Short Review

Antibacterial *N*-halamine fibrous materials

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A B S T R A C T

Pathogenic microbial contamination poses serious threats to human healthcare and economies worldwide, which instigates the booming development of challenging antibacterial materials. *N*-halamine fibrous materials (NFMs), as an important part of antibacterial materials, featuring structural continuity, good pore connectivity, rapid sterilization, rechargeable bactericidal activity, and safety to humans and environment, have received significant research attention. This review aims to present a systematic discussion of the recent advances in *N*-halamine antibacterial fibrous materials. We firstly introduce the chemical structures and properties of *N*-halamine materials. Subsequently, the developed NFMs can be categorized based on their fabrication strategies, including surface modification and one-step spinning. Then some representative applications of these fibrous materials are highlighted. Finally, challenges and future research directions of the materials are discussed in the hope of giving suggestions for the following studies.

1. Introduction

Microbial contamination and infection caused by pathogens are at the forefront of global public health awareness. This issue is highlighted by the outbreak of Coronavirus disease (COVID-19) pandemic, over 25 million confirmed cases with >900,000 deaths worldwide and increasing, which caused incalculable misery and economical loss [1,2]. To cut off the pathogen spreading by the proliferation of microbials, the commonly used strategies dealing with these challenges are the addition of disinfectants to the contact surfaces [3–5]. Despite the effectiveness of the developed disinfectants, such as metallic silver [6,7], quaternary ammonium salt [8,9], chitosan [10], and peptide [11], they still experienced the problem of drastic antibacterial performance decline induced by irreversible depletion of disinfectants. Alternatively, *N*-halamines have attracted increasing attention owing to its rapid inactivation, renewable biocidal activity, broad-spectrum antibacterial, long-term stability, and safety to humans and environments [12].

N-halamine was first proposed as halogen derivatives of nitrogen by Gmelin in their coverage of inorganic chemistry in 1927 [13]. Later in 1970, Kovacic et al. [14] presented an overall discussion of the chemistry of *N*-bromo and *N*-chloro derivatives of ammonia and alkylamines. Then Worley and co-workers were devoted in the synthesis of novel

N-halamine compounds in the late 1980s [15–17]. Nowadays, *N*-halamines can be more precisely defined as inorganic or organic compounds containing one or more nitrogen-halogen covalent bonds that obtained by halogenation of N–H groups, the halogen is chlorine, bromine, or iodine. In terms of the antibacterial function, the N-X covalent bonds can hydrolyze in the presence of water and be reduced to N–H covalent bonds, the released oxidative halogens would directly react with the vital bacterial cell constituents affecting metabolism and viability [18,19]. Once oxidative halogens are consumed, as a reverse process, the N–H groups can be facilely recharged by exposure to dilute household bleach or halogen-releasing agents, bringing renewable antibacterial activity to *N*-halamines. With the remarkable progress of diverse *N*-halamine compounds, considerable attention has been paid to developing *N*-halamine materials in various forms (fibers, nanoparticles, beads, films, etc.) for creating better antibacterial activity [20–23]. Among them, NFMs are found to be highly attractive due to their advantages like exceptional structural continuity, good pore connectivity, fine flexibility, and self-supporting capability, which show great potentials in a wide range of applications.

In this following context, we discuss state-of-the-art of studies on the design, fabrication, and functional applications of NFMs. Firstly, we briefly state the molecular structures and antibacterial behavior of *N*-

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halamine materials, and introduce their various morphologies. Then we emphasize on recent advances regarding NFMs based on the fabrication strategies of surface modification and one-step spinning. Subsequently, we comprehensively highlight the functional applications of NFMs in varieties of fields, involving bioprotective clothing, water disinfection, air purification, and biomedicine. Finally, a summary and outlook for next-generation *N*-halamine antibacterial fibrous materials is provided.

2. Chemical structures and properties of *N*-halamine materials

2.1. Molecular structures of N-halamines

In drastic contrast to traditional halogen-based disinfectants, the *N*-halamines are more diverse in their molecular structures, which could be classified into three types based on the different halogenation groups, i.e., amine *N*-halamines, amide *N*-halamines, and imide *N*-halamines (Fig. 1a). The bactericidal activities of these structures in aqueous solutions are found to be the order of imide *N*-halamines, amide *N*-halamines, and amine *N*-halamines, which is ascribed to progressively smaller dissociation constant of the *N*-halamines [24]. On the contrary, their stability follows a totally opposite tendency, the imide *N*-halamines are the least stable structure that can quickly release active halogens and be reverted to the precursor [25]. It means that imide *N*-halamines could be used for rapid inactivation, while for durable antibacterial applications, amine *N*-halamines will be the best choice. Moreover, the stability and durability of *N*-halamines is bound up with the existence or not of an α-hydrogen, a dehydrohalogenation reaction occurs under ultraviolet (UV) radiation or heat if α-hydrogen exists (Fig. 1b).

N-halmines could also be divided into small molecular *N*-halamines and polymeric *N*-halamines. In the early years of *N*-halamines studies, numerous small molecular *N*-halamines had sprung up due to their better stability than existing disinfectants, including inorganic and organic *N*-halamines [15–17,26–31]. The typical inorganic *N*-halamines such as NH_2Cl, $NHCl_2$, and NCl_3, were usually synthesized by substitution reaction of ammonia with hypochlorous acid or chlorine gas, which were found to be highly attractive in the applications of water disinfection [13]. In terms of organic small molecular *N*-halamines, some typical *N*-halamines can be subdivided according to the chemical structure of the molecule. The five-membered heterocyclic *N*-halamines like hydantoin-containing *N*-halamines (Fig. 2a), imidazolidinone-containing *N*-halamines (Fig. 2b), oxazolidinone-containing *N*-halamines (Fig. 2c), and succinimide-containing *N*-halamines (Fig. 2d). The triazine *N*-halamines, such as melamine-containing *N*-halamines (Fig. 2e), cyanuric acid-containing *N*-halamines (Fig. 2f), cyanuric chloride-containing *N*-halamines (Fig. 2g), others like acrylamide-containing *N*-halamines (Fig. 2h), 4-piperidinol-containing *N*-halamines (Fig. 2i). Despite the considerable bactericidal activity and long-term stability in aqueous solution, the major problems associated with small molecular *N*-halamine compounds were the solubility in water and the required toxicity

testing before commercial use [32,33]. Moreover, the common powder form of the compounds and the inability to directly incorporate into the substrate materials, putting limitations on their practical applications. To cope with these challenges, small molecular *N*-halamines with active groups (e.g., hydroxyl group, epoxy group, and silanol group) have attracted great attention because they could be recognized and covalently loaded on substrates by reacting with the functional groups, which provide more possibilities for the development of *N*-halamine materials [24,34,35].

Based on the research findings of small molecular *N*-halamines, polymeric *N*-halamines are rapidly emerging, which may be deemed to the derivatization of polymers with halamine groups. Benefitting from the advantages of insolubility in water, ultralow leaching amounts of free active halogens, easy to modification, good processability, and recycling properties, the polymeric *N*-halamines have become another powerful and effective way to synthesize novel *N*-halamine materials for different application requirements [36,37]. Generally speaking, four strategies are used to fabricate polymeric *N*-halamines. The first route is to graft the small molecular *N*-halamines onto polymer backbones by chemical reaction of functional groups as exhibited in Fig. 3a–d, the small molecular *N*-halamines are grafted onto nylon [38], polystyrene [39], polysiloxane [40], and polyhydroxybutyrate (PHB) [41]. Secondly, the small molecular *N*-halamines can graft onto polymer by graft polymerization. For example, Fig. 3e–g shows the polymeric *N*-halamines that are fabricated by graft polymerization of *N*-halamine monomer with polypropylene (PP) [42], cellulose [43], and poly (ethylene terephthalate) (PET) [44]. The third strategy is the polymerization of *N*-halamine monomer by reacting with themselves or other monomers (Fig. 3h–i) [45,46]. The last approach is blending or coating *N*-halamine compounds to the main polymers, which is not covalently incorporated the *N*-halamine groups into polymers [47,48].

2.2. Antibacterial behavior of N-halamine materials

Although *N*-halamines materials have received considerable attention in both industrial and academic circles, their antibacterial behavior still remains controversies. To date, three possible antibacterial pathways have been proposed, that is, contact killing, release killing, and transfer killing (Fig. 4). The first mode kills bacteria through delivering active halogens from *N*-halamines to the bacteria directly without releasing active halogen into solution, whereas the second is the dissociation of positive halogen ions from *N*-halamines to solution with the following killing. Apart from these, a third mode has been proposed by some researchers, transfer killing, which is a way of achieving inactivation through transferring the positive halogens from *N*-halamine materials to medium.

Substantial work has been performed to exploring the antibacterial mechanism of the materials. Ren et al. [49] demonstrated the contact killing behavior of fibrous membranes by carrying out a series of biocidal and leaching tests. An *N*-halamine compound, 3-(5′-methyl-5-′-hydantoinyl) acetanilide, was synthesized and blended into electrospun precursor solutions, providing the polyacrylonitrile (PAN) nanofibers with antibacterial properties after being exposed to household bleach. It was found that the release rate of *N*-halamine precursor was low even conducting with vigorous agitation, suggesting that the materials inactivate bacteria via contact killing instead of release killing. Thereafter, Bai et al. [50] investigated the antibacterial behavior of the as-prepared N–Br bond-containing *N*-halamine nanofibers using inhibition zone test, the appearance of the distinct aseptic ring around the samples validated the release killing mode. Then they tested release rate of active bromine dissociated from the *N*-halamine nanofibers under different conditions. Above 80% active bromine content maintained under a dry condition, while only 6% active bromine left when exposing into bacteria or water condition, implying that the materials inactivate bacteria by release killing mode.

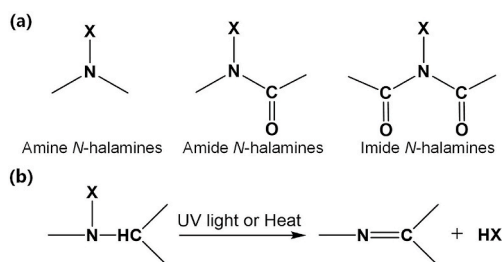The transfer killing mode was confirmed by Ahmed's report [51], the

Fig. 1. (a) Three types of *N*-halamines: amine *N*-halamines, amide *N*-halamines, and imide *N*-halamines. Reprinted from Refs. [24]. Copyright 2003 Wiley. (b) Dehydrohalogenation of *N*-halamines with α-hydrogen. Reprinted from Refs. [25]. Copyright 2013 American Chemical Society.
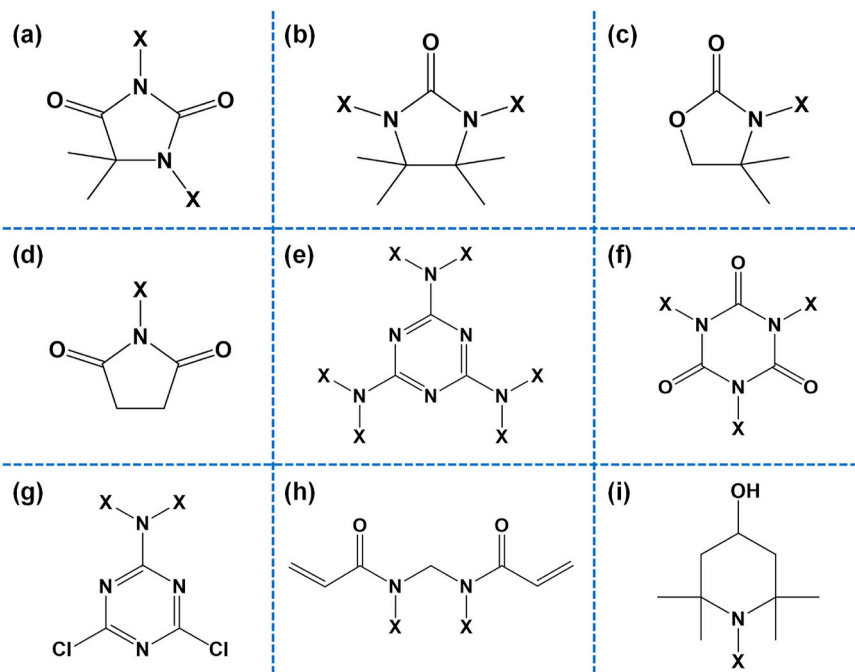
Fig. 2. Chemical structures of some typical small molecular organic *N*-halamines, X = Cl, Br, I, or H. Reprinted from Refs. [25]. Copyright 2013 American Chemical Society.
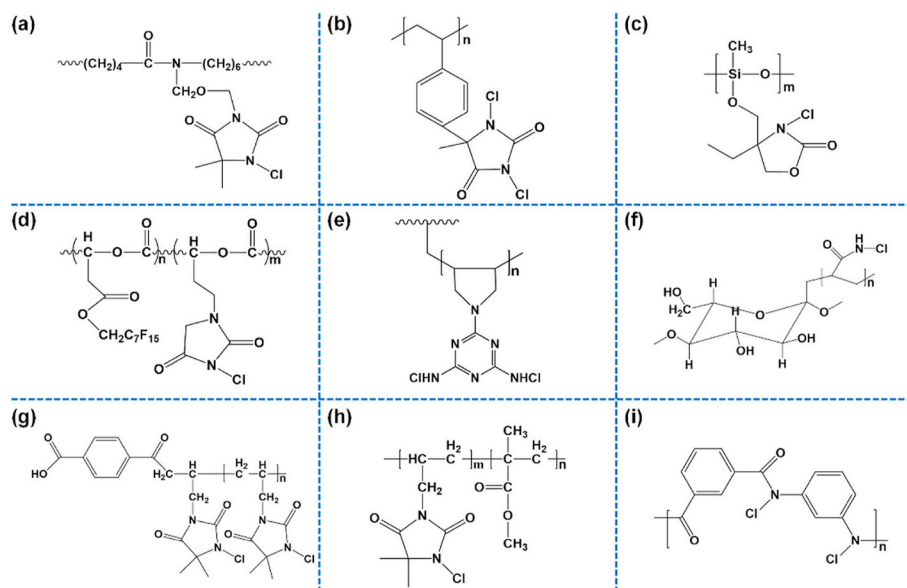

Fig. 3. Structures of some representative polymeric *N*-halamines. (a) Chlorinated 1-hydroxymethyl-5,5-dimethylhydantoin grafted nylon 66. Reprinted from Ref. [38]. Copyright 2001 Wiley. (b) Poly (l, 3-dichloro-5-methyl-5-(4′-vinylphenyl)-hydantoin). Reprinted from Refs. [39]. Copyright 1994 American Chemical Society. (c) 4-ethyl-4-(hydroxymethyl)oxa-zolidin-2-one-based *N*-halamine polysiloxane. Reprinted from Refs. [40]. Copyright 2018 Wiley. (d) Chlorinated 1-allylhydantoin and perfluorooctyl acrylate grafted polyhydroxybutyrate. Reprinted from Ref. [41]. Copyright 2018 Wiley. (e) Chlorinated poly (propylene-*g*-diallylmelamine). Reprinted from Ref. [42]. Copyright 2012 The Royal Society of Chemistry. (f) Chlorinated acrylamide grafted cotton cellulose. Reprinted from Ref. [43]. Copyright 2006 Wiley. (g) Chlorinated poly (3-allyl-5,5-dimethylhy-dantoin)-*g*-poly (ethylene terephthalate). Reprinted from Refs. [44]. Copyright 2008 Elsevier. (h) Chlori-nated poly (3-allyl-5,5-dimethylhydantoin-*co*-methyl methacrylate). Reprinted from Ref. [45]. Copyright 2015 American Chemical Society. (i) Chlorinated poly (*m*-phenyleneisophthalamide). Reprinted from Ref. [46]. Copyright 2004 American Chemical Society.

bacteria were cultured in fresh broth and in broth that are pre-treated by exposure to chlorinated polymer, respectively. The results showed that the bacteria failed to grow in the pre-treated medium, which was ascribed to the changes from the halogen exchange between the amide groups in protein and the polymer. More interestingly, they proposed that the bactericidal mode could not be explained alone but a combi-nation of these modes operating simultaneously. Bai et al. [52] studied the antibacterial behavior of the *N*-halamine containing poly (methyl methacrylate) (PMMA) fibers by referring research methods of Ahmed. The freeze-dried bacterial cells in the absence of liquid environment were used to verify the contact killing mode. An inhibition zone testing method was conducted to identify the release killing of the materials, afterward a dialysis test was further carried out to determine the release

action of the fibers. As a result, the antibacterial mode of the swatches was attributed to the combination of these two modes. Besides, Chen et al. [53] also believed that combination of these modes would be a more reasonable explanation of the antibacterial activities. Compared with the sodium hypochlorite (NaClO) solution, the inactivation prop-erties of *N*-halamine modified cotton fabrics was much higher than that of the NaClO solution, indicating that the release killing mode alone may not be enough to ensure efficient bactericidal function. Overall, the *N*-halamines containing relatively stable N-X bonds tend to follow the contact killing mode, and those containing less stable halamine func-tional groups are likely to kill bacteria by release killing. The liquid environment and media that containing N–H groups also play decisive roles in the bactericidal behavior of the materials.
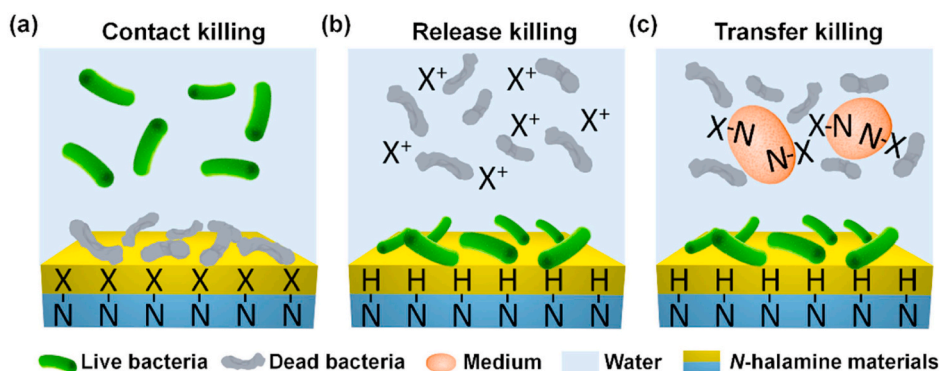
Fig. 4. Illustration showing the bactericidal modes of *N*-halamines: contact killing, release killing, and transfer killing. Reprinted from Ref. [12]. Copyright 2017 American Chemical Society.

2.3. Morphologies of N-halamine materials

The morphology of *N*-halamine materials plays a decisive role in their antibacterial activities and applications. So far, researchers have fabricated various *N*-halamine materials with controllable morphologies, mainly including sphere-shaped, film-shaped, and fiber-shaped. For sphere-shaped *N*-halamine materials, varieties of beads, microspheres, and nanoparticles have been synthesized [54–61]. The spherical morphology endowed the materials with higher specific surface area and more active sites than that of the other two morphologies, and it can be easily filled in various molds or be loaded onto other carriers for different application scenarios. Sun and co-workers [54] have firstly prepared *N*-halamine beads through suspension copolymerization of styrene and two small *N*-halamine molecular compound, 3-(4′-vinylbenzyl)-5,5-dimethylhydantoin and 3-allyl-5,5-dimethylhydantoin (ADMH), exhibiting great potentials in water disinfection. Dong et al. [60] synthesized barbituric acid-based *N*-halamines coated magnetic silica nanoparticles (SiO_2 NPs) by radical polymerization. The as-prepared SiO_2 particles displayed superparamagnetic performance and exhibited higher bactericidal efficacy than powder *N*-halamines.

Film-shaped *N*-halamine materials, combining robust mechanical strength, widespread raw materials, good transmittance, facile formability, and renewable bactericidal activity, hold great promise in fields like bioengineering and foods industry [62–70]. Qiao et al. [68] created an *N*-halamine modified thermoplastic polyurethane (TPU) film via solvent casting method. The modified TPU films displayed good biocidal efficacy, desirable rechargeability, and stability, exhibiting great potential as food contact surface materials for preventing microbial cross-contamination during food processing. Moreover, Si et al. [69] fabricated high-strength *N*-halamine grafted poly (vinyl alcohol-*co*-ethylene) (EVOH) films through combining melt radical graft polymerization with reactive extrusion method. The films rendered good antibacterial efficacy and long-term durability, which could fulfill both effectiveness and durability requirements of practical medical applications.

Fibrous materials are an important route to spread pathogenic bacteria, because the microorganism can easily adhere to the surface of the fibers [19,71]. Antibacterial NFMs have attracted great interest because of the extensive applications of fibers ranging from functional garments to medical textiles and water disinfection filters. From the early years of antibacterial modification on common cotton fabrics to the subsequent studies of antibacterial nanofibrous materials, many efforts have been made by researchers to obtain NFMs. In general, there are mainly two fabrication strategies (Fig. 5): one is surface modification of the available fibrous materials, another is to prepare materials by one-step spinning. A detailed description of these two methods will be presented as follows.
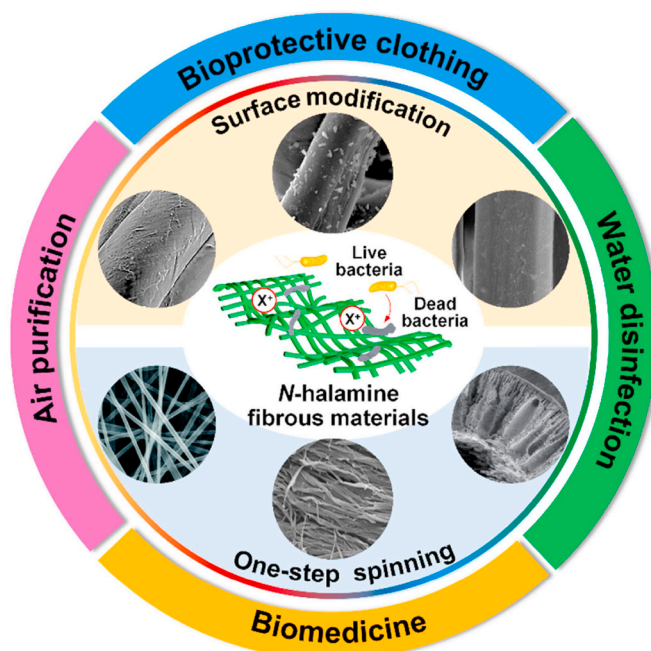

Fig. 5. *N*-halamine fibrous materials based on surface modification and one-step spinning for functional applications.

3. NFMs based on surface modification

Surface modification whereby fibrous substrates are grafted or coated with *N*-halamines is an efficient and versatile strategy for fabrication of NFMs [72,73]. The key point of this method is to find adequate ways to make *N*-halamine moieties combine with various kinds of fibrous materials. Strategies of surface modification can be classified into chemical surface modification and physical surface modification, based on whether there is a chemical bonding between *N*-halamine moieties and fibrous substrates. In the following pages, we will highlight recent advances on the above two surface modification strategies. Recently reported modification methods, fibrous substrates, and *N*-halamine compounds that have been used for the fabrication of NFMs, are summarized in Table 1.

3.1. Chemical surface modification

The chemical surface modification method can effectively incorporate the *N*-halamine moieties into fibrous substrates via covalently linkage, achieving strong chemical attachment between them.

Table 1
A summary of representative NFMs based on surface modification.

Modification method	Substrate materials	N-halamine compounds	Antibacterial reduction (%)	Reference
Surface modification by small molecular	Cotton fabrics	Oxazolidinone-containing N-halamines	100% (E. coli) 100% (S. aureus)	[74]
	Cotton fabrics	Amine N-halamines	100% (E. coli) 100% (S. aureus)	[75]
	Cotton fabrics and cotton/polyester blend fabrics	Imidazolidinone-containing N-halamines	99.9999% (E. coli) 99.9999% (S. aureus)	[24]
	PP fabrics	Amide N-halamines	100% (E. coli) 100% (S. aureus)	[76]
	PET fabrics	Cyanuric acid-containing N-halamines	100% (E. coli) 100% (S. aureus)	[35]
	PHB/PCL electrospun membranes	Hydantoin-containing N-halamines	99.91% (E. coli) 99.95% (S. aureus)	[41]
	Viscose fabrics	Polysaccharide-containing N-halamines	99.9999% (E. coli) 99.9999% (S. aureus)	[77]
Graft polymerization	Cotton fabrics	Hydantoin-containing N-halamines	100% (E. coli) 100% (S. aureus)	[78]
	Cotton fabrics	Imidazolidinone-containing N-halamines	100% (E. coli) 100% (S. aureus)	[79]
	Cotton fabrics	Amide N-halamines	99.99% (E. coli) 99.97% (S. aureus)	[80]
	Cotton/PET/Nylon-66/PP fabrics	Hydantoin-containing N-halamines	99.9999% (E. coli) 99.9999% (S. aureus)	[81]
Surface coating	Cotton fabrics	Amide N-halamines	100% (E. coli) 100% (S. aureus)	[82]
	Cotton fabrics	Hydantoin-containing N-halamines	99.73% (E. coli) 100% (S. aureus)	[83]
	PP fabrics	Imidazolidinone-containing N-halamines	99.9999% (AI H1N1 virus)	[84]
	PGA sutures	4-Piperidinol-containing N-halamines	100% (E. coli) 100% (S. aureus)	[85]
	PLA fabrics	Hydantoin-containing N-halamines	100% (E. coli) 100% (S. aureus)	[86]
Supercritical impregnation	PP fabrics	Hydantoin-containing N-halamines	100% (E. coli) 100% (S. aureus)	[87]
	PET fabrics	Hydantoin-containing N-halamines	100% (E. coli) 100% (S. aureus)	[88]

Generally, it is usually required that the fibrous substrates are impregnated in N-halamine-containing modification solutions to make a sufficient loading, and they can serve as a reactant to participate in the chemical reaction. Based on this, the chemical surface modification can be sorted by the types of chemical reaction. One is surface modification by small molecules, which means that N-halamine moieties react with
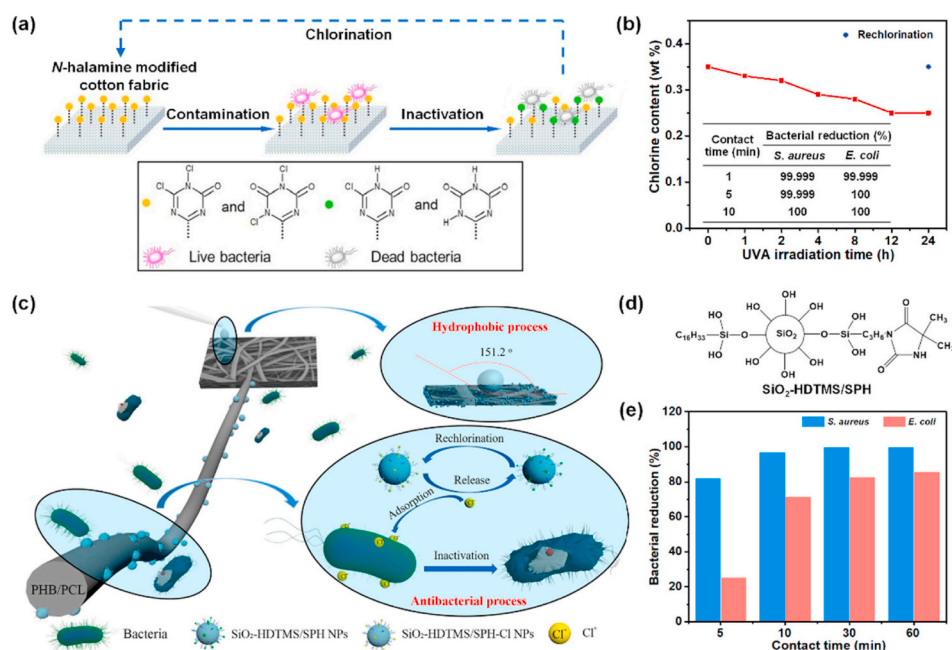
Fig. 6. (a) Schematic showing the renewable antibacterial function of N-halamine modified cotton fabric. (b) Stability of the chlorinated fabric with UVA light irradiation, the inset showing the bacterial reduction of the fabric. Reprinted from Ref. [89]. Copyright 2014 Wiley. (c) Preparation of SiO2-HDTMS/SPH NPs grafted PHB/PCL fibrous membranes and their antibacterial function. (d) Chemical structure of the SiO2-HDTMS/SPH NPs. (e) Biocidal activity of the chlorinated fibrous membranes. Reprinted from Ref. [90]. Copyright 2018 Elsevier.

active groups of fibrous substrates; the other is the graft polymerization of *N*-halamine monomers on fibrous materials.

3.1.1. Surface modification by small molecules

Surface modification by small molecules is an effective and facile method for fabrication of NFMs, accounting for primary routes to connect *N*-halamines and substrates. It is worth mentioning that the small molecular *N*-halamines used for modification should contain active groups (such as hydroxyl and epoxide ring) which can incorporate onto fibrous materials through two pathways: react with fibers directly or modify materials through other chemicals. In the former case, Ma et al. [89] described a method of controlled hydrolysis of cyanuric chloride to prepare *N*-halamine precursors, and attached the precursors onto cotton fabrics through nucleophilic substitution using a typical pad-dry-cure process (Fig. 6a). As exhibited in Fig. 6b, the chlorine content of modified fabric is 0.35 wt% after being exposed to household bleach. Moreover, around 71% of the chlorine remained after the UVA light irradiation of 24 h, exhibiting excellent UVA light stability of the fabrics. The modified fabrics also rendered high bactericidal activities against *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*) with 7 logs reductions in 5 and 10 min contact time, respectively.

In addition to the *N*-halamines that could be bonded to the fibrous substrates directly, many other substrates and *N*-halamines are not able to react with each other, a medium which serves as a bridge between *N*-halamines and fibrous materials is often required. Crosslinking agents, like 1,2,3,4-butanetetracarboxylic acid (BTCA) [91–97], dimethylol-5,5-dimethylhydantoin (DMDMH) [71,98,99], and citric acid [100], have been widely applied to react with *N*-halamines and fibers for the fabrication of NFMs due to their excellent chemical reactivity. For example, Li et al. [101] attached *N*-halamine precursor compound, 2,2,6,6-tetramethyl piperidinol (TMP), onto cotton fabrics using BTCA as a crosslinker. The fabrics were immersed in a homogeneous BTCA/TMP solutions, followed by a short drying and curing process. Upon exposure to dilute bleach solutions, the chlorinated fabrics inactivated 100% of *S. aureus* and 83.25% of *E. coli* within 10 min, highlighting great biocidal activities against common Gram-positive and Gram-negative bacterium. Inorganic nanoparticles are alternative choices for introducing *N*-halamine moieties into fibrous materials. Lin et al. [90] fabricated *N*-halamine precursors grafted SiO_2 NPs to modify PHB/poly-ϵ-caprolactone (PHB/PCL) electrospun nanofibrous membranes by dip-pad method (Fig. 6c). The SiO_2 NPs were first synthesized and modified by grafting 5,5-Dimethyl-3-(3′-triethoxysilylpropyl)hydantoin (SPH) and hexadecyltrimethoxysilane (HDTMS) to obtain SiO_2-HDTMS/SPH NPs (Fig. 6d). Then the membranes were impregnated in the mixture of azobis (isobutyronitrile) and composite nanoparticles to produce *N*-halamine containing membranes via grafting reaction. The SiO_2-HDTMS/SPH NPs could not only endow the nanofibers with bactericidal functions but also construct the superhydrophobic surface, showing great potentials in the development of food packaging. After chlorination, the resultant fibrous membranes inactivated 99.91% of *S. aureus* and 99.95% of *E. coli* O157:H7 within the contact time of 60 min (Fig. 6e).

3.1.2. Graft polymerization

Graft polymerization has become another effective and powerful way for fabricating NFMs [18,102]. Incorporating the *N*-halamine moieties onto fibrous materials through graft polymerization was usually carried out in a solution with the presence of initiators. By regulating the reaction time, grafting monomer, and initiator concentration, the *N*-halamine structure of the materials can be controlled, which finally determines their active chlorine content and biocidal activities [103–106]. Recently, Hu et al. [107] reported a two-step graft polymerization method to fabricate bi-functional co-grafted cellulose fiber. An *N*-halamine monomer, 4-[(acryloxy)methyl]-4-ethyl-2-oxazolidinone (AEO), and a quaternary ammonium salt (QAs) monomer, *N*,*N*-dimethyl-*N*-(methacryloyloxy)-ethyl-*N*-benzyl ammonium chloride (DMABn), were firstly synthesized as antibacterial components.

Subsequently, these two kinds of monomers could be grafted on cellulose fiber to obtain cellulose-graft-polyAEO (C-*g*-PAEO) (Fig. 7a) and cellulose-graft-polyDMABn (C-*g*-PDMABn) (Fig. 7b), respectively. Likewise, the two monomers could be grafted on cellulose fibers simultaneously to fabricate cellulose-cograft-polyAEODMABn (C-*g*-PAEDM) (Fig. 7c). As presented in Fig. 7d–g, more intact bacteria were found on fiber surface of C-*g*-PDMABn after contacting with *E. coli*, and the bacterial debris was observed on C-*g*-PAEDM, which corresponded to their different kinetics of antibacterial activity. That is to say, the *N*-halamine cellulose fiber exhibited rapid inactivation rate but weak absorption capacity, whereas QAs-functionalized cellulose fibers could quickly absorb bacteria without immediately killing them. Benefiting from the synergistic effect of these two mechanisms, the resulting bi-functional cellulose fibers showed a novel biocidal process and performed excellent antibacterial properties against both *E. coli* and *S. aureus* (Fig. 7h–i).

In contrast to the traditional graft polymerization initiated by initiator, electron beam irradiation method, combining the rapid free radicals generation, continuous treatment process, and energy-saving property, has been applied to modify different kinds of surfaces [108, 109]. Ren et al. [79] synthesized the *N*-halamine compound, 3-(3′-acrylicacidpropylester)-5,5-dimethylhydantoin, and grafted on cotton fabric using electron beam irradiation at room temperature. A rough and uneven surface of the modified fabric was exhibited when compared with the smooth uncoated cotton fiber. The chlorinated fabrics achieved 100% reduction of *E. coli* and *S. aureus* within 5 and 10 min of contact time, respectively. Moreover, the active chlorine was found to be regenerable and stable after UV irradiation and standard washing. By exposure to chlorination solution, the chlorine content of the sample after 50 cyclic standard washing was recovered to 50% of the initial value (0.48 wt%), and about 86% chlorine loading of the samples with 24 h UV irradiation could be recovered.

3.2. Physical surface modification

Although chemical surface modification has been performed for years in a very practical way for various applications, the indispensable prerequisite of surface tethering groups on substrates restricts their development. Alternatively, surface modification based on physical principles, as a simple way of depositing *N*-halamine compounds onto fibers without chemical bonds, plays a significant role in the fabrication of NFMs. It is feasible to regulate the varieties and dosages of *N*-halamine modifiers as well as fibrous substrates for further tailoring the morphologies and biocidal efficacy of NFMs. Generally, there are two main approaches to attain *N*-halamine functioned fibrous materials by physical surface modification, comprising surface coating and supercritical impregnation.

3.2.1. Surface coating

As a versatile and available modification method, surface coating is a facile solution treatment process that is able to be applied to various substrates, which involves dip coating and blade coating [110,111]. In a typical dip coating procedure, precursor solutions are usually prepared by dissolving or dispersing *N*-halamine compounds into suitable solvents, and then the fibrous materials are impregnated into the solutions sufficiently with a following dry process. Recently, Pan et al. [112] synthesized the *N*-halamine precursor, graphene oxide (GO) modified poly [5,5-dimethyl-3-(3′-triethoxysilylpropyl) hydantoin] (PSPH), and fabricated GO-PSPH coated cotton fabrics (cotton/GO-PSPH) via dip coating method. Then the modified fabrics were in-situ reduced to cotton/rGO-PSPH by treating with L-ascorbic acid. After being exposed to household bleach, the electrical conductivity of the cotton/rGO-PSPH-Cl was capable of monitoring their antibacterial activity according to the proportional relationship between electrical conductivity and chlorine content of the samples (Fig. 8a). The cotton/rGO-PSPH-Cl samples achieved better biocidal efficacy than that of cotton/GO-PSPH, which could inactivate 100% of *E. coli* and *S. aureus*
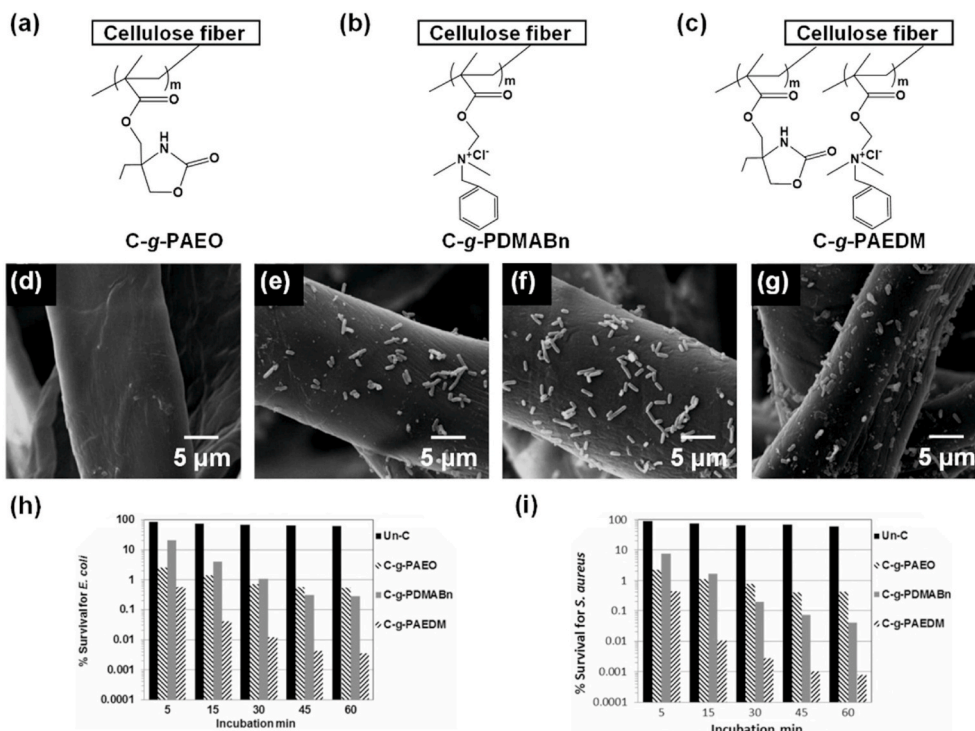
Fig. 7. (a–c) Schematic showing the chemical structures of antibacterial cellulose fibers co-grafting with *N*-halamine or (and) QAs monomer. Scanning electron microscope (SEM) images of fibers after contacting with *E. coli*: (d) untreated cellulose (control), (e) C-*g*-PAEO, (f) C-*g*-PDMABn, and (g) C-*g*-PAEDM. (h–i) Biocidal activities of grafted cellulose fibers as a function of incubation time. Reprinted from Ref. [107]. Copyright 2014 Wiley.

within 5 min of contact (Fig. 8b).

Layer-by-layer (LbL) assembly has proven to be markedly powerful method for coating fibrous substrates with *N*-halamine compound layers (usually polyelectrolytes) by dip coating [113,114]. Generally, LbL assembly process is performed by manually immersing the fibrous substrates into solutions that containing oppositely charged chemicals
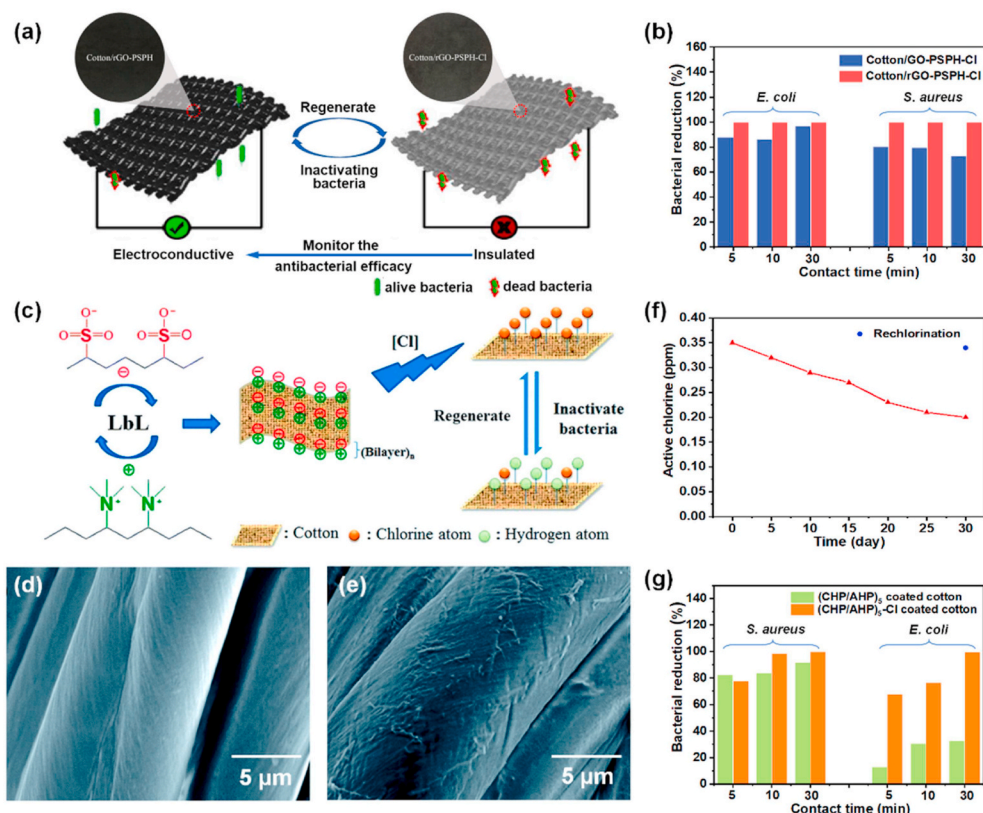
Fig. 8. (a) Schematic showing the regenerable bactericidal activity of rGO-PSPH coated cotton fabric. (b) Bacterial reduction of modified fabrics as a function of contact time. Reprinted from Ref. [112]. Copyright 2018 Elsevier. (c) Illustration of the LbL assembly method and bactericidal process of the coated cellulose fibers. SEM images of (d) the pristine cotton and (e) the coated cotton. (f) Storage stability of chlorinated fabrics. (g) Antibacterial properties of fabrics before and after chlorination. Reprinted from Refs. [82]. Copyright 2015 Royal Society of Chemistry.

alternately, followed by washing steps to eliminate unbound components [115]. The versatility, simplicity, and feasibility that LbL assembly renders make it widely used for modification of fibrous materials. Liu et al. [82] synthesized two polymeric precursors consisting of a cationic homopolymer poly ((3-acrylamidopropyl) trimethylammonium chloride) (CHP) as well as an anionic homopolymer poly (2-acrylamido-2-methylpropanesulfonic acid sodium salt) (AHP), followed by coating them onto cotton fabrics using LbL assembly (Fig. 8c). It could be clearly seen that a uniform coating layer wrapped around the cotton fiber surface when compared with the smooth surface of pristine cotton fibers (Fig. 8d–e). By exposing to household bleach, more than 50% of the original active chlorine remained in 30 days, and the lost oxidative chlorine could regain after rechlorination (Fig. 8f). The chlorinated fabrics exhibited 100% and 99.73% reduction of *S. aureus* and *E. coli* with contact time of 30 min, respectively (Fig. 8g).

Despite the versatility and effectiveness of dip coating, it still suffers from the drawbacks like uncontrollable modification layer and tedious process. Alternatively, blade coating has been found to be highly attractive in the modification of fibrous materials owing to its advantages of precise loading amount, durable coating layer, and good scale-up potentials [116]. As a typical example, the polymeric *N*-halamine precursors grafted mesoporous particles were attached onto the cotton fabric by blade coating [83]. The chlorinated samples rendered good antibacterial efficacy, which could achieve 100% and 99.99% reduction towards *S. aureus* and *E. coli* within 10 and 30 min, respectively. Moreover, the resultant cotton fabric exhibited red blood cell cohesion and better platelet adhesion, showing great potentials in the fields of biomedical applications.

3.2.2. Supercritical impregnation

Supercritical impregnation, as one of the recently developed supercritical fluid technology, has been found to be extensively appealing in surface modification of fibrous materials, owing to its environmentally friendly modification process and wide applicability, especially for inert substrates like PP fibers [40,87], polyethylene (PE) fibers [117], and PET fibers [88]. In view of the integrated merits of nontoxicity, super penetration ability, and limited solubility (only dissolve small molecules), carbon dioxide (CO_2) is usually selected as the solvent for supercritical impregnation to deliver the *N*-halamine groups to substrates. More interestingly, it is feasible to manipulate the modification

thickness and depth by optimizing the operation pressure, temperature, and time. Chen et al. [88] fabricated a CO_2-philic quaternary ammonium (quat)/*N*-chloramine polysiloxane modified PET fibers using supercritical CO_2 impregnation (Fig. 9a). The synthesized quat/*N*-chloramine polysiloxane precursors and PET fabrics were separately put in lower and upper chambers to avoid direct contact. By regulating the temperature and pressure of supercritical system, the precursors were interpenetrated into PET fibers in a controlled manner for optimal antibacterial properties. Fig. 9b demonstrated the synergistic effect of the quat/*N*-chloramine polysiloxane, that is, the *N*-halamine groups inactivate the bacteria by contact killing, and the positively charged QAs was able to attract negatively charged bacteria to promote the biocidal process. As shown in Fig. 9c and d, the surface of pristine PET fiber was relatively smooth while the modified PET fiber was found to be uneven and rough, which was ascribed to the existence of the coating layer. The modified PET swatches showed good durability and regeneration of chlorine against cyclic washing, and exhibited 7 logs reduction of bacteria within 10 min of contact (Fig. 9e).

4. NFMs based on one-step spinning

Studies on surface modification methods exhibit their effectiveness and operability for fabricating NFMs; however, they still suffer from some limitations such as unstable modification layers, inevitable leaching out of the *N*-halamine compounds, and ease of destroying original structure. Considerable efforts have been directed toward constructing NFMs by one-step fabrication process using one-step spinning, which was generally performed by spinning *N*-halamine polymers directly or blending *N*-halamine compounds in spinning precursors. Herein, we will introduce some common spinning methods for fabrication of NFMs as follows.

4.1. Electrospinning

As a typical technique for fabricating nanofibers, electrospinning technique has lately gained great attention for preparing antibacterial NFMs. Electrospun nanofibrous materials, combining their fascinating features of extremely fine fiber diameter, large surface area, and excellent pore connectivity, can not only endow the fibers with more active sites to incorporate functional moieties but also facilitate their contact
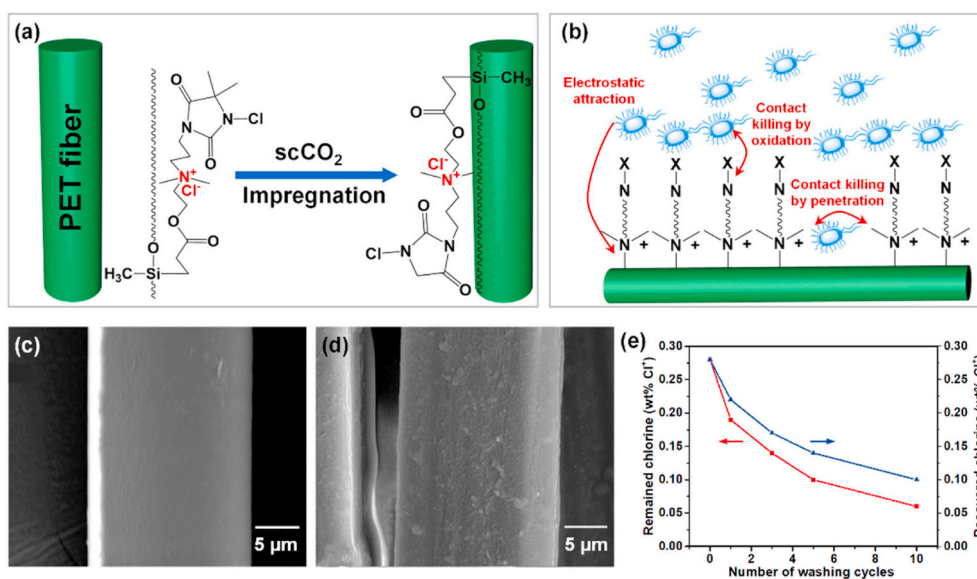
Fig. 9. (a) Schematic illustration showing the interpenetration of the CO_2-philic quat/*N*-chloramine polysiloxane into PET fiber via supercritical CO_2 (scCO$_2$). (b) Electrostatic attraction forms a bacteria-rich region which promotes the contact killing. SEM images of (c) the pristine PET fibers and (d) the PET fibers after supercritical interpenetration. (e) Washing stability and rechargeability of modified PET fibers. Reprinted from Refs. [88]. Copyright 2017 American Chemical Society.

with bacteria. The NFMs constructed by one-step electrospinning mainly comprise two types. One is blending *N*-halamine compounds which serve as antibacterial additives with other spinnable polymers, such as PAN [49,118], cellulose acetate [119–121], nylon-6 [122], polyurethane [48], or PMMA [52]. The other is employing the spinnable polymeric *N*-halamine to fabricate electrospun fibrous materials directly [123–127]. In the first case, Bai et al. [52] firstly selected two *N*-halamine compounds, 1,3-dichloro-5,5-dimethylhydantoin (DCDMH) and 1,3-dibromo-5,5-dimethylhydantoin (DBDMH), as the model *N*-halamines. Subsequently, blending DCDMH and/or DBDMH with synthesized PMMA to prepare the precursor solution and spun it into antibacterial fibrous materials by electrospinning (Fig. 10a). The bactericidal experiments were assessed using the plate counting. It was seen that the control plate exhibited significant bacterial growth with dense colonies, whereas no survival bacteria was observed in PMMA-DCDMH and PMMA-DBDMH plates, implying that the antibacterial activities of the *N*-halamine fibrous membranes come from *N*-halamines rather than PMMA (Fig. 10b). Accordingly, the survival of the bacteria is less than 0.4 after bactericidal assays of the nanofibers, indicating excellent antibacterial efficacy.

N-halamine electrospun nanofibers could be readily fabricated by physically mixing *N*-halamines with polymers, but this strategy is subjected to some annoying problems like unreasonable distribution and instability of antibacterial components. In comparison, the stability and durability of *N*-halamine electrospun fibers constructed from spinnable polymeric *N*-halamines are significantly superior to that of blending *N*-halamine materials. Generally, the spinnable polymeric *N*-halamines involve two types, polymers that intrinsically contain N–H bonds (e.g. aramid and nylon-6) and the synthesized polymeric *N*-halamines. Considering the abundant amide groups and easy-to-electrospun characteristic, Wang et al. [126] selected three kinds of *N*-halamine polymers, polycaprolactam (PA-6), polyhexamethylene adipamide (PA-66), and polyhexamethylene sebacamide (PA-610) to fabricate *N*-halamine electrospun nanofibrous membranes (Fig. 10c–d). After exposure to bleach solution for chlorination treatment, all three membranes are found to be effective in antibacterial application, and the PA-6 nanofibrous membranes presented the highest active chlorine content (907 ppm) due to the most amide groups per gram. Moreover, the PA-6 membranes exhibited excellent antibacterial activity, which inactivated 6 logs of *E. coli* within 10 min. For the synthesized polymeric *N*-halamines, Liu et al. [124] prepared the inorganic-based *N*-halamine nanofibrous membranes by combining electrospinning technique and sol−gel method. The electrospinning solution was prepared by the hydrolysis and polymerization of TEOS and the synthesized *N*-halamine
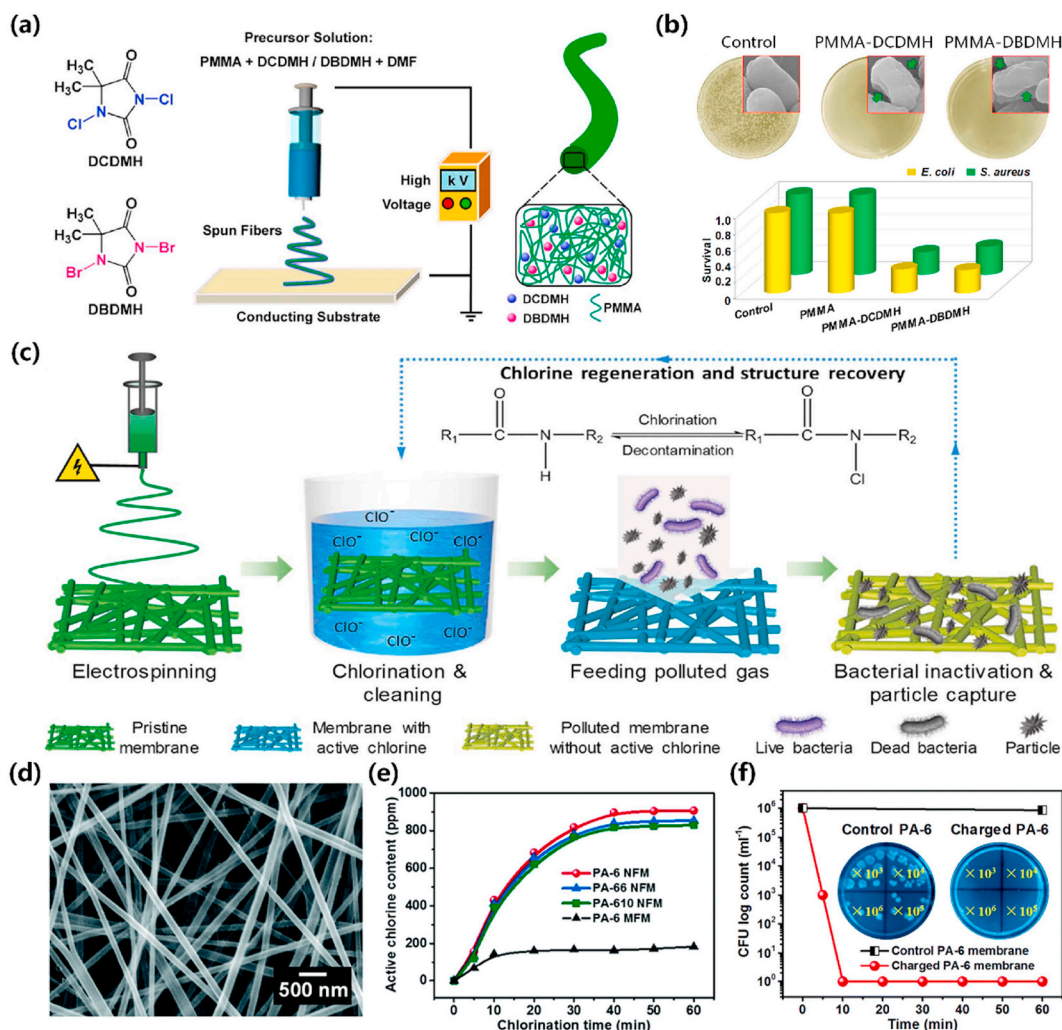

Fig. 10. (a) Schematic illustration of the fabrication pathway of DCDMH/DBDMH-containing PMMA nanofibers using electrospinning. (b) The antibacterial assays of the control, PMMA-DCDMH, and PMMA-DBDMH, respectively. Reprinted from Ref. [52]. Copyright 2016 American Chemical Society. (c) Schematic showing the design of rechargeable nylon nanofibrous membranes and renewable bactericidal activity. (d) SEM image of the nanofibrous membrane. (e) Active chlorine content of the membranes with different chlorination time. (f) Biocidal efficacy of the chlorinated membranes towards *E. coli*. Reprinted from Ref. [126]. Copyright 2019 The Royal Society of Chemistry.

silane, SPH (Fig. 11a). The resulting *N*-halamine/silica nanofibrous membranes (NSNMs) exhibited smooth fiber surface with uniform diameter of 510 ± 83 nm (Fig. 11b). Compared with the control membranes, the chlorinated NSNMs completely killed *E. coli* within 3 min according to the bacterial culture plates and the morphology changes of the bacteria (Fig. 11c).

4.2. Sea-island spinning

Sea-island spinning that produces bicomponent fibers whereby many islands fibrils of one polymer are dispersed in a sea matrix of another polymer, has dramatically accelerated the development of scientific studies on the fabrication of ultrafine fibers [128]. As for the spinning process, two incompatible polymers are melt-blended together to form fibers in an islands-in-sea morphology after the process of preheating, melting extrusion, and drawing, then the sea matrix is usually removed later to leave the island fibers [129,130]. The sea-island spinning has attracted increasing attention due to its extensive raw materials, controllable fiber morphologies, and flexible operation. Badrossamay et al. [131] utilized the synthesized *N*-halamine grafted PP to prepare antibacterial PP microfibers via sea-island spinning method (Fig. 12a). The methacrylamide (MAM), *N*-tertbutyl acrylamide (NTBA), and 2, 4-diamino-6-diallylamino-1,3,5-triazine (NDAM) were selected as functional *N*-halamine monomers to copolymerize with PP (Fig. 12b). The grafted polymers were extruded with cellulose acetate butyrate (CAB), and then immersed in acetone to remove CAB. After that the grafted PP microfibers were fabricated in the form of continuous yarn comprising fibers with different average diameter of 6 μm and 0.6 μm, respectively. Among them, NDAM grafted PP (PP-*g*-NDAM) fibers with diameter of 0.6 μm showed maximum active chloride content due to the amount of the grafted monomers in PP and the higher surface areas of finer fibers (Fig. 12c–d), thus endowing the PP-*g*-NDAM fibers with excellent bactericidal properties against *E. coli* (Fig. 12e).

4.3. Others

Besides the above-mentioned spinning methods, others like dry-jet wet spinning and wet pinning, have also been used to fabricate NFMs. For example, Kocer et al. [132] reported *N*-halamine composite fibers of cellulose, starch, and an oligomeric hindered amine light stabilizer

(HALS) by dry-jet wet spinning method. The cotton, freeze-dried starch, and HALS were dissolved in a certain ionic liquid, then the solutions were extruded and soaked in a tap water coagulation bath to obtain the composite fibers (Fig. 13a–b). After chlorination, the resulting *N*-halamine composite fibers were exposed to UV light and chlorinated repeatedly. As shown in Fig. 13c, over 70% chlorine loadings of the samples had been remained after 6 cyclic testing, indicating that the *N*-halamine fibers exhibited durable UV resistance and rechargeable chlorination properties.

In 2016, Kang et al. [133] fabricated an ultrafiltration membrane made of *N*-halamine hollow fiber by wet spinning process. The synthesized quaternarized *N*-halamine precursor, (3-chloro-2-hydroxypropyl)-(5,5-dimethylhydantoinyl-1-ylmethyl)-dimethylammonium chloride (CDDAC), was grafted onto multi-walled carbon nanotubes (MWNTs) to obtain MWNTs-*g*-CDDAC. Then it was doped in polyvinylidene fluoride (PVDF) spinning solutions to prepare PVDF/MWNTs-*g*-CDDAC hollow fiber membrane (Fig. 13d). Compared with the bacterial agar plate of PVDF membranes, few bacterial colonies were observed on the plate of modified membranes, indicating their good bactericidal performance (Fig. 13e). Moreover, the Cl$^+$ content and the bactericidal activities of the *N*-halamine membranes increased by adding MWNTs-*g*-CDDAC, and the 0.75% MWNTs-*g*-CDDAC doped PVDF hollow fiber membranes (M − 75) exhibited the best sterilization ratios of 95.2% and 92.7% towards *S. aureus* and *E. coli*, respectively (Fig. 13f).

5. Applications

Combining the unique advantages of structural continuity of fibrous materials with rechargeable bactericidal activity of *N*-halamines, the NFMs have attracted increasing attention in the past few decades and shown great potentials in different fields. This section will concentrate on the recent advances in the functional applications of NFMs, involving bioprotective clothing, water disinfection, air purification, and biomedicine.

5.1. Bioprotective clothing

Bioprotective clothing is dispensable for healthcare workers to prevent the pathogenic microbial transmission in the workplace. Current
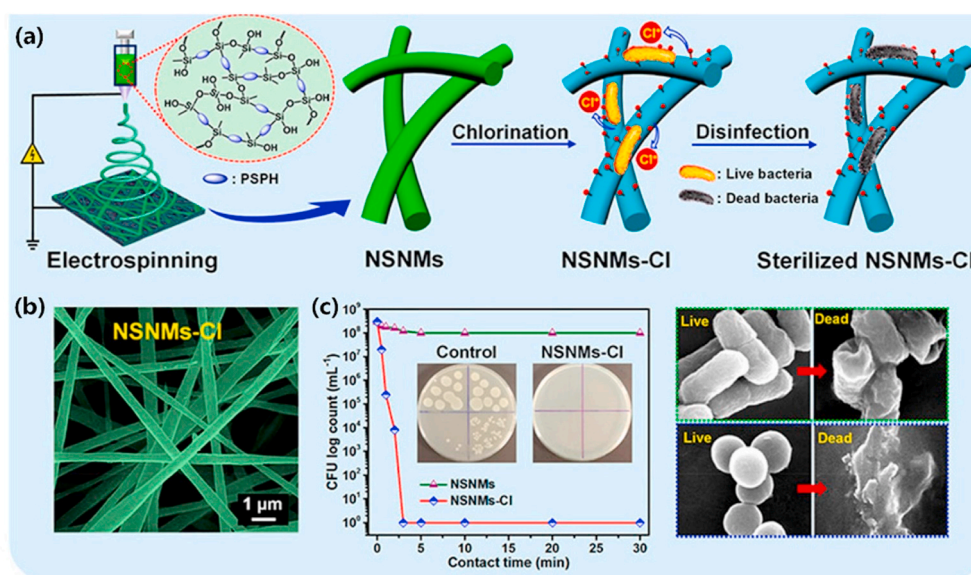

Fig. 11. (a) Schematic showing the design of antibacterial NSNMs using electrospinning. (b) SEM image of the chlorinated membranes. (c) Bactericidal activity of the membranes and the morphology changes of the bacteria before and after contacting with the chlorinated membranes. Reprinted from Refs. [124]. Copyright 2018 American Chemical Society.
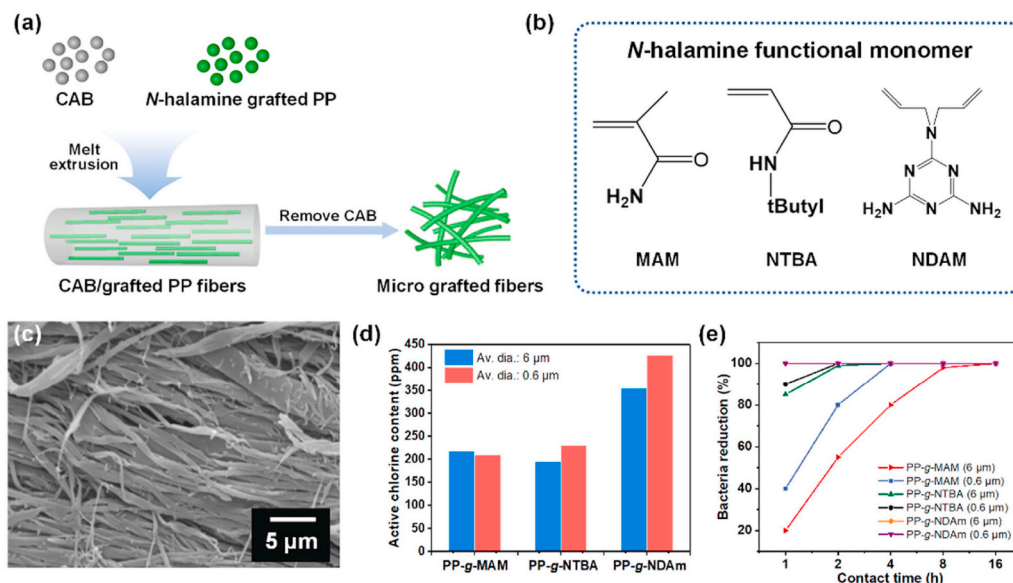
Fig. 12. (a) Schematic showing the fabrication of micro grafted fibers by sea-island spinning. (b) Chemical structures of *N*-halamine functional monomers. (c) SEM image of PP-*g*-NDAM fibers. (d) Active chlorine content of the grafted PP fibers. (e) Bacterial reduction of grafted PP fibers with different contact time. Reprinted from Refs. [131]. Copyright 2008 Wiley.
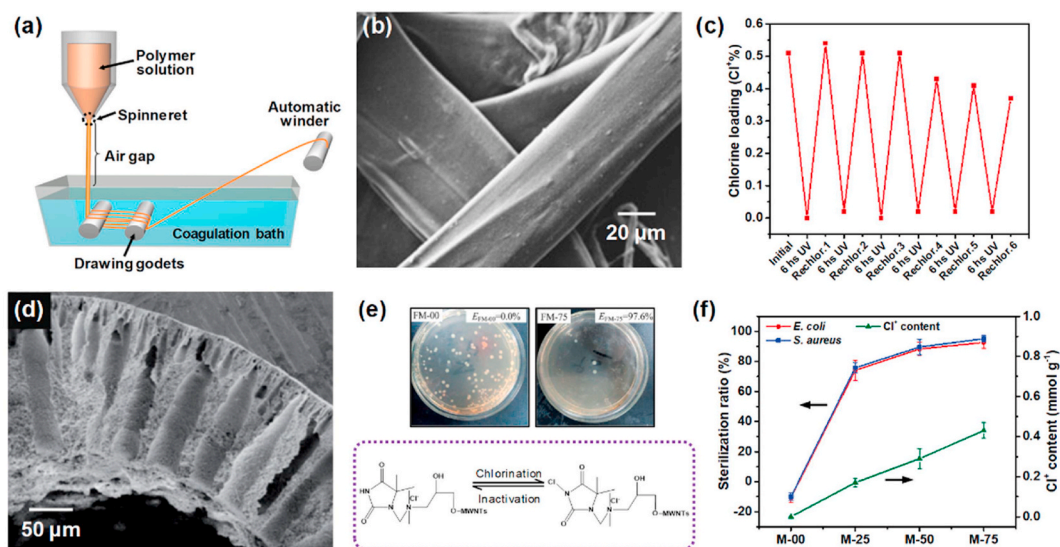

Fig. 13. (a) Illustration showing the fabrication of fibers by dry-jet wet spinning process. (b) SEM image of the cellulose/starch/HALS fibers. (c) Stability of chlorine on fibers upon exposure to UVA light. Reprinted from Ref. [132]. Copyright 2011 Elsevier. (d) Field emission scanning electron microscope image of the cross-section of PVDF/MWNTs-*g*-CDDAC hollow fiber membranes. (e) Antibacterial activity of the control and PVDF/MWNTs-*g*-CDDAC flat membranes (top) towards *E. coli*. Biocidal function of the MWNTs-*g*-CDDAC (bottom). (f) The sterilization ratio and Cl$^+$ content of the ultrafiltration membranes. Reprinted from Ref. [133]. Copyright 2016 Royal Society of Chemistry.

bioprotective clothing can effectively intercept the pathogens physically, but the sustained infection activity of pathogens could easily cause cross-contamination and postinfection [134]. Moreover, in order to make sure the thorough interception of pathogens, the clothing is usually subjected to poor breathability, undoubtedly posing a huge burden for the healthcare workers. Nowadays, the development of NFMs provides an alternative way to fabricate bioprotective clothing that can not only inactivate the pathogenic bacteria but also possess good wearing comfort.

For example, Zhu et al. [42] reported composite membranes with poly (vinyl alcohol-*co*-ethylene-*g*-diallylmelamine) (PVA-*co*-PE-*g*-DAM) nanofibers layered on poly (propylene-*g*-diallylmelamine) (PP-*g*-DAM) meltblown nonwoven fabrics, which could be used for bioprotective

clothing materials. The PVA-*co*-PE-*g*-DAM nanofibers, which was fabricated by sea-island spinning method, formed a nanoweb-like structure on the meltblown fabrics with tunable pore size (Fig. 14a). After being exposed to dilute bleach, the *N*-halamine precursor moieties would be transformed into active antibacterial *N*-halamine structures, achieving a complete kill of *E. coli* within 15 min (Fig. 14b). Besides, the wearing comfort performance of the composite membranes was evaluated by measuring air permeability and water vapor transmission. As shown in Fig. 14c, a linear increase in air resistance of the materials was recorded with the increasing concentration of nanofibers, while no distinct decrease of water vapor transmission was observed. The *N*-halamine composite membranes exhibited exceptional barrier functions towards biological and chemical toxins in aerosol form yet retaining
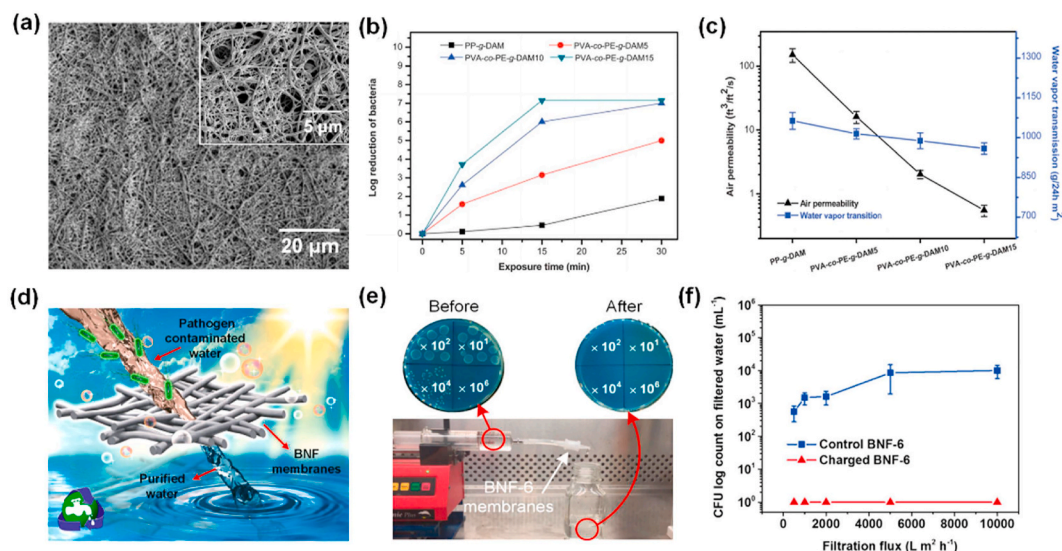
Fig. 14. (a) SEM images of PVA-*co*-PE-*g*-DAM15 nanofibrous composite membranes. (b) Biocidal activities of the PP-*g*-DAM, PVA-*co*-PE-*g*-DAM5, PVA-*co*-PE-*g*-DAM10, and PVA-*co*-PE-*g*-DAM15. (c) Air permeability and water vapor transmission of the membranes with different nanofiber content. Reprinted from Refs. [42]. Copyright 2012 Royal Society of Chemistry. (d) Schematic showing the disinfection of pathogen contaminated water by fibrous membranes. (e) Filtration apparatus for the facile water disinfection process. (f) CFU log count on filtered water as a function of filtration flux. Reprinted from Ref. [135]. Copyright 2015 American Chemical Society.

"breathable" characteristic, which could guarantee the wearing comfort of clothing.

5.2. Water disinfection

Pathogenic microbial contamination in natural and drinking water constitutes a major threat of human health and global economies [136, 137]. Disinfecting water in an efficient, reliable, and sustainable manner is a huge challenge that public health confronts today. The most popular methods of water disinfection are the addition of halogen-based disinfectants, such as free chlorine and other analogues, which could effectively address the problems of microbial-containing water with quality and supply. However, these treatment methods come with the drawbacks of infrastructure-dependent disinfection systems and irreversible decrease in biocidal activity caused by the consumption of disinfectants [138]. Interestingly, *N*-halamine fibrous materials have received great attention for water disinfection due to its high biocidal efficacy, low toxicity, and simple rechargeability. As a typical example, Si et al. [135] presented renewable bactericidal nanofibrous membranes by covalently incorporating *N*-halamine moieties into electrospun nanofibers, which could effectively disinfect contaminated water by filtration (Fig. 14d). The polymeric *N*-halamine, PVA-*co*-PE-*g*-DAM, was synthesized by melt radical graft polymerization. With the electrospinning technique and the following halogenation treatment, the nanofibrous membranes showed 99.9999% bacteria reduction at high organism conditions within 10 min of contact. As shown in Fig. 14e, no survival bacteria were found on the agar plate of the filtrate, demonstrating the high efficiency in disinfecting *E. coli*-containing water. The charged membranes showed a promising high flux of 10,000 L m^{-2} h^{-1} with 6 logs of bacterial reduction, while the control samples only inactivated 2–3 logs of *E. coli* by physical interception effect (Fig. 14f).

To address the problems of specialization, high cost, and time consuming of electrospun water disinfection membranes, Kim et al. [75] developed a cellulose filter using only water as solvent, achieving the energy-saving and improved productivity for water disinfection application. The BTCA/m-phenylenediamine *N*-halamine modification solution was attached on cellulose filter by pad-dry-curing method. The water disinfection process was employed by non-pressure-driven filtration using Buchner funnel. The bacterial solution was added to the

treated cellulose filter that placed on the funnel, and the filtrate was plated on the agar for further bacterial enumeration. As a result, it was found that the chlorinated filters could completely inactivate bacteria in water within an actual contact time of 15.9 s.

5.3. Air purification

The fatal danger of airborne microorganism and particulate pollution on health promotes the development of air purification materials [139]. Antibacterial air purification materials play a crucial role in the daily protection of human health, especially for the airborne microbial transmitted diseases. Recently, Wang et al. [125] fabricated bactericidal polysulfonamide (PSA) nanofibrous membranes by combining electrospinning method with Lewis acid-assisted chlorination, holding great promise as a functional layer for purifying contaminated air. PSA which had abundant amide groups was electrospun into nanofibrous membranes as the *N*-halamine precursor. After the creative Lewis acid-assisted chlorination treatment, the membranes were covered on the 3M surgical mask as a filtration and bactericidal layer to evaluate their air purification performance (Fig. 15a). As exhibited in Fig. 15b, no bacterial colonies could be observed on the surface of the membranes and the covered area, showing excellent biocidal activity when compared with the control area. Additionally, the membranes also exhibited high filtration efficiency (99.8%) towards the aerosol particles with a diameter of 0.3–0.5 µm, demonstrating exceptional filtration performance with low basis weight (Fig. 15c).

The above *N*-halamine polymers containing N–H bonds are highly attractive in the fabrication of air purification materials. However, the limited species of raw materials and their high cost make it difficult for practical application. Liang et al. [140] demonstrate a facile strategy to create NFMs by grafting DMDMH onto EVOH nanofibers for air purification. The resultant materials rendered rechargeable chlorination capacity with active chlorine content over 2000 ppm, exhibiting excellent inactivation efficacy of 99.9999% against *E. coli* with 3 min contact. Furthermore, the filtration performance of the materials with various basis weight were evaluated. When the basis weight of the membranes exceeded 3.2 g m^{-2}, the nanofibrous membranes showed exceptional filtration efficiency (99.1%) with a low pressure drop (105 Pa), much higher than that of commercial N95 commercial masks.
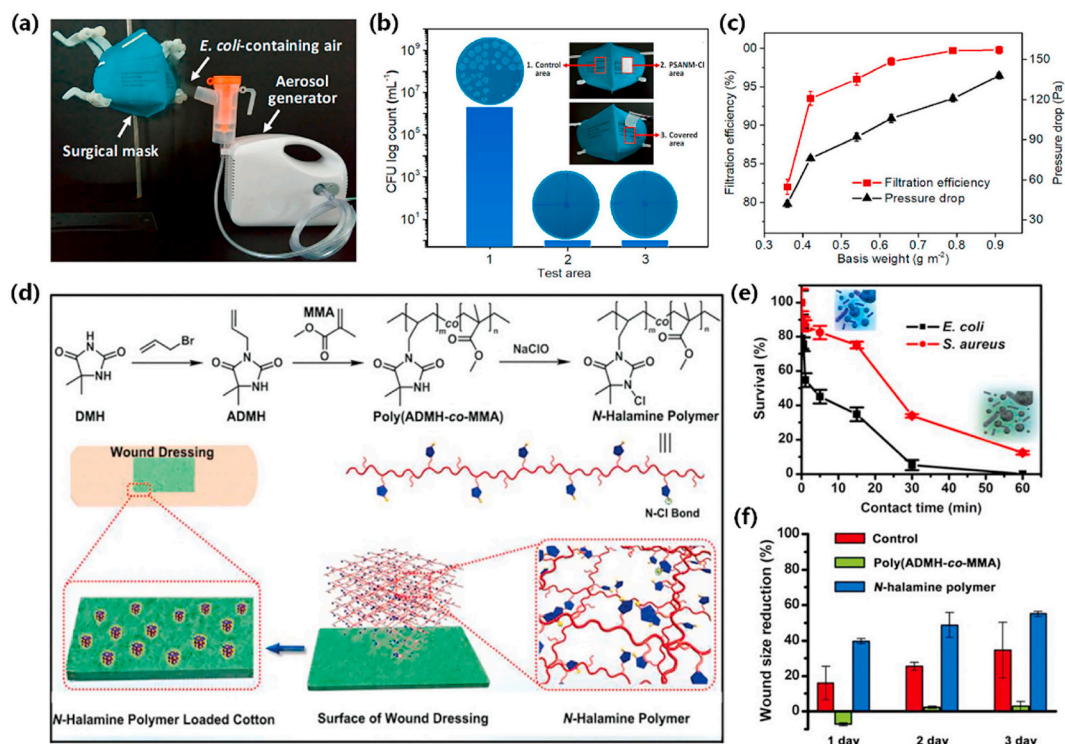
Fig. 15. (a) The interception and bactericidal experiments of a 3M surgical mask that covered with the nanofibrous membranes towards *E. coli*-containing aerosol. (b) Bactericidal activity of the selected three areas of the mask. (c) Air filtration performance of the nanofibrous membranes. Reprinted from Refs. [125]. Copyright 2019 American Chemical Society. (d) Illustration showing the synthesis of the *N*-halamine polymer nanomaterials loaded cotton for wound dressing. (e) Survival of the bacteria after antibacterial essays of *N*-halamine polymer nanomaterials. (f) Wound therapy using the synthesized *N*-halamine nanomaterials at various aging time in a normal mice. Reprinted from Ref. [141]. Copyright 2019 Wiley.

5.4. Biomedicine

The misery from wound and the possible microbial-related infection afflicted considerable patients. Wound dressing would be an effective barrier against environment contaminants, which plays a promising role in protecting wound physically and promoting wound healing [142]. Benefitting from the bactericidal function and good air permeability, the NFMs have been used as wound dressing materials recently. For instance, Gao et al. [141] constructed a *N*-halamine modified antibacterial cotton fabric, which could be used as wound dressing materials for anti-infective wound therapy (Fig. 15d). They first prepared *N*-halamine polymer based on the copolymerization of methyl methacrylate (MMA) and ADMH. Then the *N*-halamine polymer nanomaterials were loaded on the cotton substrate by negative pressure suction filtration technique. The resulting materials could almost inactivate the *E. coli* and *S. aureus* with survival percentages of 0% and 12.38% within 60 min, respectively (Fig. 15e). Moreover, the wound therapy ability of the materials has been evaluated towards the wounds of normal mice. Compared with the control and the unchlorinated polymers, the *N*-halamine polymer could effectively reduce the wound size by 55.09 ± 1.56%, demonstrating the effectiveness of the *N*-halamines for wound therapy.

6. Summary and outlook

Through years of continued efforts, impressive achievements have been engaged in the development of *N*-halamine compounds and the resultant *N*-halamine materials, as well as the antibacterial behavior of *N*-halamines. Antibacterial NFMs have been studied increasingly during the past years owing to the structural continuity, effectiveness toward a broad spectrum of microorganisms, renewable antibacterial activity, and low toxicity. Up to now, various NFMs were fabricated through surface modification method and one-step spinning. Surface

modification is a method that grafting or coating *N*-halamines onto the available fibrous materials, which can be classified into chemical modification and physical modification. Despite considerable studies on surface modification showed its versatility, effectiveness, and operability for fabricating NFMs, it is still challenging to maintain the original morphologies of the fibers and guarantee the durability of the modification layers. The one-step spinning method was a controllable and simple route for the fabrication of NFMs by spinning *N*-halamine polymers directly or blending *N*-halamine compounds in spinning precursors, but this method was limited to the spinnable, solubility, and other properties of the *N*-halamines. Taking into account the chemical and physical properties of the fibrous substrates and *N*-halamines, a satisfactory NFM could be finally obtained through these methods. Based on the synergic effect of antibacterial activity of *N*-halamines and structural characteristics of fibrous materials, the antibacterial NFMs showed great potentials in wide applications of bioprotective clothing, water disinfection, air purification, and biomedicine.

The present NFMs have shown promising results for antibacterial applications, however, there are still some crucial problems and challenges that need further exploration in the following studies. Firstly, from the fundamental antibacterial fibrous materials research point of view, less attention is given to in-depth understanding of the correlation among chemical properties of the *N*-halamines, types of fiber assembly, and the integrated antibacterial performance of the materials. Basic theories and models are needed in order to guide the design of the new NFMs. Secondly, from the antibacterial function point of view, the *N*-halamine materials have been reported to possess excellent biocidal efficacy, but the detailed inactivation reaction of the bacteria (e.g. disrupting cell membrane and inhibiting metabolism) is not entirely clear. Therefore, more research about the biological reaction during the antibacterial process should be carried out under practical conditions, which could offer some suggestions for the construction of targeted

bactericidal materials. Thirdly, from the practical application point of view, the present materials still suffer from intricate fabrication process and high cost, and most of the fabrication pathways are limited to laboratory research, which are not efficient and economical enough. Accordingly, more facile preparation methods that are suitable for industrial production should be developed.

Although much challenging work is still in front of use for the fabrication of next-generation NFMs. We believe that the endless efforts devoted to the exploration of NFMs will finally overcome the above-mentioned obstructions and push forward their rapid development. It is expected that the summarized *N*-halamine compounds, antibacterial behavior, fabrication strategies and functional applications of NFMs, combining with the well-selected references and some personal opinions, can provide some guidance and suggestions to the researchers in related fields.

Conflicts of interest

The authors declare that they have no competing interests.

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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