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A review of smart electrospun fibers toward textiles

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ABSTRACT

Electrospinning as a versatile technology has attracted a large amount of attention in the past few decades due to the facile way to produce micro- and nano-scale fibers featuring flexibility, large specific surface area and high porosity. Stimuli-responsive polymers are a class of smart materials that are capable of sensing surround environment and interacting with them. Therefore, the combination of electrospinning and smart materials could have a great deal of benefits over the development of smart fibers. In this review, it offers a comprehensive understanding of smart electrospun fibers toward textile applications. Firstly, the definition of smart fibers and the differences between interactive fibers and passive interactive fibers are briefly introduced. Then some interactive fibers made from temperature-, pH-, light-, electric field/electricity-, magnetic field-, multi-responsive polymers, as well as some polymers featuring piezoelectric and triboelectric effect which are suitable flexible electrics, are emphasized with their applications in the form of electrospun fibers. Afterwards, some passive and hybrid smart electrospun fibers are introduced. Finally, associated challenges and perspectives are summarized and discussed.

1. Introduction

Animals in nature are capable of keeping warm in cold weather by the superficial insulation layer of air trapped among their body hair on the skin, which can reduce the heat loss from their bodies [1]. However, the body hair of human beings, in the evolution, has been degraded already and the naked skin surface exposed directly to the environment suggests the loss of balance of thermoregulatory. Fortunately, our ancestors of mankind learnt to take advantage of fibers to cover their bodies for keeping warm and protection. The history of fibers is almost as old as that of human civilization. Some study show that some excavated cotton samples were demonstrated to be in 5000 BC and silkworm cultivation traces back to 2700 BC. Even some 6000 BC weaving textiles have been discovered already [2,3]. Textiles, as a crucial part to mankind, plays a significant role in the development of human beings for keeping warm and protection against the harsh surround environment. Nature fibers, such as cotton, wool, silk and linen, serving as the only option of materials, have dominated for thousands of years for producing textiles until the invention of first synthetic fiber nylon in the early last century by DuPont [4,5]. Hence, the artificial fibers and corresponding textiles, featuring more economic and high production, expand greatly the applications and enhance the development of textiles. However, the synthetic fibers derived from traditional technique usually have diameters in the range from tens of micrometers to hundreds of micrometers. Such big fibers significantly limit their applications in smart textiles because of the slow response to the external stimulus.

Going along with the development of innovative technology and science, great changes have been taking place in fibers in recent years, and probably further enriched textiles. Rather than traditional fibers, the smart ones, which are endowed with multi-functionality, are highly promising branch due to the interact ability with external environment. Electrospinning, as a versatile technology, opens a new window for smart fibers and has attracted a large amount of attention in the past few decades due to the facile way to produce micro- and even sub-nano-scale fibers featuring excellent mechanical properties especially flexibility,

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large specific surface area, high aspect ratio, surface functionality, low density, variable fiber formation from one dimension (1D) to three dimension (3D), and high porosity and their broad applications [6–17]. The charged Taylor Cone from the solution formed at the tip of the needle, which is subjected to the electric static force in an electric field, is stretched and flying towards the counter electrode or collector. Accompanied by the jet stretched process, the solvent is evaporated and result in solidification, leading to the formation of electrospun fibers. Owing to the easy setup of producing continuous micro- and nano- fibers and fibrous mats, featuring large specific surface area and high porosity, electrospinning has been considered as a promising technology to produce smart textiles. As the diameter decreases, the specific surface area of fiber will be increased dramatically. The remarkable large specific surface area allows the electrospun fibers to provide a great number of sites to interact close with external environment more effectively. The high porosity offers extreme channels for the medium to transport among fibers in the electrospun mats, thus leading to acceleration of transportation and high sensitivity. More importantly, electrospinning offers a facile way to make use of various materials from inorganic to organic matter. Smart materials, also named as stimuli-responsive materials, are capable of undertaking reversible physical/chemical change in their properties upon exposure to external stimulus, such as temperature [18–21], pH [22–26], light [27–30], electrical [31–38], magnetic [39–41], chemicals [42–46], ions [24,47], etc. It means that they possess the nature of communication with external environment. In one of our previous study, a thermoresponsive polymer was engineered into an actuator by electrospinning. Owing to the large specific surface area and high porosity, together with the temperature-stimuli responsive polymer, the actuator exhibited a remarkable ultra-fast actuation upon the temperature change [48]. Besides, in recent years, more and more efforts have been directed towards the flexible electronics which are capable of sensing mechanical motions, harvesting energy and generating current etc. The polymers having piezoelectric and triboelectric effect, as a promising candidate, are mostly engineered into flexible electronics in the form of electrospun fibrous mats. Therefore, the combination of electrospinning technology with smart materials can open a new window for the fabrication of smart textiles.

Although many brilliant review articles on electrospinning and relevant applications in textiles have been reported, many of them mainly place their emphasis on either only preparation, fabrication or some conventional fibers. Instead, the efforts on putting forward different concepts regarding smart fibers should be enhanced by not only electrospinning process, but also the introduction of some smart materials. Nevertheless, review papers emphasized on smart fibers produced by smart materials are as not yet highlighted. In this review, we will give a comprehensive understanding of conventional and smart fibers, then, especially, focus on the concrete studies concerning the passive and interactive smart fibers produced by electrospun smart polymers, as shown in Fig. 1. Finally, we will present our conclusions, challenges and perspectives of electrospun smart fibers.

2. Definition and types of smart fibers

2.1. Definition of smart fibers

Going along with the development of innovative technology and science, great changes have been taking place in textiles in recent years, which is not be used merely as warmth keeping, body protection, and fashion design. Furthermore, it can be offered distinctive properties and functions in responding to the external environment changes by adopting smart fibers, unique structure or advanced fabrication technologies. Differing from the conventional definition of fibers, smart

Fig. 1. The overview diagram of smart fibers in this review.

fibers which not only have undertaken the task of providing additional values but also have undergone alternation in order to be applied in many other fields, are in the form of either passive smart fibers or interactive smart fibers [49]. The passive smart fibers, which would not interact with or adapt to external environment changes, possess some unique functions; in contrast, the interactive smart fibers can not only sense but also react to the environment stimulus/conditions by presenting feedback. Being independent of the types of smart fibers, their "intelligences" all come from the materials, structures, fabrications or treatments.

2.2. Passive smart fibers

Passive smart fibers are defined as fiber, yarns or mats having some special functions even without receiving any stimulus from the external environment, such as anti-bacterial, self-cleaning or waterproof-breathable properties. They present less motivation when carrying out the communication with external environment. However, the intrinsic properties or structures, or the incorporation of functional components into fibers probably provide them with more or less intelligence. For example, a cotton fabric [50], with silver particles loaded on the surface, shows high effect on the reduction of *Staphylococcus aureus* and *Escherichia coli* bacterial due to the effective antibacterial effect of silver [50]. Also, according to the effect of lotus leaf, textiles can be endowed with super hydrophobicity by which they gain the ability of self-cleaning [51]. Similarly, the addition of photocatalyst TiO_2 provides textiles with self-cleaning feature of degrading dye molecules upon irradiation of solar light [52]. And many scientists have dedicated to the construction of directional water transport textiles that allow the water to transport only in one direction instead of the opposite direction [53].

2.3. Interactive smart fibers

In contrast with passive smart fibers, interactive smart fibers, being a kind of functional matter, can conduct interactive behaviors on its own automatically towards a specific requirement. Here, the interactive behaviors are general associated with information/stimulus receiving and feedback giving. Information/stimulus receiving are widely acknowledged of being stimulated by temperature, pH, light, electricity and magnetic field etc. that are significantly related to the properties of materials. And the feedback is relevant for physical/chemical properties changes, mechanical motions, shape-change, signal-output etc. Interactive smart fibers have the ability of interacting with external environment by changing itself when inputting signals and they are more motivated. For example: Gram-negative (*E. coli*) and Gram-positive (S. epidermidis) bacteria were killed by the antibiotic drug chlorhexidine released from a cross-linked gelatin electrospun mat as a result of volume change upon the alteration of surrounding pH due to its pH sensitivity [54]. As the key features of passive and interactive smart fibers illustrated in Fig. 2, it should be noticeable that there is not a sharp boundary between them, but the interactive smart fibers are interactive and more motivated, generally realized by applying smart materials, designing distinctive structures and advanced fabrication technologies.

3. Brief introduction of electrospinning and electrospun fibers

It is well known that once materials are engineered to nanoscale, they could take on some unique properties which have the great potential for great impacts in a wide range of areas. For instance, the specific surface area is inverse proportional to the size. As the diameter of the fiber decreases, the specific surface area would increase. The surface area per mass of fiber could reach up dramatically from around 10,000 to 1,000,000 m^2/kg, as the diameter falling from 500 nm to 5 nm

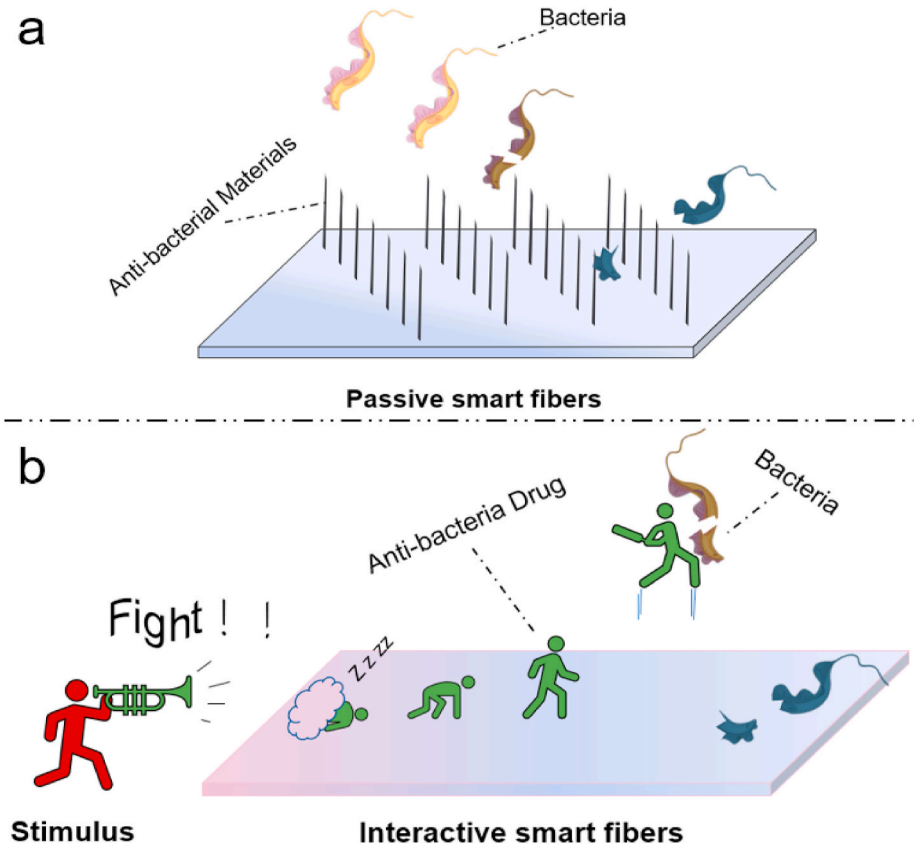

Fig. 2. The schematic illustration of key features between (a) passive smart and (b) interactive smart fibers with the function of anti-bacteria.

[55]. The fiber at nanoscale enable the relevant fibrous structure the possibility to get a high porosity of even more than 99% [56]. The remarkably high specific surface area allows the electrospun fibers to offer extremely high capacity and a notably enormous number of adsorption sites for the effective capture or release of corresponding particles, molecules, and functional groups etc [57]. This ability can make it interact close with surrounding materials and sense external environment more effectively, thus impacting sensitivity and reactivity [58].

In addition, the electrospun nanofibers further assembled into an ordered structure like bundles and yarns could increase their practical usage and expand their applications. Specifically, compared with old-fashioned yarns, the unique features of bundles and yarns, in which the number of electrospun nanofibers in a unit area of cross-section is dramatically increased, would be improved and highlighted such as flexibility and functionality. For example, it is well known that, in material science, synthetic fibers are unable to have both high toughness and high strength. In a recent research, this intrinsic conflict between them has been overcome by electrospun fibrous yarns, whose toughness and strength were comparable to those of spider silk [56]. This remarkable yarn was fabricated from poly (acrylonitrile-co-methyl acrylate) with a few poly (ethylene glycol) bisazide servicing as cross-linker, followed by annealing under tension. The resulting cross-linked aligned multi fibrillar yarns exhibit spider silk-like overall properties of a tensile strength of nearly 1.3 GPa in combination with a toughness of around 137 J/g [56]. Briefly, it is possible and attractive to generate electrospun fibers from single fiber to bundles and yarns with excellent mechanical properties by tailoring structures at multiscale and the selection of polymers whose properties are controlled by polymer architecture which is controlled by macromolecular architecture and processing.

Weaving is one of the traditional textiles manufacturing processes during which one of the two sets of yarns/threads is stretched, named warp, and the other one serving as weft are interlaced in perpendicular to the warp. It is probably to have some benefits over the integration of electrospun yarns with woven textiles. In one application of drug release, paclitaxel (PTX), a drug loaded in the twisted warp and weft yarns during the formation of electrospun fibers, was used to study the effect of packing density of plain-woven fabrics on the drug release profile. The long-term drug release profile was achieved by the diffusion effect combined with the matrix degradation [59].

More details of electrospun fibers fabrication process and other characteristics have been reported in many excellent papers already [60–62]. Therefore, electrospun nanofibers, taking a form of a continuous linear configuration, have exhibited great promising in smart fibers due to those distinct properties of fiber at nanoscale.

4. Interactive smart fibers produced by electrospinning

One of the most important considerations for fibers is the selection of materials that confers some intelligences to them. Owing to the easy-setup, a broad spectrum of materials, including organic materials, inorganic materials and their combinations, can be electrospun into nanofibers. Notably, among various kind of materials, those smart materials, also named as stimuli-responsive polymers, have greatly promote the rapid development of electrospun mats in the field of smart fibers. Stimuli-responsive polymers are a class of high-performance polymers that are capable of undertaking physical/chemical properties change upon exposure to external stimulus, such as temperature, pH, light, electrical, magnetic el al [41,63,64]. And the integration of these stimuli-responsive polymers with nanotechnology, such as electrospinning, has greatly accelerated the growth and population of smart fibers. The responsive rate, in some cases expressed as sensitivity at which the stimulus reaches the polymer chains, is governed by the mass/energy transfer diffusion. Once the stimuli-responsive polymer bulk is engineered into nano-scale or nano-fibrous fibers by electrospinning, the resultant larger specific surface area and the higher porosity can facilitate the sensitivity. The higher porosity and the larger specific surface area contribute to shorter diffusion distance and more interactive sites, respectively [65–68]. Besides, the smart properties can also be originated from special polymers having special effects like piezoelectric and triboelectric effect, which is one of the best options for the fabrication of flexible electronics.

4.1. Stimuli-responsive polymers based interactive smart fibrous fibers

4.1.1. Temperature-responsive electrospun fibers

Temperature-responsive polymers, also called thermoresponsive polymers, have the ability of performing temperature-dependent changes, which is interiorly reflected in the transition of polymer chains between two thermodynamically stable states of coil and globule in solution. The swelling behavior is mainly attributed to the coil state, at which the expanded polymer chains keep a hydrophilic coil conformation [69–71]. However, the collapsed hydrophobic globule state indicates a shrinkage. According to this temperature-dependent shifting property, temperature-responsive polymers can be characterized as lower critical solution temperature (LCST) and upper critical solution temperature UCST. As illustrated in the temperature-composition diagram, shown in Fig. 3a, LCST and UCST polymers can display a miscibility gap upon a high temperature and/or a low temperature, respectively. And the LCST and the UCST, reflected in the temperature-composition diagram, are the minimum and maximum temperatures, respectively. In terms of LCST polymers, they are soluble or swellable upon cross-linked in aqueous solution below the LCST points, whereas they turn into insolubility or show shrinkage behavior above their LCST, and vice versa for UCST polymers [72–74].

Poly(N-isopropylacrylamide) (P(NIPAM)) whose chemical structure is presented in Fig. 3b, as a typical example of LCST polymers, has been widely investigated in the past decades. It is well known that P(NIPAM) has a LCST near 32 °C at which the phase transition can be triggered in the physiological range, so that, it can be used with great benefits as a smart resource to develop fibers. In one study, an anti-cancer drug doxorubincin (DOX) was encapsulated into cross-linked P(NIPAM)/gelatin electrospun nanofibers. After heating up the nanofibers from RT to 37 °C, the nanofibers shrunk nearly half its original diameter. The in Vitro test implies an on-demand drug release profile upon the rising temperature above LCST, consequently lower the viability of human cervical cancer Hela cells [75].

In another study, Ma et al. [76]. reported a core-shell fibrous structure designed by coaxial electrospinning. In this unique structure, the thermoresponsive polymer P(NIPAM) and biodegradable material polylactic acid (PLA) were applied as shell and core components, respectively. And the temperature-dependent state of P(NIPAM) shell has a great impact in the drug release of Combretastatin A4 (CA4) from PLA core.

More importantly, P(NIPAM) copolymers, which can be synthesized easily just by radical polymerization due to the existing of double bond in NIPAM monomer, are able to provide P(NIPAM) some interesting properties and further introduce them to a broader spectrum of diverse applications. For instance, some introduced moieties designed to exhibit crosslinking function can provide P(NIPAM) with insolubility even in an environment with lower temperature than LCST. In one study, Chen et al. [77]. selected N-hydroxymethyl-acrylamide (NMA) cross-linked P(NIPAM) electrospun nanofibers as the carrier doped with an 1,10-phenanthroline-based fluorescent sensor (F-phen) for detection of metal ions. The insolubility after crosslinked makes it possible for reuse and the effectively enhanced sensing performance is contributed to high specific surface are of nanofibers which is 1–2 orders of magnitude the deep-coated films, leading to high sensitivity. Furthermore, the temperature-dependent swell-shrunk P(NIPAM) fibers could be played as a switch by which the ability to approach the sensors could be adjusted. Besides, thermoresponsive electrospun nanofibers can be

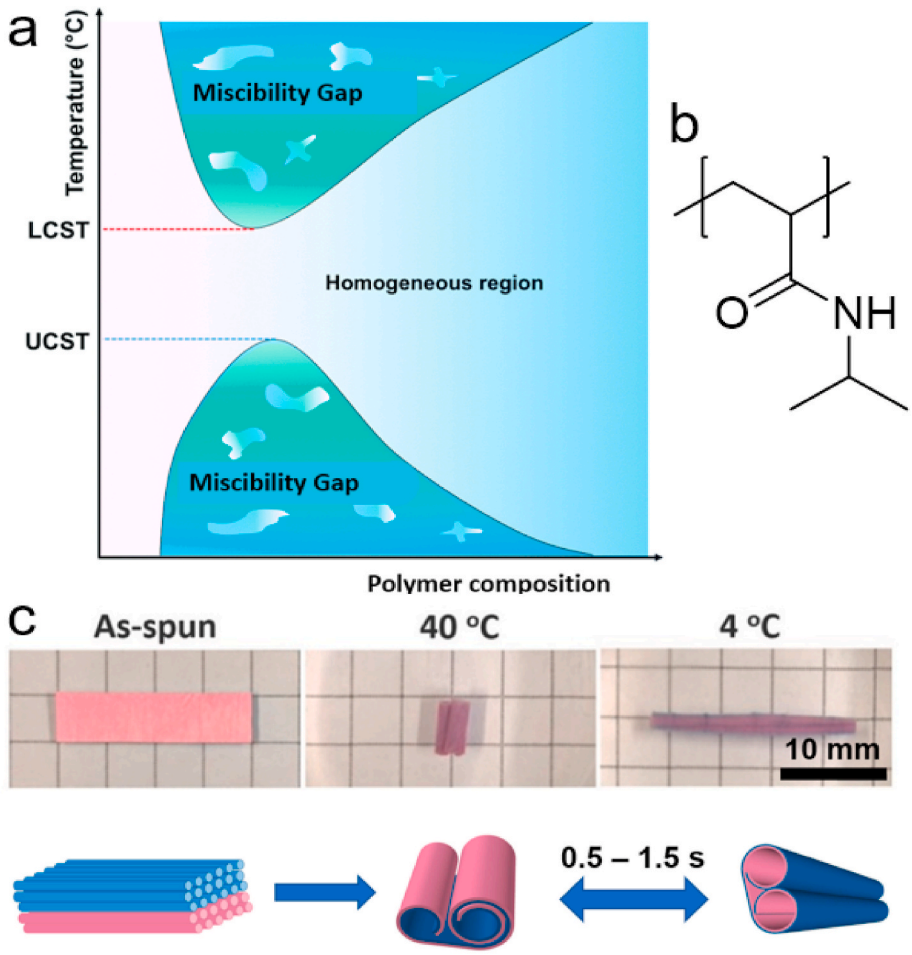

Fig. 3. (a) the temperature-composition diagram of thermoresponsive polymers aqueous solution; (b) The chemical structure of P(NIPAM); (c) a P(NIPAM) electrospun actuator showing ultra-fast and reversible actuation in 1.5 s upon the surrounding temperature change. (a) Reproduced with permission from Refs. [72]. Copyright 2017 Royal Society of Chemistry. (c) From an open access article.

served as actuator as well [78,79]. As shown in Fig. 3c, Agarwal et al. demonstrated a superfast reversible actuating behavior of a bilayered fibrous structure composed of a 4-benzoylphenyl acrylate (ABP) crosslinked P(NIPAM) fibrous membrane and a thermoplastic fibrous membrane (TPU) by electrospinning upon cooling and heating cycle between 0 °C and 40 °C. This superfast responsive ability and versatile actuation is attributed to the aligned fibers at nanoscale which can offer sufficient surface area for energy exchange.

In addition, recently, some scientists reported a facile way to fabricate surgical mesh with 4D response by coating a copolymer of N,N′-methylene bis(acrylamide) (MBA) crosslinked P(NIPAM) on a cold-plasma treated surface of PP fibers in a knitted fabric [80]. The resultant coated knitted fabric showed a 4D response upon temperature change, which may indicate one of the new generations of surgical meshes. However, compared with other thermoresponsive actuators from electrospun nanofibers [78], it is quite insensitive to the temperature, whose response time was in the range of 2–15 min. This is caused by the different specific surface area between traditional textile fibers and electrospun nanofibers.

4.1.2. pH-responsive electrospun fibers

pH-responsive polymers are a series of stimuli-responsive polymers that can respond to external pH changes by conducting physical and chemical nature changes. In terms of the mechanism, pH-responsive polymers can be defined as polyelectrolytes that contain, in their polymer chains, either weak acidic groups or basic groups which favor protonation or deprotonation varied from surround pH values. The corresponding ability to accept protons under low pH condition and release them under high pH condition of these functional groups is associated with their pKa. At pH lower than its pKa, they prefer to accepting more protons; otherwise, they are willing to releasing more protons. However, the performance the pH-responsive polymers undergone could be distinct from their classifications. Generally, there are two types of pH-responsive polymers depending on the acidic groups or the basic groups they have. Polymer having acidic groups possesses negatively charged polymer chains after releasing protons at high pH, featuring dissolution or swelling behavior, such as poly (acrylic acid) [81], poly(methacrylic acid) [82]. Those basic group-based pH-responsive polymers, such as poly((2-dimethylamino)ethyl methacrylate) (PDMA) [83], poly((2-diethylamino)ethyl methacrylate) (PEDA) [84], form positively charged polymer chains upon capturing protons at low pH, leading to dissolution or swelling behavior. These dissolutions or swelling behaviors are attributed to the electrostatic repulsive force between the same charged polymer chains. Such a unique pH-dependent transition and the ability to capture and release counter ions make pH-responsive polymers very popular in scientific area in recent years [85]. Particularly, the introduction of electrospinning makes pH-responsive polymers a promising field in a broader spectrum of applications. The high specific surface area of pH-responsive polymers electrospun fibers facilitate the interaction between two oppositely charged groups resulting from the enhancement of diffusion of ions from surrounding aqueous environment.

All these distinct properties make pH-responsive polymers incorporated with electrospinning well-suited for a broad spectrum of fields. In

efforts to pack poly(allylamine hydrochloride) (PAH) and poly(acrylic acid) (PAA), two kinds of oppositely charged polyelectrolytes, into highly confined macromolecular, Zussman et al. [86]. fabricated nanofibers from an adjusted stoichiometric ration of PAA-PAH low-pH solution by electrospinning. The results demonstrated that the polyelectrolyte complexes nanofibers exhibit a high pH-responsive ability featuring high dependency on the pH surroundings. The reversible swelling-shrinkage performance of these obtained nanofibers varied from pH 1.8 to pH 5.5, in accordance with the degree of ionization of the polyelectrolyte complexes, implying great potential in tailoring and manipulating fiber properties.

The nature of interaction between charged polymer chains with counter ions could be reflected in the switchable wettability states, featuring hydrophilicity and hydrophobicity determined by the surrounding pH values. With the help of electrospinning, one of the applications regarding to this nature is oil/water separation. Stemming from the high porosity and specific surface area, poly-(dimethyl siloxane)-block-poly(4-vinylpyridine) (PDMS-b-P4VP) electrospun mat was endowed with effective pH-responsive oil/water surface wettability as a result of the protonation and deprotonation of pyridyl groups in the P4VP segments [87].

Another important application of the pH-responsive polymers incorporated with electrospinning is to apply electrospun mat as a platform. Due to the ability of pH-responsive polymers to interact with counter ions, the electrospun pH-responsive polymeric nanofibers could be utilized as a carrier to capture, detection and detachment. Poly((2-(dimethyl amino) ethyl methacrylate) PDMAEMA as a positive charged polymer is capable of capturing negative charged groups as a result of protonation of MDAEMA segment, which could be modulated by regulating the pH value of surroundings. Owing to highly sensitive to microenvironment, pyrene-based materials are always considered to be a good candidate as a fluorescent probe. Chen et al. [88]. synthesized a copolymer poly((2-(dimethyl amino) ethyl methacrylate)-co-(stearyl acrylate)-co-((1-pyrene) methyl 2-methyl-2-propenoate)) (poly (DMAEMA-co-SA-co-Py)) via free radical polymerization, followed by electrospinning into nanofibers. As illustrated in Fig. 4, the multifunctional capture, detection and detachment of DNA were integrated in this all-in-one nanofiber carrier. The low pH surrounding leads to the electrostatic repulsion between MDAEMA segments, in accordance with the ionization of MDAEMA segments, and causes the separation of pyrene excimer, featuring the decrease in excimer-to-monomer ratio. Upon the presence of DNA, the pronated fibers perform the interaction with the counter charged group from DNA, capturing the DNA. Correspondingly, as compared to the absence of DNA, the addition of DNA contributes to more pyrene segments in proximity through electrostatic interaction, thus resulting in the increase in excimer-to-monomer ratio. Furthermore, the detachment of DNA could be conducted by modulating the pH value to 7.

4.1.3. *Light-responsive electrospun fibers*

As compared to other stimulus, light has been considered as a desirable stimulus in terms of easy-get, safe, clean, precise and flexible. Under the illumination, the light-responsive polymers have the capability to undergo physical or chemical property change. The mechanism behind this is that the light, as a kind of energy, after absorbed by the photo sensitive molecules or moieties in the polymer chains, causes a large structure change. Light responsive polymers can be roughly categorized into either photochemical or photothermal type.

The photochemical effect is often triggered by the light-induced moieties photoreaction, for instance, photo induced isomerization and dimerization. Photoisomerization is a behavior at molecular level, at which a conformational change between isomers is generated by light irradiation. Usually, it consists of ring opening-closing transition and trans-cis isomerization. The compounds of the former one undergoes bond reaction or cleavage in response to light irradiation at particular wavelengths, like fulgide and diarylethene. The example of latter one is endowed with the switch ability between the two states that compounds rotating or inversing around the double bond, such as azobenzene and stilbene.

Among the photo-responsive groups, azobenzenes are one of the most widely used type of functional molecules. Typically, at molecular level, the azobenzene group undergoes two states, trans vs cis isomers, as shown in Fig. 5a. These two states are able to be interconverted by particular light wavelengths: a UV wavelength of 300–400 nm for trans-cis conversion, to a less stable state, higher energy cis isomer and visible light >400 nm for the cis-trans conversion, back to a relaxed trans isomer [89]. In one demonstration, an azobenzene-functionalized PCL electrospun nano fibrous mat exhibit a light-dependent

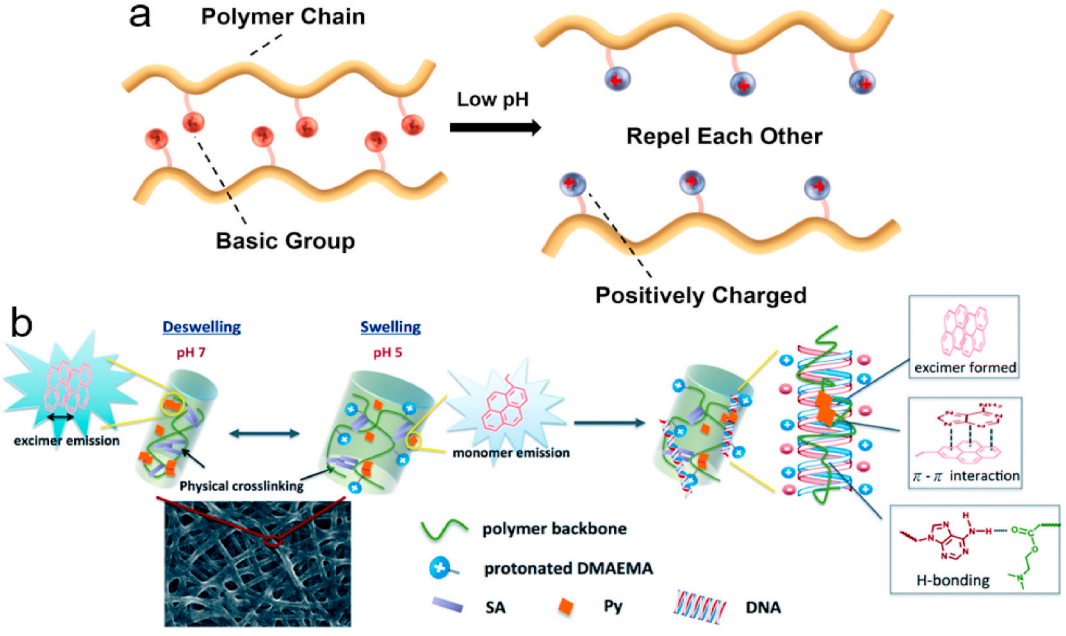

Fig. 4. (a) The illustration of mechanism of basic group-based pH responsive polymer and (b) the schematic drawing the mechanism of poly(DMAEMA-co-SA-co-Py) electrospun fibrous mat using as DNA sensor. From an open access [88].

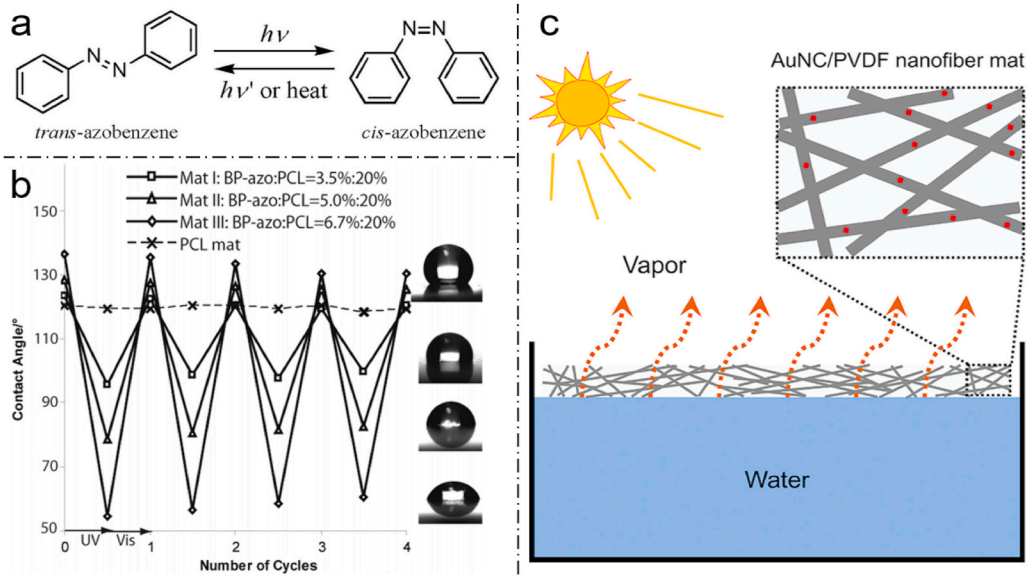

Fig. 5. (a) The illustration of trans-cis transition of azobenzene and (b) the light-driven wetting behavior of azobenzene modified PCL electrospun fibrous mat; (c) diagram presenting the application of AuNC loaded PVDF electrospun nanofibrous mat in the field of water purification via the energy from Sun. (a) Reproduced with permission from Refs. [89] Copyright 2018 Elsevier Ltd. (b) Reproduced with permission from Ref. [90] Copyright 2011 American Chemical Society. (c) Reproduced with permission from Refs. [94] Copyright 2018 Elsevier Ltd.

wettability-controlled surface, whose hydrophilic and hydrophobic behavior was tuned by the alternating UV irradiation and visible light irradiation, corresponding to cis isomer and trans isomer, respectively [90], as shown in Fig. 5b.

Owing to this special transition of azobenzene group, it is attractive in the application of remote-control drug release system in combination with the host-guest interaction between α-cyclodextrins (CDs) and trans isomer of azobenzene. Therefore, upon UV irradiation, the host-guest interaction would be suppressed during the trans-cis transition, leading to a light triggered remote α-cyclodextrin based drug release profile [91]. Based on this mechanism, in another demonstration, the introduction of CDs-based drug into poly (vinyl benzyl chloride-block-glycidyl methacrylate) poly (PVBC-b-PGMA) electrospun nanofibers realize a fast light-triggered on-demand drug release. In response to UV irradiation, a well-regulated drug release profile was obtained, whereas the same phenomenon in dark condition was hindered [92].

Beside photochemical classes, generally, regarding light-responsive polymers, they are probably associated with photothermal effect which can convert light into heat. This effect can be enabled by the photothermal polymers, including polydopamine (PDA), polypyrrole (PPy) and polyaniline, or the photothermal components as the key switch embedded in polymer forming photothermal objectives or composites, such as Au nanocages (AuNCs), carbon nanotube (CNTs), indocyanine green (ICG), reduced graphene (rGO), Fe_3O_4 particles and black phosphorus.

And the incorporation of photothermal component into polymer fabricating hybrids or composites is considered as a frequently versatile strategy. AuNCs as a considerably greater photothermal effect material with low-cost advantage has been employed in many applications already [93]. Xia et al. fabricated a remarkable nanofibrous mat for water purification by incorporating the AuNCs into poly (vinylidene fluoride) (PVDF) electrospun nanofibers. As compared to the conventional bulk heating system, this integrates demonstrated a considerably improved evaporation efficiency via distinctive photothermal effect of AuNCs and the high specific surface area, high porosity and the interconnective structure of the electrospun mat [94], as presented in Fig. 5c.

Benefiting from the effective photothermal performance of multi-walled carbon nanotubes (MWCNTs), Huang et al. fabricated a poly-L-lactic acid (PLLA) composite nanofibers loaded with MWCNTs and the anticancer drug of doxorubicin (DOX) by electrospinning. It demonstrated an improved inhibitory effect on tumor growth by the combination of the hyperthermia effect and a fair amount of DOX diffusing from fibers into tumor sites upon NIR irradiation [95].

Comparably, in another study, Szunerits et al. utilized rGO to do a similar investigation. They designed an on-demand drug release system by embedding rGO in cross-linkable poly (acrylic acid) (PAA) nanofibers with the help of electrospinning. Upon irradiation of NIR at 980 nm, the antibiotic drug of ampicillin and cefepime were released from rGO-embedded nanofibers without losing their biological activity [96].

Recently, Xia et al. reported a simple and innovative welding method by introducing photothermal dye ICG into nanofibers by electrospinning. The localized welding area of this nanofibrous mat could be well defined, taking advantages of the great photothermal effect of ICG, along with the low melting point of PCL at around 60 °C. In consequence, under NIR illumination, the exposure area of the PCL fibrous mat melts after the temperature of local area reaches the melting point of PCL owing to the photothermal effect of ICG. The morphology, mechanical strength, extent of welding and other properties of this mat could be adjusted by tuning irradiance of NIR, exposure time and the concentration of ICG [97].

4.1.4. *Electrical sensitive electrospun fibers*

Electrical responsive materials that respond to electrical field, other than other smart materials, sparked research interest in mainly developing actuators. Electroactive polymers (EAPs), which are highly flexible plastics, are a field of polymers that perform a change in size or shape during an electrical stimulation of electric field. In comparison with electronic EAPs actuator, driven by Coulomb force, those ionic EAPs-based ones offer an obvious advantage of lower voltage as low as 1–2 V. In a particular case of actuator design, ionic EAPs based actuators are driven by the diffusion or displacement of ions when stimulated by an electric field. The mechanism has been common suggested that, although still no definitively clear, upon a simulation of electric field, the negative ions fixed to the polymer chains are subjected to an attractive force from the anode, while the movement of cations toward the cathode taking place, therefore resulting in actuation. Polypyrrole (PPy) is such an ionic EAP, which is usually considered one of ideal candidates for ionic EAP actuators. In one study, as shown in Fig. 6a–c, a fiber-based actuator was fabricated by the electrochemical deposition of PPy on an Au electrode layer which was coated on the one side of substrate of an aligned electrospun poly(hexamethylene adipamide) (nylon-6/6) fibrous mat. This electrospun fiber-based actuator what may regard as the assemble of thousands of individual one-side coated bilayer fiber, shows a facilitated actuation in ion solution when electric field was applied. This is associated with the enhanced ions diffusion across the

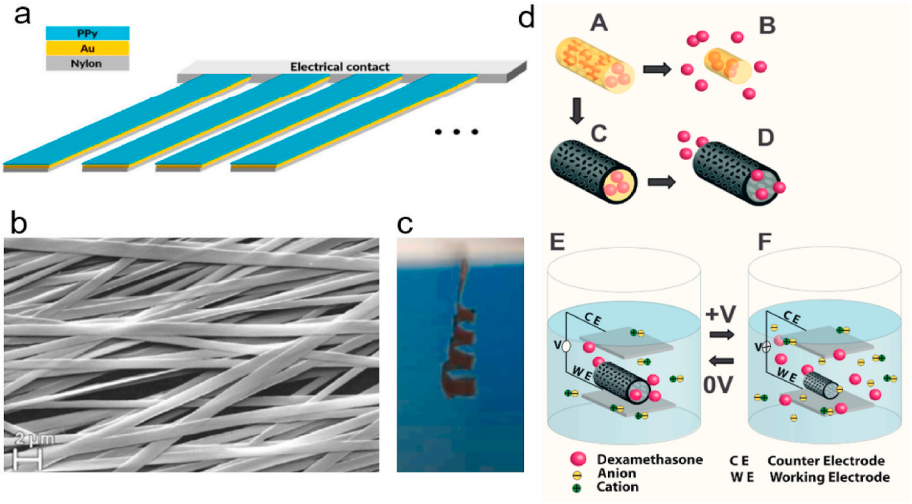

Fig. 6. (a) the configuration of nylon-based actuator; (b) the SEM image of gold coated nylon-ribbons showing the fibers aligned morphology and (c) the photograph of its actuation at a constant current; (d) The schematic illustrating the controlled release process of drug dexamethasone from PEDOT-coated PLGA electrospun fibrous mat under electric field. (a–c) Reproduced with permission from Ref. [98] Copyright 2017 American Chemical Society. (d) Reproduced with permission from Ref. [100] Copyright 2006 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

interface of PPy, which is facilitated by huge specific surface area of electrospun fibers [98].

Using a similar principal, Kee et al. fabricated an actuator made from polyaniline (PANI) nanoparticles chopped cellulose acetate electrospun fibrous mat and studied its bending behavior as a function of dopant concentration under external electrical input. As the increased concentration of PANI particles, the displacement of the composite actuator was shown much larger, since the main reason that the charged PANI particles interact with free ions inside the cellulose acetate [99]. To a certain extent, these reversible actuators paved the way to the design of artificial muscles.

Not only the design in actuator but also the application in drug release can ionic EAPs be employed. Upon the stimulation of electric field, a volume change can be induced in an ion-doped conductive polymer of poly(3,4-ethylenedioxythiophene) (PEDOT). For instance, as illustrated in Fig. 6d, owing to this electrical induced volume change property, a drug of dexamethasone controlled-release profile from PEDOT-coated PLGA electrospun fibers was achieved by applying external potential [100].

Much like other EAPs, in general, pH sensitive polymer such as poly (acrylic acid) (PAA), whose ionization feature varied from surrounding pH, is expected to be sensitive to electric field. As the deprotonation taking place, the protons or the negatively charged polymer chains of PAA prefer to moving towards the cathode or the anode, respectively, under the electric field stimulation. PAA, therefore, may particularly offer a unique advantage of electric field dependent volume change [101]. In a drug release system, it demonstrated that the swelling ratio and rate of the multiwalled carbon nanotubes (MWCN) incorporated PVA and PAA electrospun fibers are positively correlated to the applied voltage [102]. However, since the diffusion of ions inside electrolyte, these ionic EAPs need to maintain the wetness all time, which could limit the applications.

Apart from the actuator, using a hybrid approach, functionality of smart fibers can also be indirectly obtained. To generate heat from wearable fabrics, in one study, a sandwich configuration of Ag nanofibers/silk fabric/Pt nanofiber were constructed, respectively corresponding with heat generation under external current and temperature monitoring units by sputtering Ag and Pt on each surface of polyvinyl alcohol (PVA) electrospun fibers. And this integrated functional unit has the capability of remote real-time heating and temperature control through a smart cellphone [103].

4.1.5. *Magnetic electrospun fibers*

With an aim to achieve magnetic sensitive fibers, electrospinning technology has been considered the desirable way to align the magnetic sensitive particles resulting in the formation of magnetic sensitive fibers. Pure Fe and Co nanofibers were successfully fabricated, respectively, after the annealing treatment of poly(vinyl butyral) (PVB)/Fe or poly (vinyl butyral) (PVB)/Co electrospun nanofibers under an H2 atmosphere at 550 °C for 5 h, featuring magnetic properties [104]. In addition, magnetic sensitive polymers, that in particular are organometallic copolymers or composites, are of great scientific interests and have broad potential applications in numerous fields due to their shared features with metals and organic polymers. To make a magnetic sensitive electrospun fibrous mat, in comparison with the former approach, the later one of constructing composites by embedding magnetic ingredients into fibers is a simpler and more direct way.

In one study, Guo et al. found that the polyacrylonitrile (PAN) electrospun fibrous mat were endowed with magnetic properties after the incorporation of Fe_3O_4 particles, and the enhanced magnetization was attributed to weaker dipolar interaction arisen from the increased space distance between Fe_3O_4 nanoparticles [105].

In fact, electrospun fibers can be provided with multifunctionality after the introduction of superparamagnetic particles due to the magneto-thermal effect that of oscillatory magnetic field induced heat from superparamagnetic particles. In a study of cancer treatment, as presented in Fig. 7, compared with the warm water bath method, cancer cells were killed in a more effective way by the oscillatory magnetic field induced heat from the loaded Fe_3O_4 particles in the polystyrene (PS) electrospun fibers [106]. Magnetic hyperthermia, rather than photo hyperthermia, is considered to have a brighter future in the cancer treatment field, although both of them belong to remote triggering mechanisms. This is attributed to the fact that the access to the magnetothermal is more feasible in practical settings without the concern of photo path.

Moreover, owing to their electrical and magnetic properties [107–109]. Fe_3O_4 particles have been incorporated into electrospun nanofibers aiming to develop lightweight microwave absorption absorber. A Fe_3O_4 particle embedded PVC composite electrospun nanofiber was demonstrated to be a good candidate for electromagnetic radiation protection material as a result of its low microwave transmission coefficient values, transmission loss below -16 dB in the microwave frequency range of X-band [110].

Using a similar approach, Yoon et al. constructed a core-shell nanofibrous mat with Fe_3O_4 particles and polyamide (PA6) as core and shell, respectively, by coaxial electrospinning technology. The combination of Fe_3O_4 particles and PA6 shows a property of electromagnetic shielding [111]. However, the electrospinning process is always interrupted by the particle agglomeration in the needle, thus causing the undesirable morphology of the mats. To address this issue,

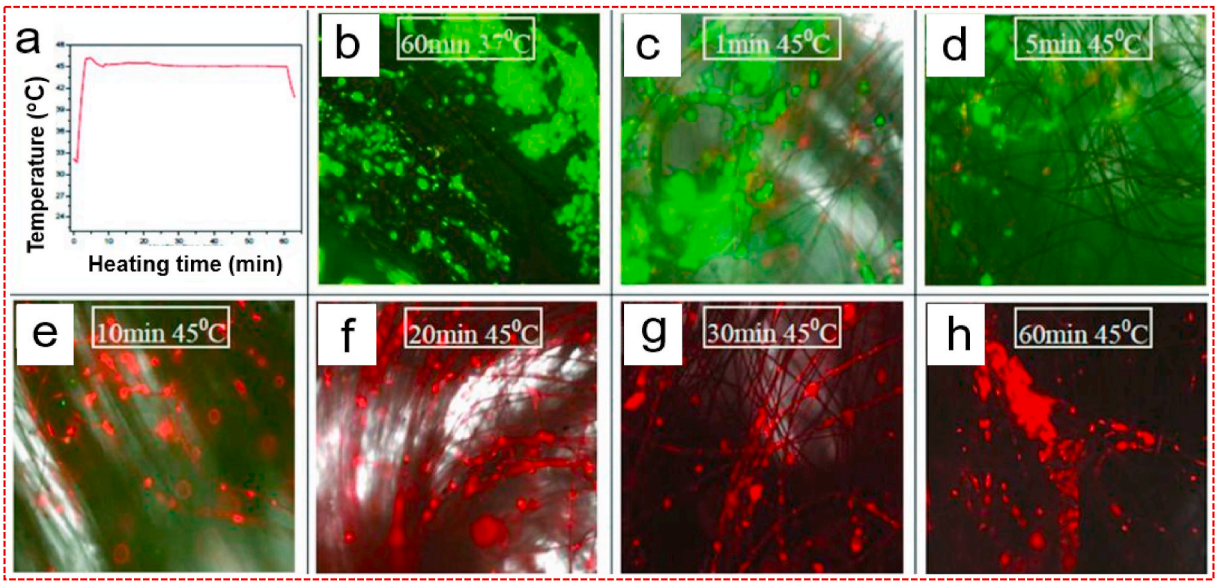

Fig. 7. (a) The profile of temperature vs time regarding to the iron oxide nanoparticles (IONP) loaded PS electrospun fibrous mat; (b) the control reference at room temperature for 60 min and (c–h) the state of ovarian cancer cells bonded to IONP loaded PS electrospun fibrous mat as a function of time, upon the heating generated by AC magnetic field. Green: alive ovarian cancer cells, Red: dead ovarian cancer cells. Reproduced with permission from Ref. [106] Copyright 2012 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

scientists have made numerous efforts to separate particles and then prepare well-dispersed nanoparticles suspension. In general, two main approaches have been pursued; the first involves the addition of surfactant in the particle suspension and the second relies on the surface modification of particles.

Ultrasonic treatment is always employed to separate pure particles so that those individual particles could be capped possibly better by surfactant. As a matter of fact, both of the surfactant approach and the surface modification method are associated with "coating". The same as surfactant, the primary role of surface modification by polymer capping the particles is to prevent agglomeration as a result of the interparticle van der Waals attraction in a dispersion medium by offering either electrostatic repulsion or steric [112].

During a growth process of Fe_3O_4 particles, the colloidally-stable suspensions of magnetite Fe_3O_4 particles were formed in an iron salts chemical coprecipitation reaction in the presence of hydrophilic graft polymer that caps the Fe_3O_4 particles for steric stabilization of the Fe_3O_4 particles against agglomeration [113,114]. By electrospinning, then, the PVA electrospun fibers with well-dispersed Fe_3O_4 particles were endowed with superparamagnetic properties and enable a deflection in the field of external applied magnet [115].

4.1.6. Multi-responsive electrospun fibers

To design smart fibers, the stimuli-responsive materials must fulfill the requirement in terms of multi-responsive ability. The materials are needed to be sensitive to not only one stimulus, but also, most time, multi-stimulus as well. Generally, the approaches to create multi-responsive ability involve constructing block polymer and loading functional ingredients into stimuli-responsive materials etc. Poly (N-isopropylacrylamide-co-acrylic acid) (P(NIPAM-co-AA)) is a typical dual responsive polymer, that comprising thermoresponsive and pH-responsive segments, are sensitive to external temperature and surrounding pH value change. Therefore, the properties of electrospun fibrous mat made of (P(NIPAM-co-AA) can be adjusted by both temperature and pH.

As one study we did before, in which (P(NIPAM-co-AA) was selected as the materials to fabricate a dual-responsive electrospun fibrous actuator whose actuation could be fast precisely controlled by changing temperature and pH value, which expand the application in compared with the thermoresponsive or pH-responsive actuator [81], as illustrated in Fig. 8. This study only showed only dual responsive ability, but we believe it could be also stimulated by the electric field due to the protonization/deprotonization process of acrylic acid segment.

Similarly, as described above, dual responsive materials could be created as well as by the loading of functional ingredient into smart materials [116,117]. In another study, an ion-, pH- and temperature-responsive random copolymer, poly(2-(2-hydroxyl-4-(5-(acryloxy) hexyloxy]phenyl)benzoxazole)-co-(N-isopropylacrylamide)-co-(stearyl acrylate)) (poly(HPBO-co--NIPAAm-co-SA)), was synthesized by radical polymerization. Besides the thermoresponsive ability coming from NIPAAM moiety, the ion and pH-responsive functionality are attributed to the HPBO segment which would turn into zinc complex or phenolate anion with regarding to aqueous Zn^{2+} solution or basic condition, respectively. The electrospun fibrous mat from this multi-responsive polymer solution showed a thermo-, metal ion- and pH-responsive ability featuring hydrophilicity-hydrophobicity transition and fluorescent emission [118].

Numerous of multi-responsive fibrous mats fabricated by electrospinning have been created either through constructing multi-responsive copolymers, or combining several responsive polymers, or embedded functional ingredients into responsive polymers [119–122].

4.2. Flexible electronics from electrospun fibers

Nowadays, regarding to the smart or intelligent fibrous mat, it always gives the impression of flexible electronic. In general, flexible electronic are envisioned to possess functions of powering, sensing, communication, and controlling etc. To address this issue, the fibrous mat generally should be a conductive part or as a generator by the incorporation of conductive matters or some unique materials that possessing piezoelectric/triboelectric effect, respectively.

4.2.1. Flexible electronic produced by incorporation of conductive matters

It is very well known that carbon nanofibers by the carbonization of polyacrylonitrile by calcination [123], and the way of electrospinning

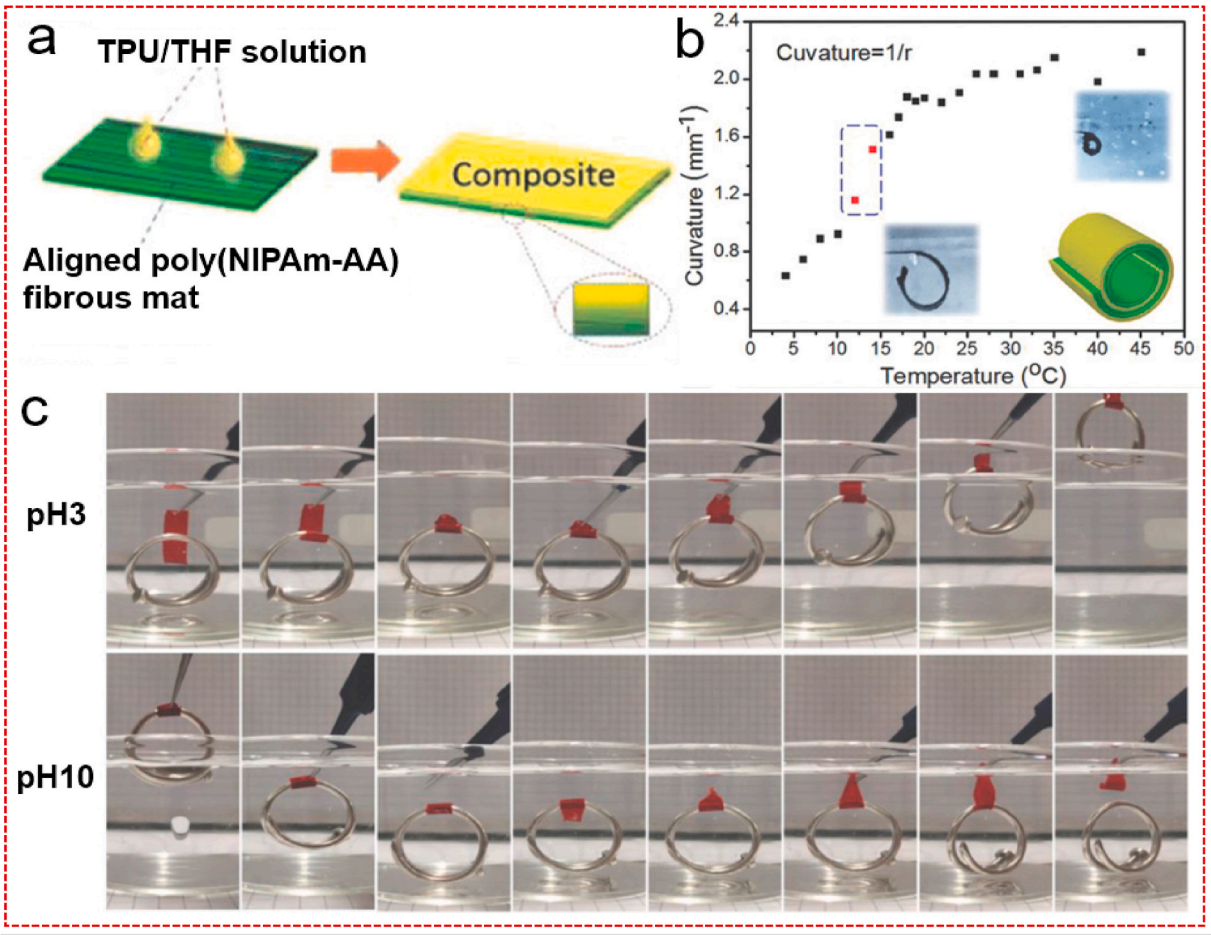

Fig. 8. (a) The schematic illustrating the fabrication of dual-responsive composite actuator; (b) the actuation degree in the form of curvature as a function of temperature showing thermoresponsive ability; (c) the photograph of the silver ring (2471.3 mg)-lifting and -release process of this composite actuator with the weight of 5.8 mg upon the pH change. Reproduced with permission from Ref. [81] Copyright 2018 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

conductive agents, like carbon nanotube, graphite, can give insolate fibers conductivity. However, a key challenge to the widespread application in this field is the brittle property of the carbon fibers and unstable fabrication process caused by the aggregation of particles, respectively [124]. Instead, blending conductive nanofibers with general insolate electrospun fibers is one possibility to fabricate conductive fibrous mat. In one study, the reduced graphene oxide (rGO) as conductive path was localized uniformly on the surface of electrospun polyurethane (TPU) fibrous mat through ultrasonication. This constructed flexible composite structure possessing both of good stretchability and high sensitivity was used as a good candidate for sensor in human motion monitoring [125]. Apart from the deposition of

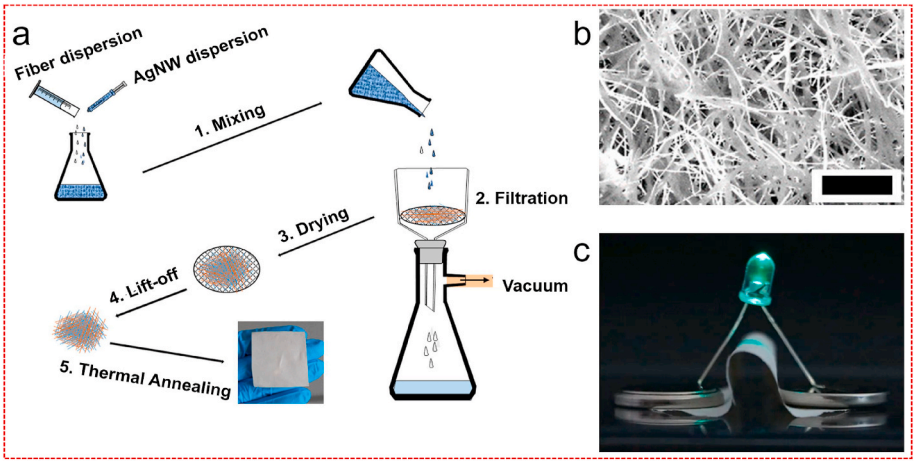

Fig. 9. (a) The schematic of fabrication of the PAN/PCL/AgNW nonwovens; (b) the SEM image of the morphology of the resulting PAN/PCL/AgNW nonwovens (scale bar: 1 μm); (c) the photograph of a lighted LED demonstrated the flexibility and conductivity of PAN/PCL nonwoven with around 1 vol% AgNWs. From an open access article [126].

conductive materials on the surface, conductive fibers could be assembled with other conventional base fibers as well. Greiner et al. fabricated a composite with the metal-like electrical conductivity of 750,000 S/m by homogeneously distributing silver nanowires (AgNWs) among electrospun short poly(ε-caprolactone) (PCL) fibers through the filtration of AgNWs and PCL fiber suspension, as shown in Fig. 9. This research provided a promising in portable applications [126].

In addition, Ding et al. created a flexible electrospun fibrous mat with a large conductivity of more than 980 S cm−1 by electrospinning of poly(tetrafluoroethylene) (PTFE) and poly(vinyl alcohol) (PVA) with the crosslinking agent of boric acid (BA), followed by oxidation and pyrolysis, as illustrated in Fig. 10. This outstanding conductivity, and flexibility that showing no cracking after many deformations could make it a promising candidate in flexible electronics [127].

4.2.2. *Flexible electronic by means of piezoelectric and triboelectric effect*

According to the piezoelectric effect and triboelectric effect, scientists have carried a tremendous amount of research work in energy harvesting/storage, self-powered and heater generator systems in combination of electrospun fibrous mats.

Piezoelectric materials are a certain class of materials that has the capability to generate electric charges upon the mechanical stress. As one of the most important semi-crystalline materials, it is able to convert mechanical force into electricity due to the β crystalline phase who features the piezoelectric sensitivity. In 2011, Lin's group discovered that the electricity could be generated directly from electrospun PVDF fibrous mat even without the procedure of any extra poling treatment upon receiving a mechanical impact [128]. And in another study, Zhu et al. conducted electrospun PVDF fibrous mat, on the surface of which a secondary rough nanostructure is constructed, as active layer in insole. As the mechanical to electricity conversion during the human walking procedure, the maximum generated voltage could reach 210 v [129].

Triboelectric nanogenerator is capable of harvesting energy from external mechanical motions and turn it into electricity by a conjunction of electrostatic induction and triboelectric, and are usually to be used to design flexible electronics. Since it was firstly demonstrated by Wang in 2012, it becomes more and more popular and presenting more possibilities for the development of flexible electrics. For enhancing the triboelectric effect in this kind of nanogenerator, materials with high surface electron affinity are always considered. Recently, Wang et al. fabricated an innovative nano-micro triboelectric yarn which shows the energy harvesting features, together with the fabrics made of this yarn. As illustrated in Fig. 11, PAN & PVDF and silver wires were fabricated as core and shell components, respectively, by electrospinning followed by the formation of yarn. When conducting 2.5 Hz mechanical drive, this yarn is able to generate high output of 40.8 V, 0.705 μA cm^{-2} and 9.513 nC cm^{-2} and the resulting smart electrospun fibrous mats present the biomechanical sensing features [130].

Similarly, Ding's group has also succeeded in developing a triboelectric effect dependent wearable fabrics generator, by which the mechanical energy from human motions can be harvested and converted to electricity. This fabric generator was fabricated by the deposition of PTFE particles and PVDF nanofibers on traditional textiles, such as cotton, silk, PP, PET, through simultaneously sprayed and electrospun technology. Owing to the roughness surface of the fabric (PET), which is attributed to the modification of PTFE particles and PVDF nanofibers, the triboelectric effect is therefore enhanced. And then the electric output performance of the fabric generator is significantly boosted, by which serious of LEDs could be lighted up [131].

5. Passive smart fibers produced by electrospinning

Conversely, passive fibrous mats possess less motivation when carrying out the interactive behavior with external environment. Compared with the communication process of interactive fibrous mat with external environment by changing their chemical/physical properties actively, the passive ones prefer to doing nothing but rely on the intrinsic characterizations without the change of their chemical/physical properties, such as waterproof and breathable fibrous mat and antibacterial fibrous mat.

5.1. *Waterproof and breathable textiles*

The air permeability, a critical parameter for clothing, is tightly

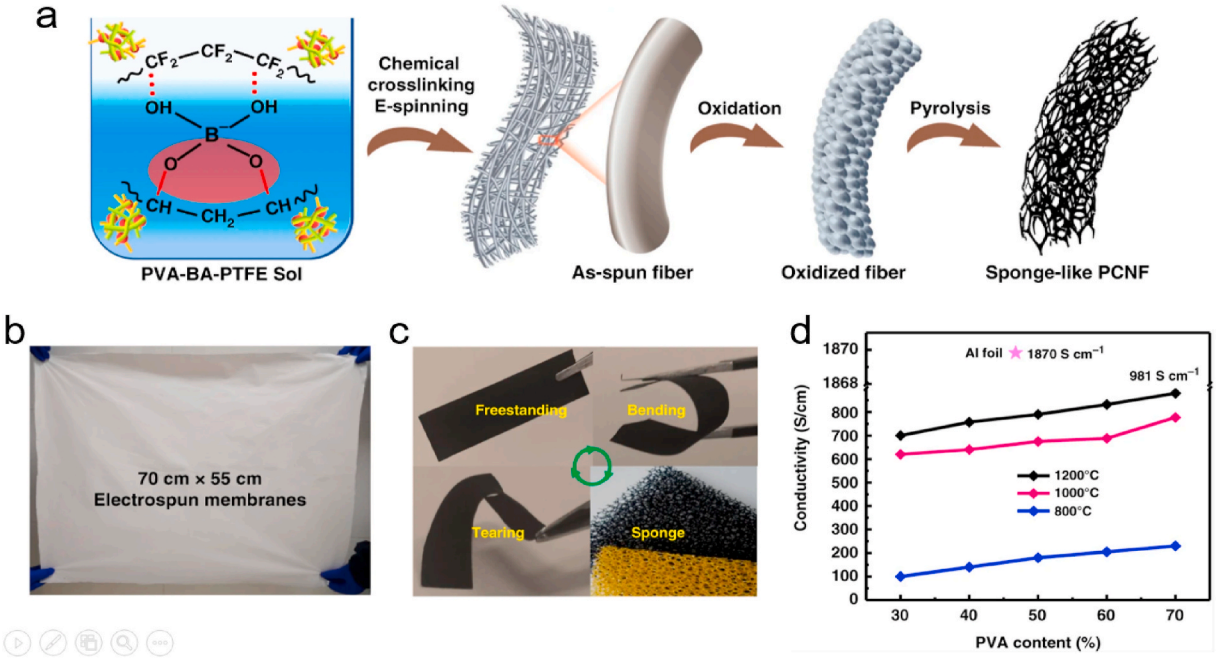

Fig. 10. (a) The schematic of fabrication of conductive PVA-BA-PTFE fiber; (b)the photo of as-spun fibrous mat before oxidation; (c) the deformation of the conductive PVA-BA-PTFE fibrous mat presenting flexibility; (d) the conductivity of PVA-BA-PTFE fibrous mat as a function of PVA contents. From an open access article [127].

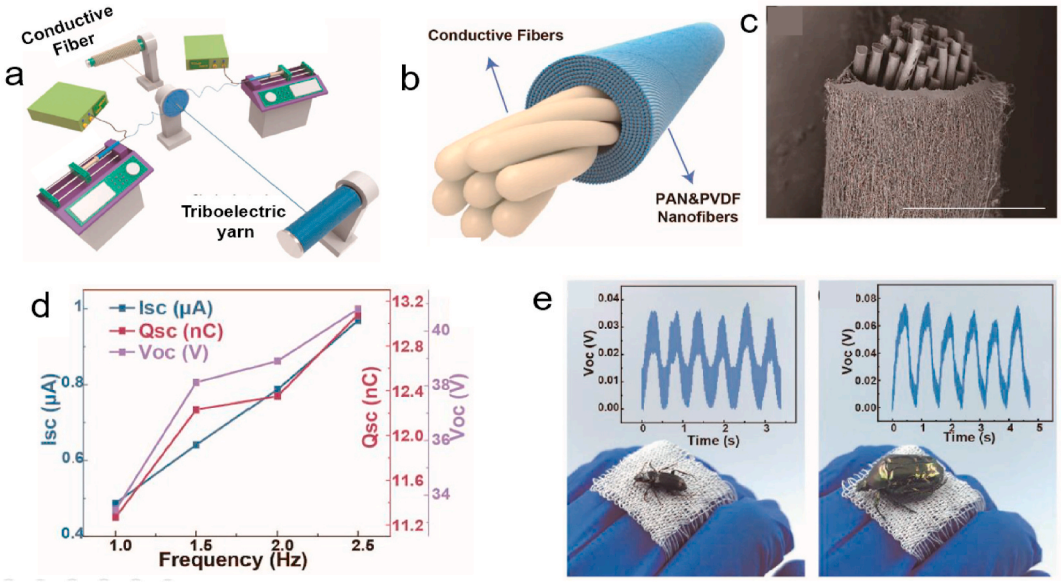

Fig. 11. (a) The fabrication of triboelectric yarn; (b), (c) the illustration and SEM image of the triboelectric yarn showing the core-shell structure; (d) the generated voltage, current and charge quantity upon different frequencies; (e) the sensitivity measurement of the fabric as a result from the triboelectric yarn. Reproduced with permission from Refs. [130] Copyright 2020 American Chemical Society.

related to the porosity which of electrospun mats can easily reach up to 90%. Higher porosity can provide more channels for air to go through the textile. The diameters of rain droplets are between around 18 and 28 μm or even larger [132]. And the pore sizes among those intersecting fibers can be controlled in the range from 0.1 to 0.8 μm by adjusting the process parameters during electrospinning and the overall porosity of the mat [55]. Therefore, the high porosity and the well-designed pores guarantee the possibility of waterproof and moisture permeable textiles by offering them the selective permeability for water droplet or vapor, as shown in Fig. 12a. Consequently, it is to conclude that the pore size of an electrospun mat can be well fabricated for moisture-permeable but impervious to water droplets on rainy days. In a fabric system, the electrospun PU nano-fibrous mat showed better performance in the situation of water vapor- and air-permeability than that PU and PTFT coated fabrics [133]. Furthermore, the performance of textiles in waterproof feature, that of hydrophobicity, can be enhanced by introducing hydrophobic rough surface, as illustrated in Fig. 12b. And electrospinning has been demonstrated as such a kind of versatile tool for fabricating superhydrophobic mats, which is attributed to the wide selection of hydrophobic polymers with low-surface energy [134–136] and the facile way to construct rough surface with ability to trap amount of air [137–142]. A simultaneous electrospraying of silica particles was employed during the electrospinning of PVDF and the resulting mat, that exhibited superhydrophilicity with the water contact angle of 163 °C

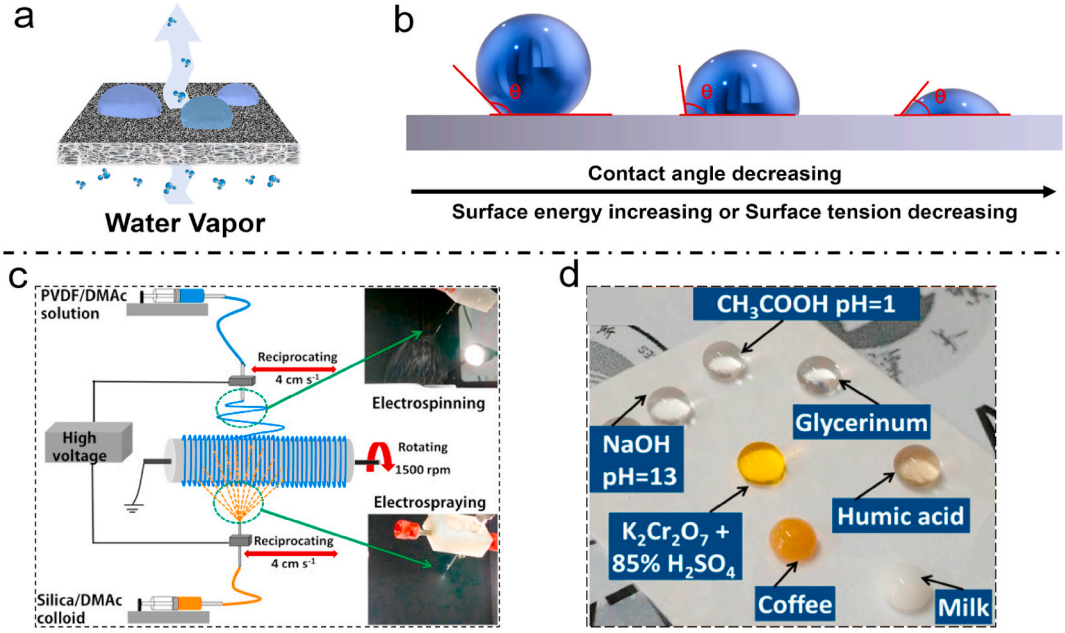

Fig. 12. (a) and (b) The mechanism of waterproof and breathable textiles; (c) and (d) the fabrication of PVDF based electrospun textile with waterproof and breathable ability and the corresponding performance of repelling to various other liquids. (a) Reproduced with permission from Ref. [144] Copyright 2019 Elsevier B.V. (c) and (d) Reproduced with permission from Ref. [143] Copyright 2016 Elsevier B.V.

and a high porosity of 85%, is considered as a good candidates of filter and waterproof and moisture permeable textiles [143], as presented in Fig. 12c and d.

5.2. Antibacterial fibers

The key to impart antimicrobial activity to the fibrous mat is creating an antimicrobial surface on the fibrous mat, which can be functionalized in a diversity of ways. Except constructing antibacterial polymers terminated with quaternary amine groups which are able to kill bacterial by the cation formation [145], the other common way to fabricate antibacterial fibrous mat is the incorporation of antibacterial components into fibers. Silver ions have been demonstrated to kill bacterial due to the ability of reaction with thiol group that most of bacterial has in enzymes [146]. Similarly, copper as one of nature antimicrobial materials has also shown the same property as well, although the mechanism is not very clear [147]. When the silver or copper agent is engineered into nanofibers by electrospinning, the resultant fibrous mat, as a carrier, can offer thousands of loading spots due to the large specific surface area and high porosity. In one study, silver and copper nanoparticles originated from $AgNO_3$ and $Cu(CH_3COO)_2$), respectively, are incorporated into cellulose electrospun nanofibers, and the resulting fibrous mats shows superior antibacterial activity [148].

6. Hybrid smart electrospun fibers

When discussing the characterizations of interactive and passive smart fibers, it should be noticeable that there is not a sharp boundary between them. Sometimes there are always some types of smart fibers neither from stimuli responsive nor from piezoelectric and triboelectric effect polymers, that we cannot just simply term them as either interactive or passive ones. Shape Memory Polymers (SMP) feature a shape shift between the temporary shape and the permanent shape upon receiving stimulus from surrounding environment, such as heat. The fibrous conformation guaranteeing an effective heat transfer due to their porous structure can allow a fibrous SMP to perform a faster response. The large specific surface area of electrospun fibers endow them with versatile surface functionality, therefore, electrospun fibrous structure can be designed to act as a promising platform to construct structural coloration to mimic the natural color of some insects, like butterfly wings, without using any dye by manipulating the nano-, microstructures on the fibers according to the Bragg's Law. Electrospinning also make it possible to fabricate coaxial structure at nanoscale, consequently, different functional components or reaction agents can be incorporated into nanofibers acting as core part and separated by the shell materials. When these functional agents leak out from the core and touch with each other, some "smart" action probably starts showing some smart properties, like self-healing fibers. Be different from those smart fibers made by stimuli-responsive polymers or conductive ones, generally, these hybrid smart electrospun fibers have to rely on fiber assemblies including other introduced materials to show a "smart" response.

6.1. Shape memory fibers

Shape Memory Polymers (SMP) are an emerging class of materials that allow the shape to be a reversible transition between a deformed state and an original state upon exposure to an external stimulus, like temperature. In general, the SMP effect mechanism relies on two inherent incompatible phases in the polymer. These two phases, a reversible soft phase and a frozen hard phase acting as a competition, account for the shift between the temporary shape and the permanent shape, respectively. Upon an external stimulus, generally, like temperature, a temporary shape is created and subsequently frozen when a mechanical deformation is employed due to the compromised polymer chains movement of reversible soft phase, while the frozen hard phase still keeping its stiff state. And the transition from a temporary state back to a permanent state is attributed to the resulting strain during the deformation from the frozen hard phase [149–156]. A typical polymer meeting these requirements is polyurethane (PU) which is composed of soft and hard segments respectively corresponding to the reversible soft phase and the frozen hard phase. As the temperature exceeding the glass or melting transition, the recovery actuation will be triggered. Rather than bulk film, the Shape Memory Effect (SME) employed in fibers at the micro- or nano-scale probably promotes the research of textiles in situations of immediate control due to the high porosity [157]. In an early study, PCL based shape memory PU fibrous mat was produced by electrospinning, which showed excellent shape recovery with 98% and 80% shape fixity [158]. In another study, as shown in Fig. 13, Bao et al. succeed in fabricating poly(D,L-lactide-co-trimethylene carbonate) (PLMC) fibrous mat by electrospinning, which was demonstrated a fast recovery actuation in seconds upon the heating at 39 °C as a result of enhanced heat transfer caused by the superiority in high porosity of electrospun fibrous mat [159]. Additionally, the incorporation of some other functional components can bring about remote-controllable ability other than direct heating. The dual-shape transition behavior was achieved by the incorporation of Fe_3O_4 particles acting as magnetically responsive parts and multiwalled carbon nanotubes serving as physical cross-linking points during the electrospinning of PCL [160].

6.2. Structurally colored fibers

Color gives human the sense of beauty in life. Dye, either natural or synthetic one, enables the coloration of textiles by the manipulation of light in the form of reflecting and absorbing etc. Even so, the pollution of dyeing procedure brought about by the chemical process cannot be ignored as well as the undegradable residual colorants. As an alternative to dye, structural coloration which is easy to be found in nature, such as butterfly wings, provides another route for the textile color generation [161,162]. The color generated from structure, rather than from dye, is more environment friendly due to its unique nature of dye-free and fadeless process. Be analogous to the colorful butterfly wings, structural coloration arises from photonic band gap of ordered photonic-crystal structure [163,164]. According to the Bragg's Law, the corresponding mechanism relies on the ability of the periodic micro- or nano-structure to manipulate the incident light, that of light refraction, scattering and diffraction as a result of the interaction between light waves and tailored configurations possessing the same order of size as the wavelength [165, 166]. Electrospinning, featuring the easy access to the desirable morphology and structure of nanofibers, has been subject to intensive study in structurally colored textiles by scientists. In one work, presented in Fig. 14, the colors of the samples were tuned by tailoring the nanostructure of electrospun colloidal nano fibers through employing various size of poly-(styrene-methyl methacrylate-acrylic acid) (P(St-MMA-AA)) particles from 220 nm, 246 nm–280 nm, leading to green, red and purplish-red, respectively [167]. Another strategy is referred to as core-shell structure in which the thickness of shell accounts for the color. For example, the colors of blue, green and red were constructed by controlling the thickness of polystyrene/poly(N-isopropylacrylamide-co-acrylic-acid) core-shell particles which have the potential to enable the colorful textiles by coating them on textiles [168].

6.3. Self-healing fibers

Self-healing is an effective and innovative function to address the issues that materials are most of time vulnerable to damage and the crack sites are hard to be localized. The self-healing materials can automatically detect and repair the cracks upon the damage. Considering this remarkable property, the long-term durability of materials during the application are supposed to be easily achieved. The mechanism relied on the reaction happening to the cracks suggests that two

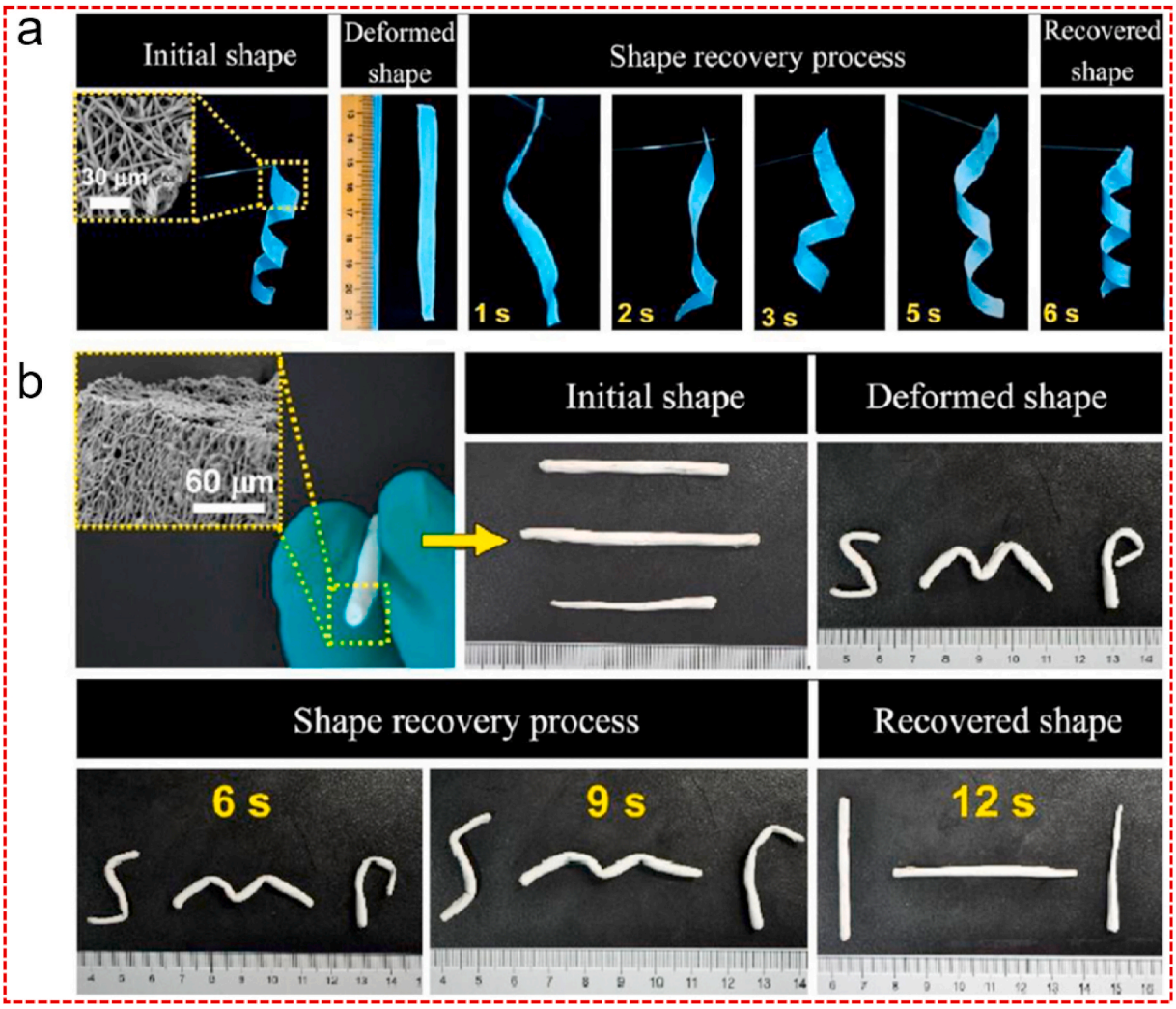

Fig. 13. The image of shape memory actuation process of (a) PLMC electrospun fibrous mat and (b) cylindrical bars showing fast response due to the large surface area and high surface area of electrospun products. Reproduced with permission from Refs. [159] Copyright 2014 American Chemical Society.

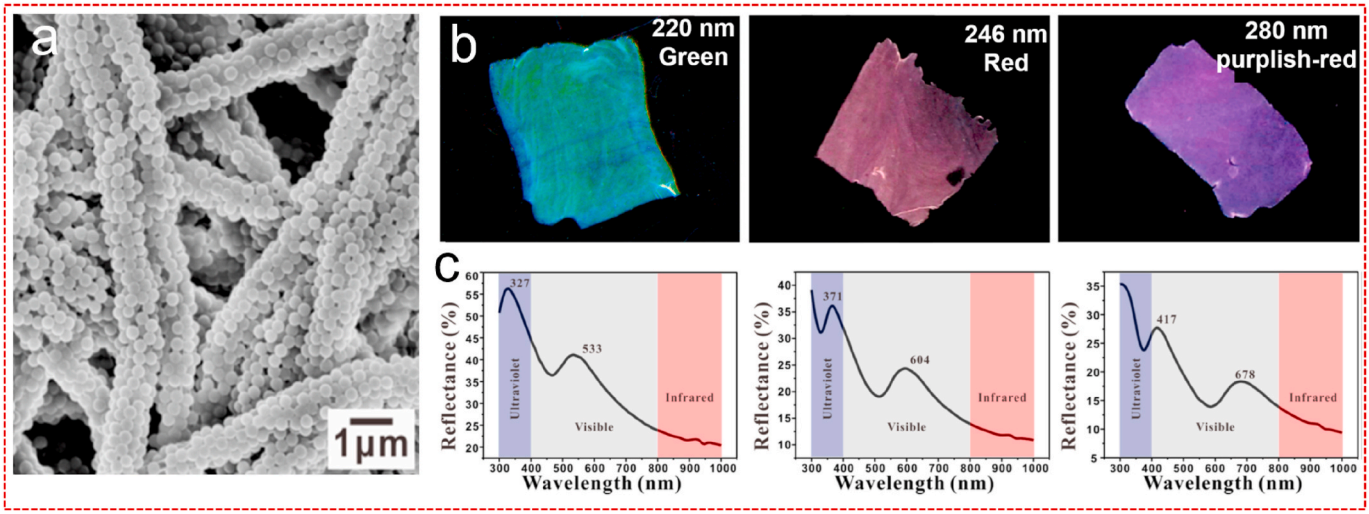

Fig. 14. (a) The SEM image of fibrous mat with 220 nm particles and (b) photographs of colorful electrospun colloidal nanofibrous mats from green to purplish-red according to the size of particles and (c) the corresponding reflective spectra. Reproduced with permission from Refs. [167] Copyright 2015 American Chemical Society. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

reagents not ought to meet each other until the cracks are created [169, 170]. For instance, the nutrients are not supposed to be delivered towards the wound site to encounter the injured cells and tissues initiating the healing process until a cut or a wound on human skin [171]. Some typical strategies have been developed to accomplish self-healing materials by constructing the healing agent fluid flow, as a key feature, to mimic that nature process. The melting polymer flow can be generated easily by employing PCL with low-melting point at 60 °C. In one study, a cut crack on a PCL electrospun fibrous mat was healed by the re-bonding process at the crack point as a result of the melting PCL fluid flow, serving as healing agent, upon the temperature at 80 °C [172]. Alternatively, healing agents which start reacting once they encounter each other, are separated by the shell structure, generally, in the form of core-shell configuration. When one of the agents is released from the crack site, caused by the deformation or the broken of shell, touching the other one outside the shell, then the reaction will be initiated automatically in situ, thus starting the self-healing. In one demonstration, a cut-induced polymerization was initiated in an electrospun nanofibrous mat reinforced composite by the meeting and the reaction of two reagents, that of curing agent (dimethyl methylhydrogen siloxane) and liquid monomer (dimethyl siloxane), respectively, from the core of PAN electrospun fibers and the epoxy matrix. As a consequence, the cut spot was repaired by this effective healing process after 2 days [173]. Similarly, healing agents could be fabricated into different core-shell structures as well. As illustrated in Fig. 15, Khorasani et al. encapsulated two healing agents, including two ingredients composed of a low viscosity epoxy resin and its amine-based curing agent, into nanofibers with the shell of styrene acrylonitrile (SAN) by electrospinning, respectively. These two types of core-shell nanofibers were loaded into resin region covered by two carbon fabric layers creating a self-healing composite whose crack was repaired and the mechanical properties were restored back to its original performance after a damage was employed [174].

7. Conclusions and future perspectives

In summary, smart electrospun fibers have a great potential towards textile applications. As the development of science and technology, fibrous structure like fibrous mats are taking more responsibilities to meet the development requirements of textiles in future which are not only regarded as the roles of protection, insulation and decoration. In terms of fibers, understanding the differences between interactive and passive fibers will dramatically aid in our ability to establish the concept of smart textiles, to identify them and to pave the way for the design of novel textiles. Nano fibrous mats, which have unique larger specific surface area, higher porosity and more flexibility, to a certain extent, can serve as a man-made skin against external harsh environment. Electrospinning provide a facile way to produce nanofibers with a broad selection of materials from inorganic to organic matters [175,176]. And the combination of electrospinning technology and smart materials open a new window for the fabrication of smart fibers and their innovative applications in drug release system, actuator, self-powered matters, wearable electronic devices, human motion monitors and sensors. Although many researches on these smart electrospun fibres have been proceeding, more efforts should be carried forward in practical usage. For example, in the battle against coronavirus starting at the end of 2019, a variety of masks are suggested being worn to prevent the spread of disease caused by the coronavirus, but most of them are the old-fashioned surgical masks and anti-smog face mask N95, which, relying on the passive functionalities in their short life service, are failing to adapt to the virus mutation. Therefore, the electrospinning

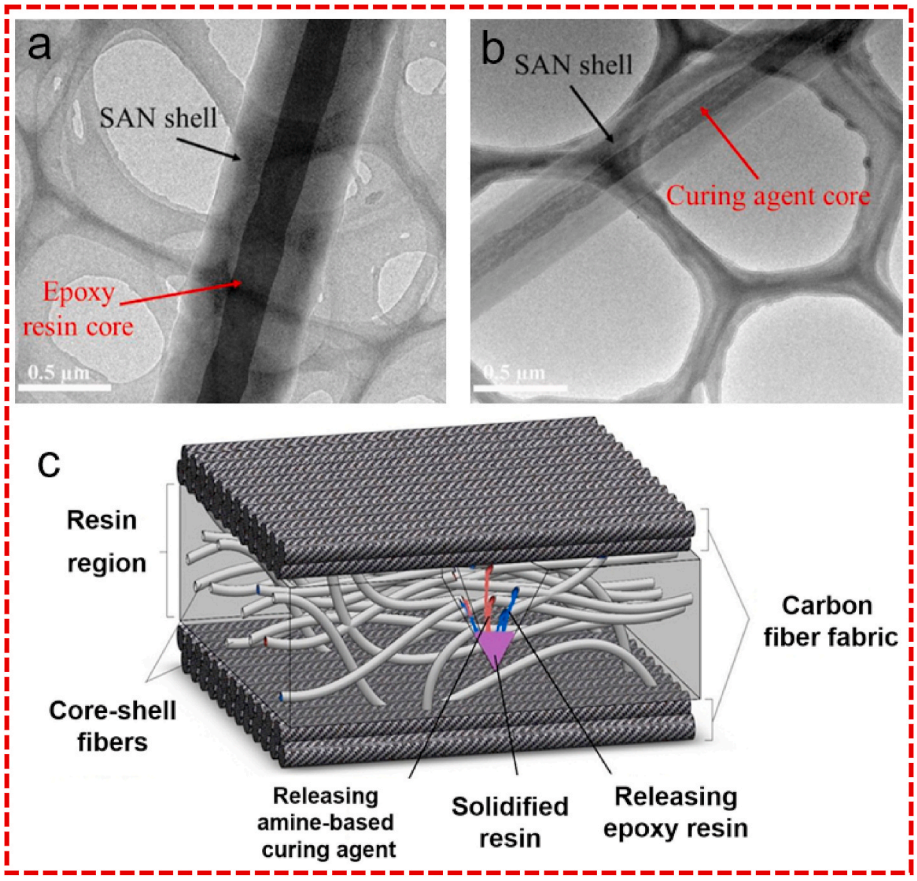

Fig. 15. (a) and (b) The SEM images of core-shell fibers with the same shell of SAN but two different core components of epoxy resin and curing agent, respectively; (c) the schematic of this core-shell structural based self-healing mechanism. Reproduced with permission from Refs. [174] Copyright 2017 Elsevier Ltd.

technology combined with novel smart materials probably access the fibers including fiber, yarn, mat or textile with passive or interactive ability which suggests a bright future. Additionally, with the aid of development of computer science, smart electrospun fibers would be endowed with a new role in the applications of artificial intelligence (AI), man-machine interaction and soft electronic devices. However, the other confronting challenge for the smart electrospun fibers, which is the low production of electrospun fibers, is hindering their commercialization. There are already some companies, such as Jiangxi Xiancai Nanofibers Technology Co., Ltd. and MANN-HUMMEL, etc., which have dedicated to the industrial-scale mass production of electrospinning and showed actual perspectives, but the work toward high yields and industrialization all over the world should be kept on carrying out. And on the way of this work, anther new challenges should be addressed, that of the industrial-scale mass production of smart materials and the massive toxic solvents used in the electrospinning process. Other than the rather simplistic way to synthesize and employ materials in the laboratories, the economic cost plays a significant role in the commercialization process of materials. Moreover, most of time, it is inevitable to apply organic solvents for electrospinning which are toxic and harmful to our environment. Therefore, it is necessary to select low-toxic even non-toxic solvent to minimize the related negative effect. Anyway, smart electrospun fibers, serving as functional parts, are unnecessary to taking the place of every areas of those traditional textiles, but preferably integrated into them.

Compliance with ethical standards

The authors declare that they have no conflict of interest.

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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