al. utilized nano-TiO₂ coating on silk-based respirator paper to attain a paper respirator with antibacterial and high dust filtration efficiency. In that study, the bacteriostatic efficiency of the silk paper increased by increasing the amount of nano-TiO₂ intercepted in the fiber network (Sha and Zhao 2012). Generally, coating the surface of the mask with photocatalytic materials can enhance its antibacterial properties. Among all semiconductor photocatalysts, TiO₂ is the most widely used one due to such properties as low cost, chemical stability, strong activity in photocatalytic reactions, non-toxic properties, and capability of coating as a thin film on a layer. In the paper respirator, a TiO₂-coated surface reacted directly or indirectly with cell components while being exposed to ultraviolet (UV), visible, or solar light, leading
to bacteria killing or prevention of bacterial growth (Zhang et al. 2018; Wahyuni and Roto 2018).

Hashmi et al., for the first time, used copper (II) oxide NPs as an antibacterial agent in a breathing mask in 2019. One of the reasons for selecting CuO nanoparticles was their good antibacterial properties and economic production compared to gold, silver, and copper NPs. The main purpose of that study was using copper oxide as an antibacterial agent. Thus, copper oxide was loaded at 0.25%, 0.5%, 0.75%, and 1% concentrations in the PAN nanofiber membranes. Based on the findings, the PAN/CuO nanofibers containing 1% CuO NPs significantly increased tensile strength. Besides, the addition of CuO NPs increased the antibacterial performance and improved air permeability of the breathing masks (Hashmi et al. 2019).

Following the COVID-19 pandemic, a report was published on the antiviral effects of a silver nanocluster/silica composite coating. This coating could be deposited on various surfaces including metal, polymer, glass, ceramic, and different filtering materials. The immunity of daily exposure to the SARS-CoV-2 was increased in crowded environments. The antiviral effects of this coating on the FFP3 respirators was investigated, and virus infectivity tests showed that it could reduce the titer of SARS-CoV-2 to zero (Balagna et al. 2020).

The application of metal oxide NPs or composites is limited in the literature. In addition to silver nano composite, TiO₂, and CuO NPs, there is enough space in this area for more modifications and applications. In spite of the useful properties of this nanomaterial, the nanotoxicity of some of these compounds should be taken into account during the design process.

Carbon nanomaterial

Because of the high surface area, unique adsorption property, and capability for functionalization, carbon nanomaterials have been applied in different masks and respirators. Previous studies conducted on carbon nanotubes (CNTs) including single-walled carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (MWCNTs) and their features have been presented in Table 2. Accordingly, Zou et al. evaluated the air flow resistance of filtration materials composed of CNTs and compared its bio-filtering efficiency to commercial FFRs (Zou and Yao 2015). Although most studied medical masks and N95 FFRs had approximately >90% and >99% filtration efficiencies, the SWCNT-0.20 filters had a considerably higher biological aerosol filtration efficiency compared to N95 FFRs and medical and activated carbon (AC) masks (87% and 70%, respectively) (Zou and Yao 2015).

Jahangiri et al. made a composition of an AC and carbon nanofiber (AC/CNF) in order to enhance the adsorption of volatile organic compounds (VOCs) by the AC adsorbent containing the organic vapor (OV) cartridges of the respirators. They evaluated the efficacy of the prepared adsorbents for the adsorption of VOCs like benzene, toluene, and xylene (BTX). Although the prepared cartridges from walnut shell-activated carbon met the minimum breakthrough time of 70 min based on the EN 14,387:2004 Standard, the results showed that the cartridges with CO₂ activated AC/CNF had a higher breakthrough time compared to those with walnut shell-based activated carbon with the same adsorbent weight (e.g., the cyclohexane breakthrough time: 117 vs. 85 min) (Jahangiri et al. 2013).

Shchegolkov et al. investigated the role of carbon nanostructures and graphene-modified paraffin as a heat exchanger in respiratory protective devices (RPDs). The results demonstrated that graphene could be utilized as one of the heat storage modifiers for RPDs since it generated pleasant conditions for users’ breathing by improving the cooling efficiency to around 24–40 °C (Shchegolkov 2017).

Carbon nanomaterials have been used as antibacterial elements in some kinds of mask. Huang et al. assessed the bacterial killing efficiency using laser-induced graphene (LIG). According to the results, the inhabitation rate of the bacteria was about 81% that reached 99.998% after combination with the photothermal effect within 10 min, which confirmed the safe usage of the masks (Huang et al. 2020). Based on this research, combination of some kinds of carbon nanomaterial with some metal or metal oxide NPs could enhance the antibacterial or even antiviral properties that could be useful for emerging microbial infections in the near future. Yet, further research in this field is warranted.

In the works discussed in this section, carbon nanomaterials were used as adsorption/removing elements in masks. Carbon nanomaterials have also been applied as sensing elements in gas masks. In the
| No | Nanomaterial type                        | Chemical composition                                           | Mask type                      | Size of nanomaterial | Target pollutant                  | Efficiency | Ref                                      |
|----|-----------------------------------------|----------------------------------------------------------------|-------------------------------|----------------------|-----------------------------------|------------|------------------------------------------|
| 1  | Polymeric/metal NPs composite nanofiber | Polyvinyl alcohol/silver nanoparticles composite nanofiber (PVA/AgNPs) | Particulate respirator        | D = 207 nm           | Particles and pathogens          | 92.60%     | Xianhua et al. 2020)                    |
| 2  | Polymeric nanofiber/metal NPs           | nylon6 nanofiber/silver nanoparticle                           | Surgical mask                  | N6 (D = 150–250 nm/ Th = 2 nm) AgNPs (D = 16 nm) | Bacteria (Escherichia coli) and nanoparticle | NR         | Khamis Aloufy and Abdel-Moneim El-Messiry 2013 |
| 3  | Polymeric nanofiber/metal NPs           | Polyacrylonitrile (PAN) nanofiber/silver nanoparticles          | Surgical mask                  | PAN (D = 257 nm) AgNP (D = 40–50 nm) Nanocomposite = 125 nm | Bacteria (S. aureus and E. coli) | 99%        | Selvam and Nallathambi 2015             |
| 4  | Metal NPs                               | Nano gold (as catalyst)                                        | Respirator cartridge for gases | NR                   | Carbon monoxide and chemical, biological, radiological, and nuclear (CBRN) situations | NR         | Croll et al. 2010)                     |
| 5  | Metal NPs                               | AgNPs                                                         | Surgical mask                  | D = 10–15 nm         | Bacteria (Escherichia coli and Staphylococcus aureus) | NR         | Hiragond et al. 2018)                  |
| 6  | NPs                                     | Mixture of silver nitrate and titanium dioxide                 | Surgical masks                 | D = <100 nm          | Infectious agents (Escherichia coli and Staphylococcus aureus) | 100% reduction | Li et al. 2006a)                      |
| 7  | NPs                                     | Mixture of silver nitrate and titanium dioxide                 | N95 respirator/surgical mask   | D = <100 nm          | Bacterial                          | NR         | Li et al. 2006b)                       |
| 8  | Metal oxide nanoparticles               | TiO2                                                           | Respirator mask                | G.S = 6 nm           | Bacteria                           | NR         | Sha and Zhao 2012)                     |
| 9  | Metallic nanocluster/composite nanomaterial | Silver nanocluster/silica composite                            | FFP3 respirator                | …                    | Coronavirus SARS-CoV-2            | NR         | Balagna et al. 2020)                   |
| 10 | Polymeric nanofiber + metal oxide NPs   | 99% polyacrylonitrile (PAN) nanofiber + 1.00% copper oxide NPs (PAN/CuO) | Breath mask                   | D = 197 nm PS = 17.5 Å | Microbe                           | NR         | Hashmi et al. 2019)                    |
study performed by Gao et al., a fiber gas sensor was fabricated from CNT-based sensing elements including SWCNTs, MWCNTs, and ZnO quantum dot-decorated SWCNTs (SWCNTs@ZnO). After that, the fiber gas sensor was integrated into face masks. The flexible smart face mask could distinguish some target gases including ethanol (C₂H₅OH), formaldehyde (HCHO), and ammonia (NH₃) at room temperature by reading the corresponding LED lights with different colors. The fiber gas sensor-integrated smart face mask had a good sensitivity and recovery time, long-term stability, high device mechanical bending ability, and excellent wearable functionality (Table 3) (Gao et al. 2018b).

### Conclusion remarks

Because of the significant advantages of nanomaterials in different branches of science and technology, their application for enhancing the filtration efficiency of RPEs cannot be ignored. Enhancement of the surface area in the filtration material and increase of biological activity against bacterial or viral infections can be expected from nanomaterials in RPEs (Fig. 3). Although some polymeric nanofibers, metal or metal oxide NPs or nanocomposites, and carbon nanomaterials have been used in RPEs, there is enough space for research on the application of other kinds of nanomaterial for increasing usability, regeneration after exposure, and efficiency against new viral infections such as SARS-Cov-2 in future. In this context, CA, PVDF, nylon, PAN, polysulfone, and PBI nanofibers can be denoted as the most common materials applied for the preparation of nanofibers or nanoporous materials in RPEs, which are commonly fabricated using electrospinning.

Another important point that should be considered in future research is the co-application of nanofibers and pure metal, metal oxide, or their composites, which can possess antibacterial or antiviral properties or enhance the selectivity of capturing target pollutants. There are also promising expectations from carbon nanomaterials such as carbon nanofibers, nanotubes, and graphene sheets as highly efficient substrates for capturing VOCs or particles for future studies. Overall, the great advantage of carbon nanomaterials is their compatibility in functionalization or

| Table 2 (continued) | Chemical composition | Mask type | Efficiency | Size of nanomaterial | Target pollutant | Mask type | Size of nanomaterial | Target pollutant | Efficiency | Ref |
|----------------------|----------------------|-----------|------------|---------------------|-----------------|-----------|---------------------|-----------------|------------|-----|
| 11                   | Nanofibrous material (polymeric nanofiber/carbon nanomaterial) | Respirator mask | NR | NR | Bacteria and virus | NR | NR | Bacteria and virus | NR | NR | Ahmed et al. 2020 |
Table 3  Application of carbon nanomaterials in the production of various types of masks and respirators

| No | Nanomaterial type | Chemical composition | RPE type | Size of nanomaterial | Target pollutant | Efficiency | Ref |
|----|-------------------|----------------------|----------|----------------------|-----------------|------------|-----|
| 1  | Single-walled carbon nanotube (SWNT) | Carbon nanomaterial | Respirator mask | \(D = 1 \text{–} 2 \text{ nm} \quad L = 10 \text{–} 30 \text{ mm}\) 0.2 mg/cm\(^2\) CNT loading | Biological aerosols, aerosols, and particles | 87% 70% | Zou and Yao 2015 |
| 2  | Nanotubes (SWCNT—MWCNT—ZnO quantum dot@ SWCNT) | Carbon nanomaterial | Smart sensing mask with gas sensor | NR | C\(_2\)H\(_5\)OH, HCHO, and NH\(_3\) | NR | Gao et al. 2018b |
| 3  | Nanofiber | Carbon nanomaterial | Respirator cartridge | \(D = 10 \text{–} 20 \text{ nm} \quad \text{P.S} = 3.84 \text{ Å}\) | VOCs, such as benzene, toluene and xylene (BTX) | NR | Jahangiri et al. 2013 |
| 4  | Graphene | Carbon nanomaterial | Portable respiratory devices | O.D = 2–70 nm \(L > 2 \text{ um}\) | – | NR | Shchegolkov 2017 |
| 5  | Laser-induced graphene | Carbon nanomaterial | Surgical mask | NR | Bacteria | 81% | Huang et al. 2020 |
| 6  | Nanofibrous material (polymeric nanofiber/metal oxide/carbon nanomaterial) | Matrix of polylactic acid and cellulose acetate containing copper oxide NPs and graphene oxide nano sheets (CuONPs/GO@PLA and CuONPs/GO@CA nanofibers) | Respirator | NR | Bacteria and virus | NR | Ahmed et al. 2020 |

Fig. 3  Different kinds of nanomaterial from various chemical natures, shapes, and sizes for improving the protection efficiency of PPE
modification during grafting with other nanomaterials or organic/polymeric reagents.

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Declarations

Conflict of interest The authors declare no competing interests.

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