



Materials in advanced design of personal protective equipment: a review

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ABSTRACT

The outbreak of the Covid-19 pandemic has aroused tremendous attention toward personal protective equipment (PPE) in both scientific research and industrial manufacture. Despite decades of development in PPE design and fabrication, there's still much room for further optimization, in terms, of both protection performance and wear comfort. Interdisciplinary efforts have been devoted to this research field in recent years. Significantly, the innovation of materials, which brings about improved performance and versatile new functions for PPEs, has been widely adopted in PPE design. In this minireview, recent progress in the development of novel materials and structural designs for PPE application are presented in detail with the introduction of various material-based strategies for different PPE types, as well as the examples, which apply auxiliary components into face masks to enrich the functionalities and improve the personal feelings in the pandemic period.

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1. Introduction

The Covid-19 pandemic has dramatically changed the world since its outbreak at the end of 2019. Up to now, more than 184 million people have been infected, with 3.98 million deaths caused worldwide [1]. Despite the recent development of vaccines, which are still skeptical in preventing infections and causing side effects, the most effective approach to slow down the spread of the Covid-19 coronavirus is to wear PPEs, which include not only face masks and shields for ordinary people but also protective clothes and glasses for medical workers surrounded by a high concentration of the coronavirus. In this context, the research of PPE has been greatly boomed. According to the searching result in Web of Science, the PPE related literature has been dramatically ramped up from 357 in 2019 to 1734 in 2020 indicating the unprecedented enthusiasm in this field amongst the scientific society. Besides, PPE manufacture is also an industry worth billions of dollars. The productivity of face masks in China has reached more than 110 million

per day in 2020 [2] and will be sure to continuously increase before the attenuation of the pandemic.

Except for the PPEs for coronavirus protection, there are multiple types of PPEs applied in various scenarios, such as the armors and helmets for the protection from mechanical impacts, respirators and gloves to resist the chemical toxicants, as well as protective clothes to block the thermal hazards and electromagnetic radiations. Each of them has undergone at least several decades of development and commercial products have been massively manufactured. However, there is always room for progress in PPE design and fabrication. For example, surgical masks, which most people wear in this pandemic, have high filtration efficiency only toward particles larger than 300 nm [3], while the coronavirus is 65–125 nm in diameter [4], which could still penetrate through the surgical mask and infect the wearer. The N95 masks have better filtration efficiency toward small particles, while it could also block the air flow for breath, and the wearer could develop both physiological [5] and psychological syndromes [6] after long-term use of N95 masks. Therefore, there's great motivation for the optimization of face masks to achieve high filtration efficiency while maintaining breathability. Besides, the insufficient protection property, high weight and bulkiness, as well as the low breathability and long-term durability also necessitates the innovation in PPE design. On the other hand, smart elements could be introduced to PPEs to bring in new functions to assist the protection process, such as

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sensors and energy harvesters. The development of PPEs is an interdisciplinary subject combining materials science, textile engineering, ergonomics and medical science, and so on, which aims to protect people from various hazards to the most extent.

In this minireview, recent advances in the novel strategies to improve PPE performance in recent years will be discussed. We will first provide an overview of the materials and structural designs for personal protective application, divided by different PPE types. Then we will give an introduction to the state-of-the-art commercial masks with auxiliary designs, which represents the recent efforts in developing smart PPEs for everyday use. This minireview is ended by the discussion of the prospects and challenges in future PPE design and optimization.

2. Functional materials and structural design for improved PPE performance

Despite the wide application of PPEs in various occupational and civil scenarios, there are still great efforts to develop new materials and structures for improved protection performance. In this section, we will introduce the materials in advanced PPE design in recent years, which is divided based on the specific PPE type.

2.1. PPE with mechanically functional materials and design

PPEs against mechanical impacts, such as helmets and armors, are essential in both military and civil applications. There are two basic requirements in the design of mechanical PPEs. The first is enough strength to prevent the PPE from broken apart, and the second is the capability to absorb the impact energy so that the load transferred to PPE wearers could be minimized.

In ancient society, armors are the most common type of mechanical PPE for the abundance of wars. To effectively avoid the penetration of spears and bullets, the armors are usually made of intrinsically hard materials with high mechanical strength, such as metals and ceramics. However, owing to their undeformable nature, the impact load could be ballistically transferred to the wearer, which still causes injury. Besides, the rigid and heavy armor could cause dramatic discomfort to the soldier by limiting his mobility. In modern society, safety helmets have been increasingly used to protect the wearer against the impact of high-velocity or high-weight objects. Typically, the safety helmets are comprised of the rigid outer shell, which is made of stiff plastics such as polycarbonate and acrylonitrile butadiene styrene, and buffer layer, which is made of deformable paddings such as polyurethane (PU), and expanded polystyrene [7]. In recent years, polymers reinforced by high modulus fibers are also applied in assembling the mechanical PPEs for improved strength and reduced brittleness compared with plastics. Composites with high mechanical performance have been prepared by embedding aramid fibers, polybenzoxazole fibers, carbon fibers, and glass fibers, and so on into polymer matrix [8,9]. And the mechanical properties of the final composites are dramatically affected by the continuity, as well as the weaving architectures of the fibers [10,11]. Compared with single-component polymers, the preparation of fiber reinforced composite is relatively laborious, especially for the synthesis of fibers. Recently, Lin et al. [12] tackled this issue by extracting Kevlar fibers and low-melting polyester (PET) fibers from the selvage of discarded fabrics and assembled these recycled fibers together with nylon fiber into a non-woven fibrous network. A sandwiched structure was constructed by enclosing the high strength PET interlayer with two as-prepared fibrous networks (Fig. 1a and b) [12]. Together with the dramatic advantage in the reduction of feedstock consumption and textile waste, the resulted composite also demonstrates optimal burst strength and tensile strength of

1957 N and 425 N. The lightweight, environmentally friendly and mechanically robust composite serves as a promising candidate in mechanical PPE application.

For materials as mechanical supports, there's usually a trade-off between mechanical strength and flexibility. The tradeoff could be effectively overcome by the introduction of shear thickening fluids (STFs). STFs are usually concentrated colloidal suspensions. Upon the infliction of shear force, the suspended particulates could aggregate which dramatically increase the viscosity of the suspension [13]. Therefore, STFs-based mechanical PPEs provides simultaneously more flexibility and comfort in daily wear and enough protection upon mechanical impact. Fowler et al. [14] encapsulated an STF composed of silica nanoparticles and poly (ethylene glycol) into a spacer fabric, which decreases the peak force by 66% upon impact, compared to the pure fabric. Because STFs sometimes brings about problems in sealing because of their liquid nature, a solid-state shear-thickening gel was developed and impregnated into the Kevlar fabric for ballistic protection (Fig. 1c) [15]. With the addition of carbon black into the gel, the composite could not only adsorb 21.6% of the impact energy (Fig. 1d) but also monitor the impact intensity through the change of electrical resistance when integrated into a protective helmet.

Except for the selection of material, novel structural designs have also been adopted for reinforcing the mechanical strength, absorption of more impact energy, and prevention of crack propagation in PPEs. Because a porous structure usually has a lower modulus than its bulk counterparts, it could deform both elastically and plastically in a controlled manner under the impact, which efficiently absorbs and dissipates the input mechanical energy [16]. Foam structures with uniform and periodic porosity are relatively easy to be prepared, while they could still collapse under high load due to the global buckling behavior. In comparison, a hierarchical graded porous structure demonstrates higher strength and energy absorption ability because of the structural response to compressive stress by stages [17]. That is, when the compressive stress is small, the softer parts of the graded structure undertake the main deformation, while with the increase of stress, the stiffer parts begin to deform. Such behavior renders a better-organized structural adaption toward the applied pressure and more sufficient absorption of the input mechanical energy [18,19]. With the development of additive manufacturing, various complex hierarchical structures with microscale feature sizes could be facilely prepared [20–23]. The graded honeycomb structure could also be applied as a liner of a helmet demonstrating nearly twice the energy absorption rate and 37% lower transferred load than homogeneous honeycomb structure [24]. On the other hand, reinforcement of the foam structure by continuous cushioning fillers could efficiently improve the structural stability without much sacrifice in flexibility [25]. For example, the filling of flexible PU into the pores of 3D printed polylactide (PLA) lattice could decrease the jerk by 9%, displacement by 17% and increase the energy adsorption by 23% under the impact at an expense of 21% mass increase [26].

Despite the high mechanical strength for anti-impact PPEs, small defects inevitably exist within them, which could develop into cracks upon mechanical impacts. To this end, there are also novel designs to improve the fracture toughness of the anti-impact PPEs. The introduction of a discontinuous staggered structure could be a solution, for the crack propagation could cease at the interface between staggered layers. Inspired by the structure of conch shells, a 3-layer prototype was prepared by 3D printing in 2017. (Fig. 1e and f). Within each layer, stiff VeroMagenta plastic serves as the base, with soft Tangoblackplus rubber lamellae periodically sandwiched within the VeroMagenta plastic. For the restraint of crack propagation, the orientations of the Tangoblackplus rubber

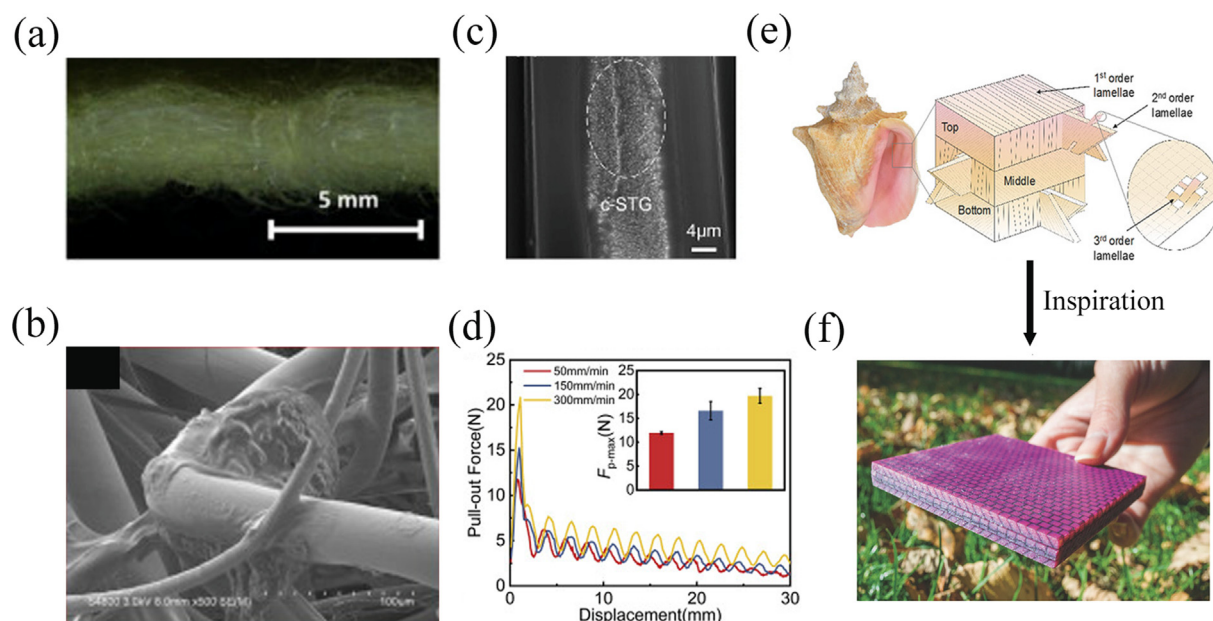


Fig. 1. Mechanically functional PPEs. (a) Nylon/Kevlar/low melting point fibers non-woven surface layer after annealing treatment. (b) The SEM image of the fiber reinforced structure. Reprinted with permission from the study by Lin et al. [12] (c) The SEM image of shear thickening gel infiltrated Kevlar fabric. Reprinted with permission from the study by Zhao et al. [15] (d) The damping of impact force by shear thickening gel infiltrated Kevlar fabric. Reprinted with permission from the study by Zhao et al. [15] (e) The schematic of the three-tier cross lamellar structure for conch shell. (f) The man-made 3D printed three-tier cross lamellar structure. Reprinted with permission from the study by Gu et al. [20]. PPE, personal protective equipment; SEM, scanning electron microscopy.

lamellae in each layer are staggered by 45°, so that the propagated cracks could be arrested at the interface between layers [20]. The 3-layer hierarchical structure demonstrates 85% and 70% higher energy absorption than the bulk VeroMagenta plastic and 1-layer sandwich structure, respectively. One drawback of this prototype is that cracks could still propagate freely within each layer. Recently, Wu et al. [27] developed a fibrous Bouligand structure with fibrils lamellae twisted continuously over depth, like a spiral stair. The propagation of cracks follows the twisted lamellae which absorb greatly increased energy than propagating in a straight line so that the crack toughness is dramatically improved.

2.2. PPE with chemically functional coatings

Chemical hazards are ubiquitous in many occupations. For example, doctors should be protected from the viruses and bacteria in the aerosol around the hospital; soldiers should stay away from chemical warfare agents (CWAs) on the battlefield; environmental workers should reduce the inhalation of volatile organics. Even ordinary human beings also suffer from growing air and water pollution. Therefore, great efforts have been devoted to the design of novel PPEs for chemical protection. Reducing the pore size of face respirators and chemical protection clothes down below the particulate size could isolate the protege from certain chemical hazards, such as microorganisms, while it also brings difficulty in breathing and releasing the thermal stress [28]. Materials with high surface area, such as activated carbon [29], have been commonly applied for assembling face masks and chemical protective clothes due to the strong physical adsorption ability and low fabrication cost, while the low filtration efficiency, the easy saturation by non-toxic adsorbents, as well as the risk for secondary toxicant release, still restricts its application in high-risk occupational circumstances. In this section, we focus on PPEs that could chemically interact with the chemical hazards by permanently convert the toxicants into harmless agents or generate alert signals to the proteges.

PPEs with different chemical modifications are usually applied for different target toxicants for protection. Metal-organic framework (MOF), which contains metal nodes bridged by organic ligands, have been widely applied for assembling the chemical protective clothing for their high porosity, chemical stability and abundant functionalization sites [30]. Among various MOF types, Zr-based MOFs, such as UiO-66-NH₂, are particularly suitable for the degradation of organophosphate-based CWAs [30–33]. One issue concerned in the application of MOF in PPEs is the poor adherence between the modified MOFs and the underlying fabric. To this end, an oxide-based interlayer could be introduced to anchor the MOF molecules. For example, a highly efficient CWA protective fabric could be obtained by conformally coating a polyamide-6 fiber mat with atomic layer deposited TiO₂ film, followed by *in situ* growth of UiO-66-NH₂ (Fig. 2a) [32]. The as-prepared CWA protective fabric could decompose the nerve agent soman by 50% in merely 2.3 min (Fig. 2b). Since the introduction of rigid oxide layer decreases the flexibility of the PPEs, alternative solutions include directly mixing the MOF and fiber precursors followed by electrospinning [34,35], as well as using hot pressing to ensure strong bonding between MOF and fibers [35]. Besides, the warning function could also be introduced in MOF modified chemical protective clothes. Making use of the decolorization of the toxicants during the degradation process, the functionality of the chemical protective clothes could be real-time monitored [36]. The introduction of colorimetric warning dramatically alleviates the potential danger from the dysfunction of the PPEs.

Antimicrobial PPEs are essential to protect medical workers from possible infections. Deposition of Ag nanoparticles (AgNPs) on polymeric fiber mats is a simple way to endow antimicrobial properties on PPEs [37,38], while the antibacterial tests for AgNPs coated PPEs are usually conducted in solution, the performance in a gaseous environment is doubtful. Organic macromolecules with nitrogen-halogen moieties usually demonstrate strong oxidative properties by releasing oxidative halonium ions in an aqueous environment [39] and could be decorated onto fiber mats for

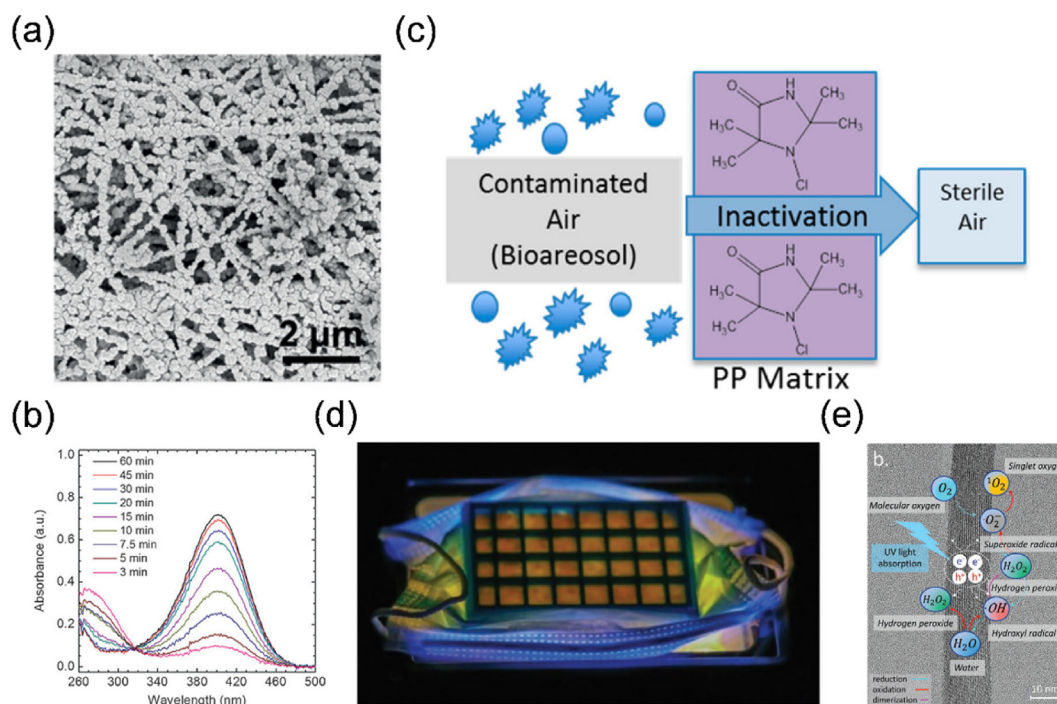


Fig. 2. Chemically functional PPEs. (a) The SEM image of Zr-based MOF on a polyamide-6 fiber mat. (b) The degradation of CWA with time. Reprinted with permission from the study by Zhao et al. [32]. (c) The schematic for the deactivation of airborne pathogens by H-halamine. Reprinted with permission from the study by Demir et al. [42]. (d) A face mask integrated by TiO₂ nanowire network. (e) The mechanism for the photocatalytic degradation of microbial targets. Reprinted with permission from the study by Horvath et al. [45]. CWA, chemical warfare agent; PPE, personal protective equipment; SEM, scanning electron microscopy.

antimicrobial applications [40,41]. Among various macromolecules of this type, N-halamine is most commonly applied despite its weak intrinsic toxicity [39,42]. In contrast with AgNPs, ion release by N-halamine could take place using the environmental humidity, facilitating its application for inhalation protection (Fig. 2c) [42]. To further enhance the biosafety and environmental friendliness of the antimicrobial PPE, textiles functionalized by botanic extracts have been designed [43,44]. With natural antimicrobial ingredients such as phenolic compounds, some bionic extracts are lethal to a variety of microorganisms. Usually, the bionic extracts are volatile and easily oxidizable, which necessitates proper encapsulation for a controlled release and lasting functionality. Compared with N-halamine, the efficiency for bacteria-killing is far inferior for natural bionic extracts (hours vs days), indicating that PPEs with bionic extracts could only be used in the ambient environment and not suitable for pathogen abundant environments, such as hospitals.

Except for using the intrinsic chemical reactivity for degrading the toxicants, there are also chemical PPE designs relying on external stimulus, mostly light, for the generation of reactive oxygen species (ROS), which could attack pathogens and organic toxicants and protect the PPE wearers. A prominent advantage of photocatalytic detoxification is the rechargeability of the reactivity, which is different from the abovementioned chemical reagents, which are irreversibly consumed by toxicants. A face mask integrated with TiO₂ nanowire networks was prepared by Horváth et al. (Fig. 2d), which could deactivate various pathogenic viruses under UV illumination (Fig. 2e) [45]. Because the percentage of UV in solar radiation is very low, the applicability of the TiO₂ nanowire integrated mask is limited. A rechargeable daylight driven bioprotective nanofibrous membrane could be achieved through modifying electrospun PVA-co-PE film with benzophenone derivatives, which could efficiently generate ROS under visible light [46]. The bactericidal and virucidal efficiency reaches 99.9999% and 99.999%, respectively. Moreover, the ROS generated by light could be stored, which still kills pathogens under dark conditions.

Although versatile chemical PPEs have been designed and prepared by introducing functional coatings to conventional textiles, the long-term functionality should also be further evaluated for the possible degradation and detachment of the functional coating. Besides, the cost issue also needs to be considered before the substitution of passive PPEs by chemically functionalized PPEs in practical scenarios. For the future research of chemical PPEs, the combination of detoxification and sensing of the chemical hazards could be further explored.

2.3. PPE with electrically functional materials

The introduction of electricity to PPEs, whether by building a functional electrical circuit or generating electrical charges on them, could dramatically enrich the functionality of PPEs. In this section, three scenarios of electrically functional PPEs are introduced. First, a smart PPE could be endowed with a sensing function, which could either detect the external stimulus or record the physiological signals of the wearer. Second, PPEs could be integrated with energy harvesters to provide the power supply of essential electrical devices. Third, tribo/piezoelectric charges could be induced in air filters which benefits the adhesion of particulate matters (PMs).

As illustrated in the last section, toxic gases have been a serious threat in many occupations. Although chemical PPEs could isolate or detoxify them to protect the wearer, there's still danger from the unconscious failure of the PPEs. Quick and reliable detection of toxic gases could effectively assist the protection process by warning people of the chemical hazards in the surroundings for which gas sensor integrated PPEs have been developed. Carbon nanomaterials, such as carbon nanotube (CNT) and graphene, have been widely adopted in building chemical sensors for the adsorption of analytes dramatically affects the carrier transport within the nanostructures [47,48]. To prevent the exfoliation of carbon nanomaterials from the textile substrate, Wang et al. [49] directly

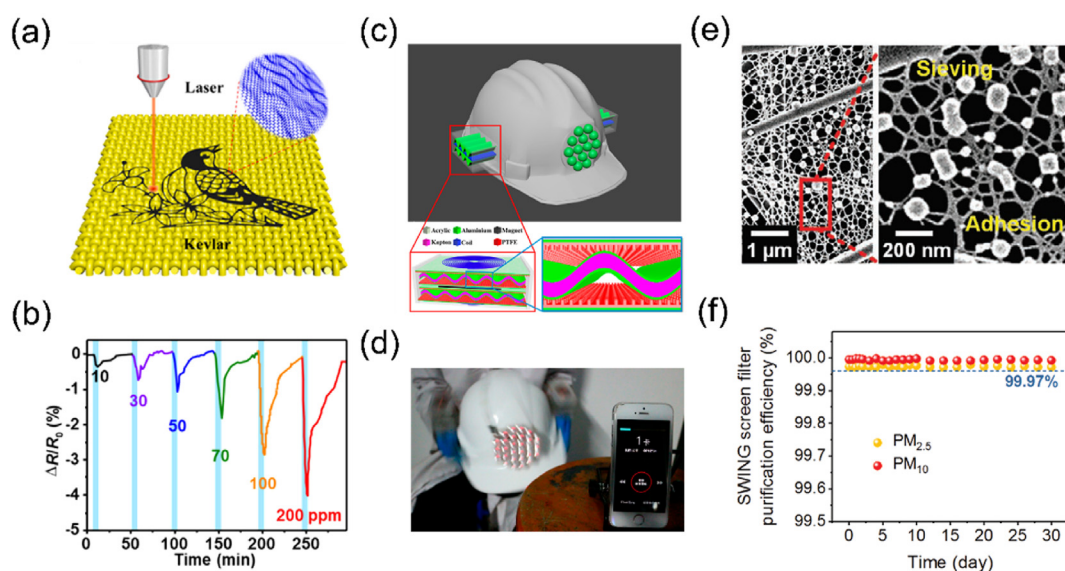


Fig. 3. Electrically functional PPEs. (a) Schematic for the preparation of graphene on Kevlar fabric by laser writing. (b) The electrical response of graphene/Kevlar textile to different NO_2 concentration. Reprinted with permission from the study by Wang et al. [49]. (c) The schematic of TENG integrated helmet. (d) The photo showing TENG integrated helmet powering LEDs and a wireless pedometer. Reprinted with permission from the study by Jin et al. [58]. (e) The SEM image showing the PMs adhered on PVDF fiber mat. (f) The long-term filtration efficiency for $\text{PM}_{2.5}$ and PM_{10} by PVDF fiber mat. Reprinted with permission from the study by Zhang et al. [61]. PM, particulate matter; PPE, personal protective equipment; TENG, triboelectric nanogenerator.

transformed Kevlar fabric to graphene at pre-defined positions through laser irradiation (Fig. 3a). The *in situ* carbonization process guarantees a seamless bonding between graphene and the underlying substrate. A self-powered NO_2 sensor based on the graphene/Kevlar fabric was integrated into a face respirator which has a low detection limit of 10 ppm (Fig. 3b). On the other hand, gas sensor integrated PPEs should be capable to distinguish different toxic gases and avoid crosstalk. To this end, a smart face mask that could separately detect ethanol vapor, methanal and ammonia gas was developed [47]. The three gas sensors are constructed by coating a nylon fiber with single-walled CNTs, multi-walled CNTs and Zn nanoparticles decorated single-walled CNTs, respectively, followed by weaving the fiber sensors into a face mask. Each sensor is sensitive to one type of toxic gas and insensitive to the others so that the three types of gas could be separately distinguished.

The mechanical impact to the head could be lethal. The measurement of the impact force is significant for both medical treatments of the injured person and investigation of the accident. Typically, the operational range of most piezoresistive and capacitive pressure sensors is in kPa level, while the impact force during an accident could reach several MPa. Therefore, a pressure sensor with an extended operational range should be designed. Wang et al. [50] encircled the side face of a cylinder PDMS by a fabric strain sensor, which could record the normal pressure within the range of 0–8 MPa with a sensitivity of 1 MPa^{-1} . Such pressure sensor could be integrated into helmets or armors for measuring impact force. Furthermore, a feedback system could also be introduced for better protection from blast triggered impact [51].

For people working in a harsh environment, real-time monitoring of their physiological parameters is essential to guarantee their well-being. Besides, the high weight and low breathability of PPEs could inflict much mechanical and thermal stress to the wearer, which also necessitates physiological monitoring to avoid the heatstroke and asphyxia of the wearer. Breath flow monitoring could be achieved through the design of a smart face mask integrated by piezoresistive [52] or triboelectric [53,54] pressure sensors, which could reflect both the respiration condition of the

wearer and the functioning status of the face mask. PPEs capable of comprehensive physiological monitoring are also developed by integrating various sensors, such as temperature sensor, heart rate sensor, respiration sensor and motion sensor into the PPEs [55,56]. With advanced computing technologies and artificial intelligence (AI), a comprehensive assessment could be made for the PPE wearer so that timely feedback is provided before the occurrence of severe health problems.

Further efforts in sensor integrated PPEs lies in the display, storage and transmission of the sensing data so that the wearer himself or the supervisor could readily get the information and take measures. The integration of LEDs [47] or electrochromic devices [57] could be a solution for visible demonstration of the data, while they are still too rough in displaying the result. Reliable data transmission necessitates advanced connectivity solutions, such as Bluetooth, WIFI and mobile network (5G). Intelligent sensing systems with decision making and feedback ability is also being pursued with improved functionality and reduced size.

For people working in remote areas, there could be a serious deficiency of electric power, which brings great inconvenience and even danger to them. Because batteries are usually bulky and heavy which are suitable to carry along, the utilization of biomechanical energy could be a novel solution to provide an essential power supply. PPEs could be applied as the platform for the integration of generators. For example, a triboelectric nanogenerator (TENG) and an electromagnetic generator (EMG) made by the double-deck structure of Al-Kapton-Al could be integrated into a safety helmet, which could harvest the biomechanical energy from head motion (Fig. 3c) [58]. After AC-DC transformation by rectifiers, the TENG could power an LED and a wireless pedometer (Fig. 3d). Generators could also be mounted on gloves, which collect the biomechanical energy from hand motion [59,60]; and masks, which harvest the mechanical and thermal energy of the respiration airflow [54]. In all, generators within PPE could bring about life-saving significance to the wearer working in a harsh environment, while the necessity of rectifying devices and low power output could be the limitation for biomechanical energy harvesters.

The most common and efficient approach for the filtration of PMs is to wear face masks. However, there's always a tradeoff between filtration efficiency and air permeability in the design of pore size for face masks. The introduction of electrical potential within face masks could dramatically improve the filtration efficiency of PMs by electrostatic adsorption (Fig. 3e and f) [61], without losing much breathability. The typical approaches to introduce electrical potential in face masks include mounting TENGs [62,63] and integrating electret materials (PVDF, BaTiO₃ et al.) [61,64,65], by which a voltage of several hundred volts could be generated under the respiration airflow. Because in both ways, the generated electrical potential increases with the speed of airflow, which further raises the adsorption efficiency of PMs, the deterioration of filtration efficiency under high-speed airflow could be largely prevented [61]. Despite the advantages above, the adsorption of PMs could clog the porous fiber mats, leading to degraded performance after long-term operation.

2.4. PPE with thermally functional materials

Thermal hazards are common for many occupations, such as firefighting and the metallurgical industry. Besides, as mentioned in previous sections, the long-time wearing of PPEs could bring about much thermal stress and discomfort to the wearer causing the rise in body temperature and heart rate, which may further lead to heatstroke and cardiovascular diseases [66,67]. PPEs with thermal insulation interlayers could isolate the wearer from the environmental heat, while the thermal stress is even harder to be released from the wearer [68–70]. To this end, thermally functional materials, as well as structural designs have been introduced to PPEs to overcome this tradeoff so that both external and internal heat could be kept away from the human body. In this section, two types of thermally functional PPEs will be introduced, one is PPEs integrated with heat-absorbing materials, including phase change materials (PCMs) or liquid coolant; the other is PPEs with engineered pore structure which could dissipate heat through thermal radiation.

Because the phase change process of PCMs could absorb or release much heat without temperature change, the PCMs could be regarded as a thermal reservoir that helps to stabilize the local temperature upon massive heat input. PCMs could be integrated into protective clothes and helmets to block thermal hazards in a specific workplace. The thermal protection performance of PCM-based thermal liner depends dramatically on the phase change temperature and latent heat, which necessitates the careful selection of PCM type. With phase change temperature close to skin burn temperature and high latent heat, paraffin is the commonest PCM type in PPE application [71]. In addition, the phase change in the temperature of paraffin could be tuned by changing the number of carbon atoms for fitting the application in different scenarios. Pure paraffin usually has low thermal conductivity, causing insufficient absorption of heat. To this end, fillers with high thermal conductivity could be added, such as graphene, CNTs and metal nanoparticles [72]. Besides, because paraffin is not fire retardant, it should be encapsulated when applied in firefighting clothes [71,73].

Liquid cooling is a common strategy for thermal protection of industrial facilities, which is also applied in the design of thermal PPEs. Water-containing channels could be knitted into cotton fabrics, which resulted in a liquid cooling garment [74]. The liquid cooling garment could resist temperature rise by not only the high heat capacity but also the circulation of water to carry local heat away. High electrical voltage up to several kV could be applied to accelerate the circulation of dielectric coolant in a stretchable pump, while the safety issue should be considered (Fig. 4a) [75].

Skin simulant with penetrating channels connecting a water reservoir was also prepared, which serves as an artificial sweating system under heat exposure [76]. The evaporation of sweat could dramatically enhance energy absorption, as well as weight reduction of the whole system.

Radiative heat transfer contributes greatly to the thermal exchange between the human body and the outside world. Because the human body could dissipate heat by emitting infrared radiation with wavelength ranging between 7 and 14 μm , there is also designs in PPE to boost this radiative cooling process for personal thermal management. In 2016, Hsu et al. [77] first developed this idea by preparing a nanoporous polyethylene (PE) membrane with pore sizes ranging from 50 to 1000 nm. Because of the comparability in feature size, visible light is scattered by this membrane which renders the membrane opaque in naked eyes. On the other hand, PE contains mostly C–C and C–H bonds with narrow absorption peaks around certain wavelengths (3.5 μm , 6.8 μm , 13.9 μm). Therefore, it is transparent to most IR radiation which facilitates the dissipation of heat (Fig. 4b and c). As a result, the skin temperature covered by the PE membrane is 2.7 °C lower than that covered by cotton (Fig. 4d). Compared with IR transparent materials, IR emissive materials could actively absorb heat and convert it to IR radiation, which enables the dissipation of heat from both external environment and the human body [78]. For the blockage of radiant heat flux in the specific working scenario, such as firefighting and metallurgical industry, increasing the reflectance of thermal PPEs by deposition of metal nanoparticles could be adopted [79,80].

Despite the rapid development in the design for thermal PPE, there are still limitations in the as-mentioned systems. The introduction of PCMs and cooling liquid brings about extra weight for the PPE wearers, which could induce ergonomic problems. Besides, the encapsulation of PCMs and cooling liquids should be meticulously conducted for their leaking could bring danger to the wearer. For the radiative cooling system, there might be a privacy concern for the IR transmissive membrane could be transparent under the IR camera.

2.5. PPEs functionalized by anti-radiation materials

UV radiation, taking up ~5% of total solar radiation, could partially penetrate through the ozone layer and harm the skin of ordinary people. Besides, hazardous radiations, such as UV, X-rays, and high-power lasers, are common in many working scenarios (e.g. medical tests, materials processing and characterizations, optical communications). PPEs for radiation shielding have been developed for both specialized and civil use. For textiles without a specific anti-radiation design, a high textile thickness and compactness is needed for complete radiation blockage, which dramatically increases the discomfort for the wearer [81]. Therefore, novel materials for absorbing electromagnetic radiation, especially UV, could be introduced for building the anti-radiation PPEs.

The radiation shielding materials could be divided into inorganic and organic ones. The mechanism of radiation shielding in inorganic systems is the absorption of the electromagnetic wave for the transition of electrons from the valence to the conduction band. Because of the proximity between the bandgap and the UV energy, TiO₂ (3–3.2 eV) and ZnO (3.37 eV) are the most commonly used inorganic UV shielding materials so far [82]. Because the adhesion between inorganic oxides and textiles is usually poor, the oxides could be hybridized with organic matrices, such as PET, before coating on the textile substrate for UV blockage [83]. Besides, strongly bonded ZnO nanowires on cotton fabrics could be

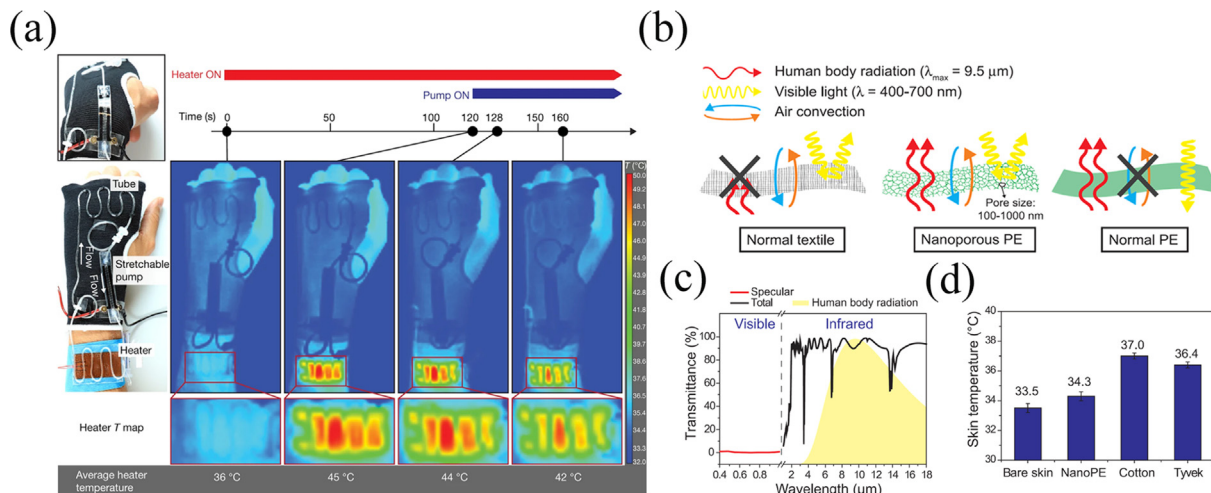


Fig. 4. Thermally functional PPEs. (a) Stretchable pump integrated into a glove for thermal regulation. Reprinted with permission from the study by Cacucciolo et al. [75] (b) The schematic for the comparison of normal textile, nanoporous PE and normal PE film in terms of transmittance of human body radiation, visible light and air. (c) The transmittance spectrum of nanoporous PE within the visible and infrared range. (d) The comparison of skin temperature by different coverings under constant heating. Reprinted with permission from the study by Hsu et al. [77]. PE, polyethylene; PPE, personal protective equipment.

achieved by *in situ* growth process. The ZnO nanowires deposited on the inner surface of cotton fibers are durable upon more than 50 washing cycles, retaining a high ultraviolet protection factor of 100 [84]. On the other hand, inorganic coatings are usually rigid and undeformable. To this end, Liang et al. [85] designed a stretchable UV shielding skin by layer-by-layer assembly of electrospun PU fiber mat and spray coated TiO₂ layer (Fig. 5a). The UVF of the UV shielding skin reaches 10,810 at 0% strain and still maintains 5685 at 200% strain (Fig. 5b and c), thanks to the recoverable sliding of fibers under strain. A potential drawback of this system could be the low breathability because of the densely packed structure leading to poor wearing comfort. As for the protection against electromagnetic waves with higher energy than UV, such as X-ray, heavy metals could be adopted in PPE design [86].

Compared with inorganic radiation-shielding materials, the organic ones could be directly made into fiber mats or combined with existing textile substrates with high affinity rendering improved durability for the resulted anti-radiation PPEs. Organic UV shields usually contains aromatic structures with carbonyl groups which demonstrates conformational change upon UV absorption [82]. However, chemical reactions are usually accompanied by conformational change, which could release detrimental chemicals and ROS, leading to harm to the human skin. Besides, the ultraviolet protection factor for organic UV shields is usually below 100, which is inferior to the inorganic ones [87,88].

For the future development of anti-radiation PPEs, there should be multiple considerations except for improving the protection efficiency. The safety issue should be taken into a prioritized account, considering the possible permeation of inorganic nanoparticles into the skin, as well as the detrimental decomposition products for organic radiation shielding materials. Besides, the ergonomic and esthetic issue also needs to be considered, especially for the civil UV shielding applications.

3. Functional designs of masks in pandemic period

Thanks to the advanced novel materials applied in PPE fabrication in laboratory research, many PPE manufacturers have turned scientific advancement into commercial products. Especially, after the outbreak of the Covid-19 pandemic, face masks have been a must in everyone's daily life [89]. While the negative influence of face masks on people's comfort, as well as the communications between people, has motivated the design of smarter face masks, which provide auxiliary functionality besides passively isolating the coronavirus. In this section, commercial face masks with auxiliary functional components are introduced, which could represent the new trends in industrial PPE development.

Wearing masks hinders the communication between people by both muffled speech and coverage of facial cues. Transparent face masks made of plastics have been prepared [90]. While at the expense of low wearing comfort because of the poor air permeability and large mechanical mismatch with skin, the plastic mask facilitates only facial expressions in the environment with enough brightness. Aiming to further facilitate the communication between people behind the mask, a company named Razor developed

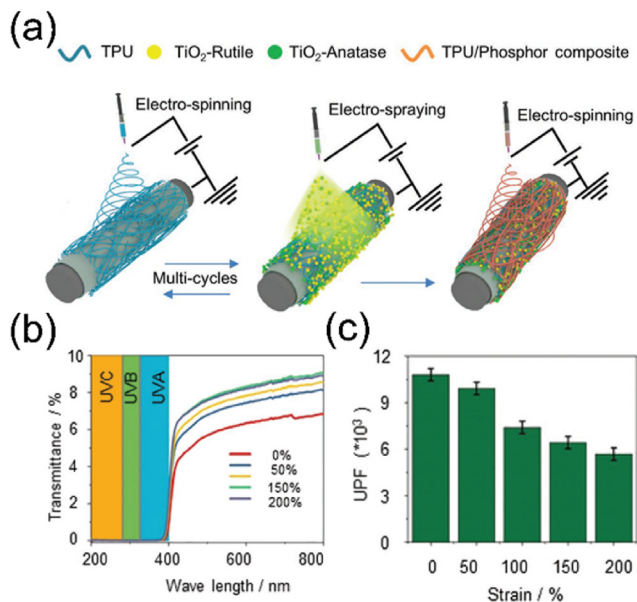


Fig. 5. Anti-radiation PPE. (a) The schematic for the fabrication of the UV shielding skin. (b) Transmittance spectrum of the UV shielding skin under different tensile strain. (c) UPF value of the UV shielding skin under different tensile strain. Reprinted with permission from the study by Liang et al. [85]. PPE, personal protective equipment; UPF, ultraviolet protection factor.

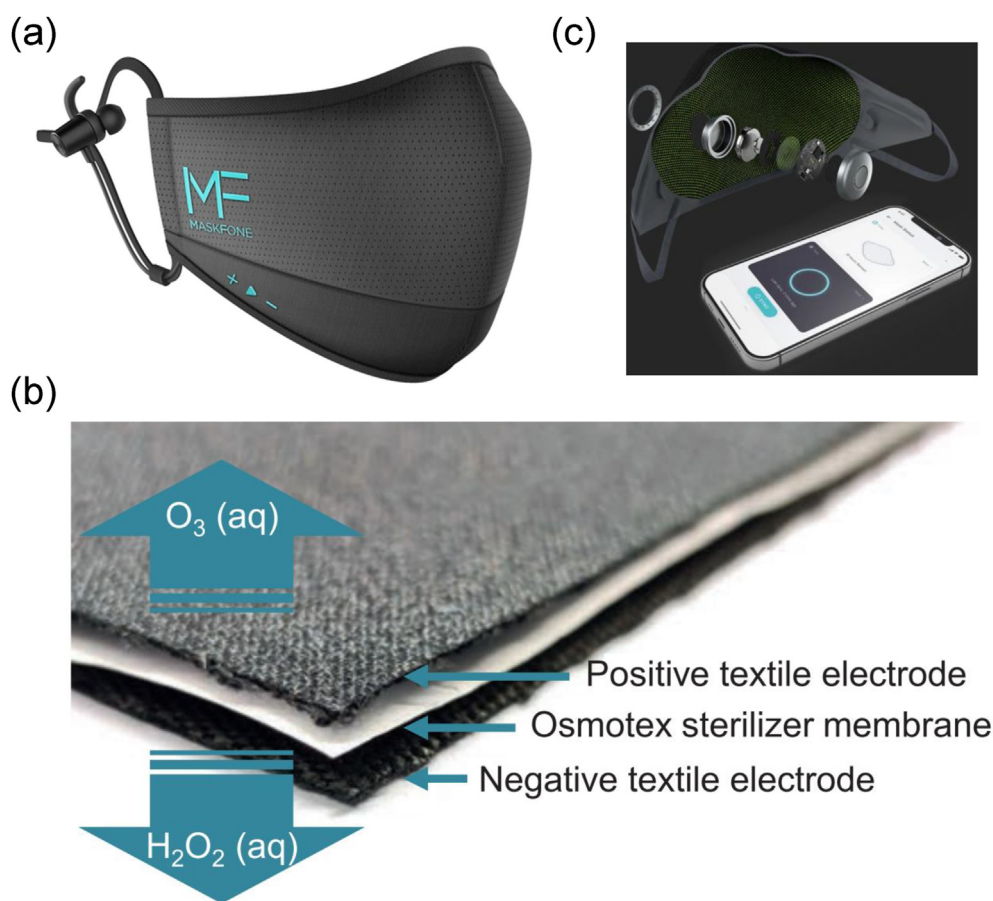


Fig. 6. Demonstration of commercial smart face masks. (a) The mask incorporated with earbuds [92]. (b) The sandwiched structure of the self-disinfecting mask which could be purified by built-in high voltage [97]. (c) The schematic of sensor embedded smart mask and the display of recorded data on mobile phone [98].

a novel face mask last year that could convey both facial and vocal language regardless of the environmental brightness [91]. In addition to the plastic covering which is intrinsically transparent, luminous additives are introduced which could light the plastic, so that facial language could even be exchanged in the dark. Furthermore, for the amplification of voices, a microphone is embedded within the mask, which ensures a clearer conversation behind the mask. In another waterproof N95 face respirator called MaskFone designed by Binatone company, an earbud is incorporated for making better quality phone calls (Fig. 6a) [92]. In another conceptual product, an LED array is stitched into a face mask, by which the motion of the mouth is represented by specific light patterns [93]. The C-Face mask designed by Donut Robotics company took a step further by embedding a translator within the mask, by which the spoken words could be real-time translated into 8 other languages [94]. The daily wearing comfort of the electronics embedded mask still waits to be examined, despite the claim by Razor company that ergonomic design has been adopted to prevent the contact between the electronic module and the face.

Although the multiple-layer design could effectively isolate the virus from entering the respiratory system, the virus could accumulate outside the mask after long-term wearing, which still brings about danger to the wearer. To this end, the LG company developed a face mask named Puricare, which uses UV light to deactivate the microbes on the mask. The UV-LED is powered by rechargeable batteries, which could sustain for up to 8 h after a single charging. As a consequence, 99.97% of the particulates (<0.3 μm in size) in the air could be blocked [95]. For a similar aim, scientists from the

Massachusetts Institute of Technology (MIT) incorporated a copper mesh into the mask. By applying an electrical current through the mesh, large amounts of ohmic heat are generated, which greatly raise the local temperature, and the microbes are killed [96]. Another approach to kill the aerosol pathogens adhered to the mask relies on the radical species produced by a high electric field (Fig. 6b) [97]. A self-disinfecting mask designed by Swiss researchers has a sandwich structure with two conductive fabrics separated by a dielectric layer. A voltage of several volts is applied by a rechargeable battery which could ionize the air and generate radical species. And the pathogens could be inactivated in only several minutes. After the purification process, the mask could be recycled for use. Despite the reduction of waste, volatile compounds released upon the applied voltage should be further assessed in terms of their safety concern.

Because the respiration process contains much information about health, the collection of respiration parameters, such as respiration rate, flow, as well as concentration of certain constituents could facilitate the monitoring of health conditions. To this end, commercial smart masks embedded with respiration sensors have been designed. For example, the Airpop company developed a smart mask that incorporated a sensor network for recording the respiration rate of the wearer (Fig. 6c) [98]. Besides, the smart mask could also monitor the air quality in the surroundings. The manufacturer claims that the data could help to monitor the sleep condition of the wearer. The above-mentioned Puricare mask also contains a respiration sensor and a ventilator with dual fans [95]. Through tracking the respiration

flow of the wearer, the ventilator could automatically adjust the fan speed which facilitates the air exchange across the mask. Another smart mask designed by Vita Innovations company comprises a 3D printed resin as the supporting substrate with a series of biometric sensors embedded [99]. The sensors could simultaneously measure the heart rate, blood oxygen level, body temperature and respiration rate of the mask wearer. These data could be transmitted to external devices for display, and an alarm could be triggered when abnormal physiological data appears. The as-designed mask is greatly helpful in the hospital for monitoring the health condition of patients, especially, for those waiting for emergency treatment.

The above-mentioned functional components of face masks represent the efforts of manufacturers to make the world better under the long-lasting Covid-19 pandemic. Despite the abundance of novel smart mask products, the price of them is still too high compared with regular surgical masks (tens of cents for each) and even N95 respirators (~1–2 dollars for each). The cost issue also exists in other types of smart PPEs, such as protective clothes, helmets, and gloves. The reduction of costs in the preparation of smart PPEs necessitates the further innovation of materials and processing techniques in this field, as well as the establishment of an industrial production line for increased productivity so that more people could afford them and enjoy the convenience of new technologies.

4. Conclusion

In this minireview, advanced materials and structural designs applied for various types of PPEs have been introduced, as well as examples of smart face masks for achieving improved efficiency and additional functionalities. New materials and structures have been proposed, and various additives have been introduced in PPEs to improve the performance for resisting the mechanical, chemical, thermal, and radiative hazards. Sensors are also embedded in PPEs for daily monitoring and early warning of potential danger, which serves as an effective support for passive personal protection. Novel smart PPEs have been not only designed and fabricated in the lab but also industrially manufactured for daily applications. With the construction of the infrastructures all over the world, as well as the growing air and water pollution, the development of PPEs will continuously be a research hotspot in the future, even after the end of the Covid-19 pandemic. As the basis for the upgrading of PPE functionalities, the innovation of materials will definitely be focused to achieve better protection performance.

Despite the increasing focus and rapid development of this field, there are still limitations in applying advanced materials in smart PPE fabrication. First, the durability of the protection performance of the as-designed PPEs should be assessed, especially for PPEs with additives of organic or biological molecules for specific capture of pollutants because of the degradation of these additives with time. Besides, side-effects should be taken into account when improving certain properties of a PPE by introducing new materials. Sometimes, the improvement of protection performance is at the expense of decreased personal comfort, and some additives used in PPEs are intrinsically detrimental to some extent. Last but not the least, the high price is always the bottleneck for the popularization of the smart PPEs amongst ordinary people. The cost for smart PPEs preparation could be lowered down by mass production through the standardized production line, while the risk for technology disruption and the uncertainty of market demand should also be concerned.

In all, the advancement of materials science has greatly motivated the revolution of PPEs, rendering improved protection efficiency, functionality and wearing comfort. The development of PPEs will not cease with the recession of the Covid-19 pandemic, and more efforts will be enrolled in this field to bring more safety and convenience to the people in need of care.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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