

Polymer Complex Fiber: Property, Functionality, and Applications

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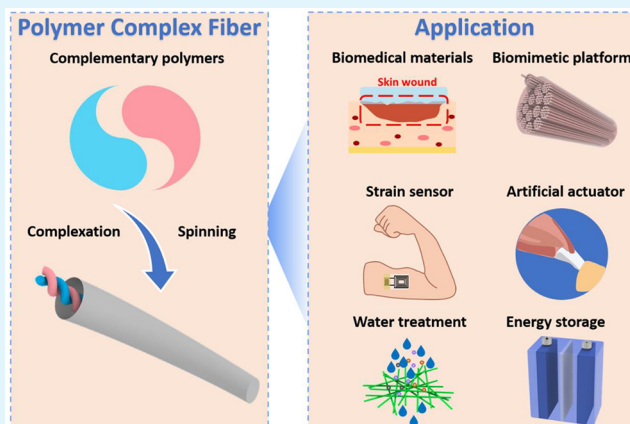
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ABSTRACT: Polymer complex fibers (PCFs) are a novel kind of fiber material processed from polymer complexes that are assembled through noncovalent interactions. These can realize the synergy of functional components and miscibility on the molecular level. The dynamic character of noncovalent interactions endows PCFs with remarkable properties, such as reversibility, stimuli responsiveness, self-healing, and recyclability, enabling them to be applied in multidisciplinary fields. The objective of this article is to provide a review of recent progress in the field of PCFs. The classification based on chain interactions will be first introduced followed by highlights of the fabrication technologies and properties of PCFs. The effects of composition and preparation method on fiber properties are also discussed, with some emphasis on utilizing these for rational design. Finally, we carefully summarize recent advanced applications of PCFs in the fields of energy storage and sensors, water treatment, biomedical materials, artificial actuators, and biomimetic platforms. This review is expected to deepen the comprehension of PCF materials and open new avenues for developing PCFs with tailor-made properties for advanced application.

KEYWORDS: polymer complex fibers, spinning techniques, energy storage, sensor, water treatment, biomedical materials, actuator, biomimetic platforms



1. INTRODUCTION

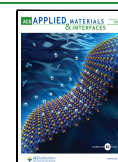
Polymer complexes possess unique structures and kinetic behaviors, resulting from polymer complexation wherein one polymer overcomes the intramolecular and polymer–solvent interactions to associate noncovalently with other polymers to form stable assemblies.^{1,2} Polymer complexation is considered to be one of the key processes that relates to the origin of life.^{3,4} A variety of biomacromolecule complexes in living systems, such as double-helix DNA and membraneless organelles, exert crucial functions to precisely regulate biological activities and maintain life.^{2,5} Inspired by these and other natural systems, polymer complexes thus have received increasing attention in multiple research fields including polymer physics, colloid chemistry, materials science and engineering, and life sciences.^{6–11} One of the most attractive features of polymer complexes are their dynamic nature originating from noncovalent interactions among polymer chains, which leads to numerous desirable properties. These properties such as reversibility, adaptiveness, self-healing, and stimuli-responsiveness, allow for the construction of multifunctional and intelligent materials.¹² Shaping polymer complexes into fibers further endows the resulting materials with the character inherent in fibrous structures and hence extends the properties and functionalities beyond simple

polymer complexes. As a type of one-dimensional material, fiber has both a large aspect ratio and a high specific surface area, which facilitates high loading capacity and the capability to quickly detect or respond to environmental variations. The flexible and aligned structure also introduces excellent mechanical properties and allows the fiber to be woven on demand into different shapes.¹³ Therefore, a growing number of research groups have participated in the exploring the wide possibilities offered by polymer complex fibers (PCFs). The work about PCF can be dated back to 1970s, in which stable biopolymer fiber was obtained by extruding a protein/alginate (ALG) mixture into a calcium chloride (CaCl_2) bath, opening up new opportunities to investigate and develop ALG-based complex fibers for biomedical application.^{14,15} In 1994, Kitao et al. reported the PCF prepared through synthetic polymers, in which, poly(D-lactic acid) (PDLA)/poly(L-lactic acid)

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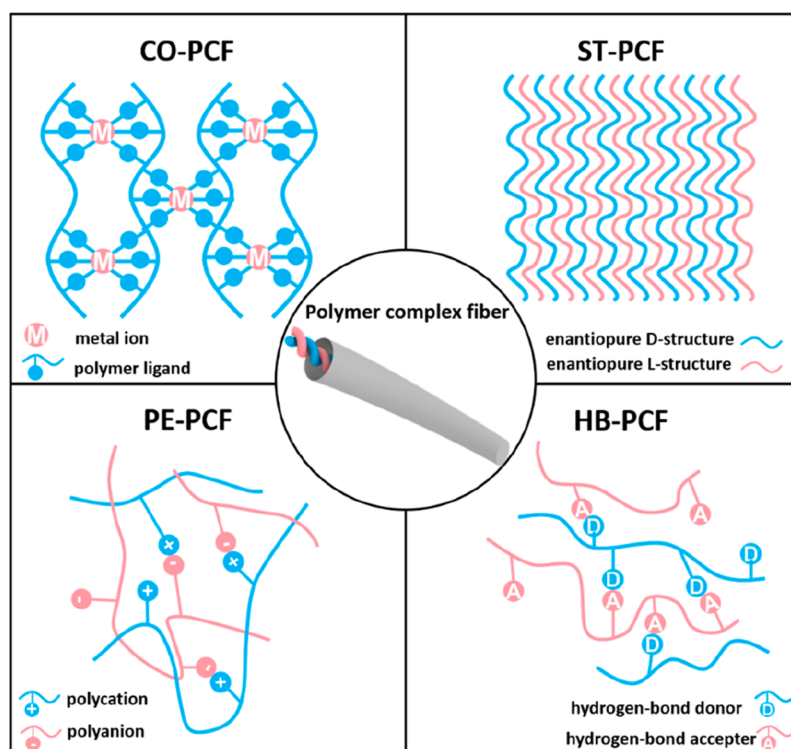


Figure 1. Schematic illustration of four kinds of PCFs based on molecular interactions, including coordination complex fiber (CO-PCF), stereocomplex fiber (ST-PCF), polyelectrolyte complex fiber (PE-PCF), and hydrogen-bonded complex fiber (HB-PCF).

(PLLA) complex fiber was successfully fabricated by wet spinning, exhibiting a melting point 50 °C higher than pure poly(lactic acid) (PLA).¹⁶ This method has been widely used to improve the thermostability of PLA. In 1998, Yamamoto et al. reported PCFs prepared through interfacial drawing of two oppositely charged polymers at the interface in the aqueous solution, which paved the way to process polyelectrolyte complexes into fibers.¹⁷ Afterward, with the deepening understanding of fundamentals and the development of technologies, tremendous efforts have been put into designing and engineering PCFs to enrich their functional properties and explore their versatile applications.

More recently, several excellent review papers have discussed PCFs from different aspects.^{18–21} Wan introduced the formation mechanism of polyelectrolyte-based fibers prepared through interfacial drawing, summarizing their physical properties and applications for tissue engineering and drug delivery.¹⁸ Brettmann concentrated on the studies of molecular interactions in electrospinning and reviewed the effects of molecular interactions on rheological properties and fiber processing.¹⁹ Subsequently, Steckl and Schiffman independently surveyed coaxial electrospinning technique relevant for fiber preparation.^{20,21} Their reviews involved the research of polyelectrolyte complex fibers (PE-PCFs) but primarily focused on the fundamentals of coaxially electrospun composite nanofibers (e.g., formation mechanism, parameter adjustment, and process modification) and their applications. Previous review articles emphasize PE-PCF generally, at most discussing a single fabrication type, such as interfacial drawing or electrospinning only. Herein, we aim to extend the discussion beyond polyelectrolyte fibers to other types of PCFs and provide a comprehensive overview of the various fabrication methods with their characteristics and their recent advances in applications. Classification of PCFs according to

their chain interactions is first introduced in this review. We will further summarize the progress in PCF fabrication through comparison of fabrication techniques and applicable scenarios for each method and assess the effect of processing parameters on fiber formation and properties. In addition, composition–structure–property relationships, and the diverse properties of PCFs will be addressed. In the last section, we highlight the functionality and the up-to-date applications of PCFs for advanced materials in various fields, including energy storage and sensors, water treatment, biomedical materials, artificial muscle actuators and biomimetic platforms. We hope this review will deepen the comprehension of PCF materials, invigorate new works within the field, and provide researchers a quick guideline to develop PCFs with tailored properties for advanced applications.

2. CLASSIFICATION OF PCFS

The assembly of polymer complexes can be driven by a variety of noncovalent associations, such as metal coordination, stereoselective interaction, electrostatic interaction, hydrogen bonding and so on. Different molecular interactions and bonding within polymer chains influence the formation mechanism, preparation method, properties, and thus the application of polymer complex-based materials. To date, there are four types of PCFs being well studied, and they are classified according to the dominant noncovalent interactions, as coordination complex fiber (CO-PCF),^{22,23} stereocomplex fiber (ST-PCF),^{24–27} polyelectrolyte complex fiber (PE-PCF),^{28–31} and hydrogen-bonded complex fiber (HB-PCF) (Figure 1).^{32–35}

The CO-PCF consists of polymers and metal ions where the metal–ligand coordination is the driving force for the fiber formation. For this type of PCF, ALG/Ca coordination fiber is

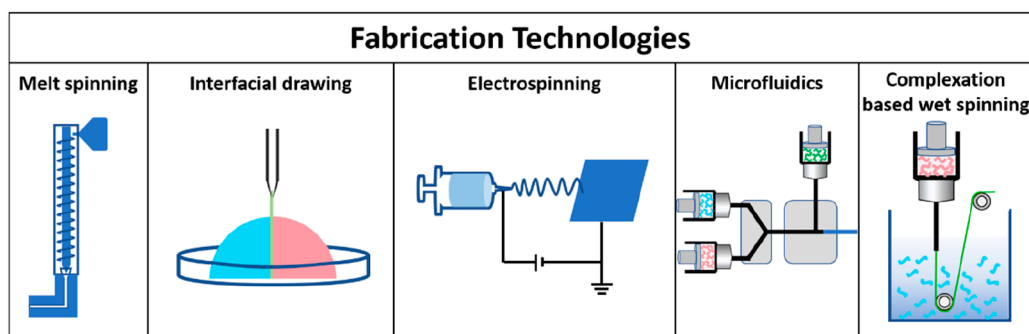


Figure 2. Schematic summarization of five fabrication technologies, melt spinning, interfacial drawing, electrospinning, microfluidics, and complexation based wet spinning.

the most studied system because of the strong interaction between divalent metals and carboxylate groups from ALG. With rigid structure and biocompatibility of ALG in addition to large coordination bond energy, ALG-based coordination complexes are expected to construct tough fibers for tissue engineering scaffolds and drug carriers.^{36,37}

Stereocomplexes are generally produced via packing of two complementary stereoisotactic polymers into the crystalline state.^{38,39} Currently, poly(methyl methacrylate) (PMMA) and PLA are commonly used polymers for the preparation of stereocomplexes.^{24,25,40} The association of syndiotactic and isotactic PMMA results in PMMA stereocomplexes, which could further be processed into fibers through electrospinning.^{24,25} Many researchers have focused on the formation mechanism and crystalline structure of PMMA stereocomplexes. One study reported in 2014 revealed that the tactic PMMA fiber exhibited better biocompatibility in cell culture, with enhanced cell attachment and proliferation compared to pristine PMMA fibers, demonstrating the potential of PMMA ST-PCFs for biomedical applications.²⁵ For PLA ST-PCFs, different techniques such as wet spinning, dry spinning, melt spinning, and electrospinning have been conducted as a means to control fiber properties through fabrication.^{16,41–48} It is reported that the dry-spun PLA ST-PCF had higher tensile strength and melting temperature compared to the wet-spun counterpart. This could be explained by the increased surface defects generated in wet-spun fiber during solvent exchange, and more stereocomplex crystals forming upon drawing at 140 °C in the dry-spinning process.¹⁶ The ST-PCF prepared by electrospinning possessed an increased tensile modulus and strength than the PLLA or PDLA fibers.⁴⁵ Another work showed that the PLA ST-PCF obtained by melt spinning presented greater thermostability than pure PLA, with a crystalline structure tunable through annealing process, enabling its usage in commodity fields as an engineering material.⁴⁹ Thus, the thermal resistance and/or mechanical properties of ST-PCF can be tuned through choice of preparation method, which broaden the practical applications of PLA fibers.^{50,51}

Polyelectrolyte complexes are the coacervates or precipitates produced when the two oppositely charged polymers are mixed in an aqueous solution.² Based on the polymer origins or intrinsic properties, polyelectrolytes are categorized as natural and synthetic polyelectrolytes, or strong and weak polyelectrolytes; various combinations can be made to form polymer complex materials according to different needs. PE-PCFs were first constructed using natural polymers (e.g., gelatin, chitosan (CHI), ALG, gum, and albumin) by the

Yamamoto group.^{52–57} Stiff PE-PCFs were spun by drawing the liquid-like complexes in ethanol or water, and their foundational work paves the way for the fabrication and application of PE-PCFs. Nowadays, natural PE-PCFs hold great potential to be applied for biomedicines, owing to their commercial availability, biocompatibility, biodegradability, and low toxicity. Polymer complex materials can also be prepared using synthetic polyelectrolytes which include weak polyelectrolytes (e.g., poly(acrylic acid) (PAA) and poly(allylamine hydrochloride) (PAH)) and strong polyelectrolytes with completely ionized groups (e.g., poly(diallyldimethylammonium) (PDADMA) and poly(styrenesulfonate) (PSS)). With the tunable ionization degree and favorable stability, the synthetic polyelectrolytes are widely used to study the fundamentals in polyelectrolyte complexation process, including the effects of ions and water molecules on chain conformation, assembly and disassembly of polyelectrolyte complexes.^{58–61} In another work, the “mixed” polyelectrolyte fiber comprising PDADMA (the synthetic polyelectrolyte) and ALG (natural polyelectrolyte) was fabricated through complexation based wet spinning. The obtained fibers showed humidity sensitive behavior with their mechanical strength changing in response to the surrounding humidity.⁶²

Owing to the contribution of hydrogen bonding, two different polymers (a hydrogen bond donor and acceptor) can associate to form polymer complexes. Common polymers that are hydrogen bond donors are PAA and poly(methacrylic acid) (PMAA), and hydrogen bond acceptors are poly(ethylene oxide) (PEO), poly(vinylpyrrolidone) (PVPON), poly(2-ethyl-2-oxazoline) (PEOX), and poly(vinyl alcohol) (PVA). The hydrogen-bonded complex PAA/PEO was first reported in 1959 and its counterpart HB-PCF was reported in 2016.^{33,63} Hydrogen bonds can be broken and reconstructed reversibly according to the pH variations that endow HB-PCFs with outstanding pH responsive behavior. As the pH is modulated, the fibers show reversible dilation-contraction, which could be used to build artificial pH-driven actuators.⁶⁴

3. FABRICATION TECHNOLOGIES

Since the first reported PCF in 1970s, various techniques have been investigated and optimized for PCF fabrication, in order to achieve the desired materials with controllable and tunable properties. In general, the preparation method should be selected based on chemical characteristics, physical properties, and molecular interactions of the participating polymers in fiber formation. On the other hand, it is also essential to take the unique features of each technique into consideration

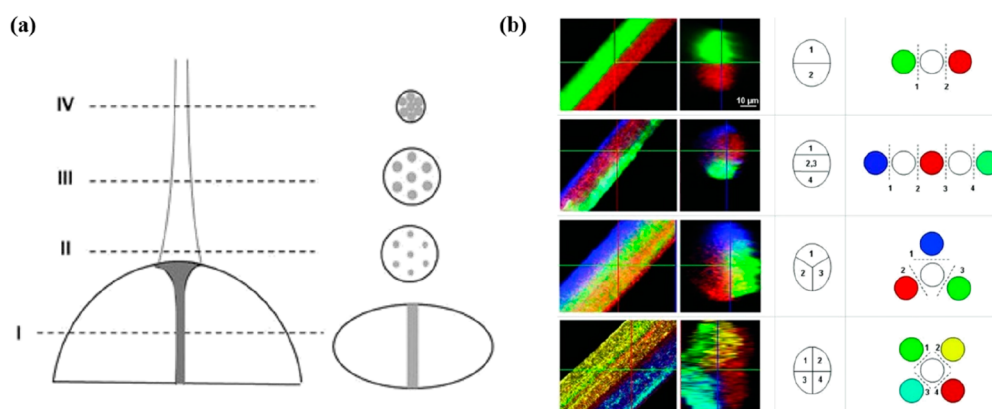


Figure 3. (a) Schematic illustration of four-step formation mechanism of interfacial drawing; (b) the process of multicomponent fibers involving two interfaces to four interfaces. Redrawn and reprinted with permission from ref 65. Copyright 2012 John Wiley and Sons.

because process parameters (e.g., nozzle extrusion, traction, or external field) and conditions (e.g., temperature and the viscosity of spinning dope) of manufacturing will significantly influence the structures and behaviors of resultant fibers. Herein, we will provide a description of modern technologies for PCF fabrication including melt spinning,^{42,43,49} interfacial drawing,^{65–71} electrospinning,^{44,72–77} microfluidics,^{78–83} and complexation based wet spinning (Figure 2).^{33,62,84}

3.1. Melt Spinning. Melt spinning is a simple method in which the thermoplastic polymers are spun from the melting state without solvent.⁸⁵ The basic requirement for melt spinning of single-component polymer fibers is that the polymer's melting temperature should be lower than its degradation temperature. In melt spinning, the polymers are first heated to form a polymer melt, followed by extrusion through the spinning jet into an air chamber. After cooling and solidification, the continuous fibers are drawn out of the air chamber and wound on fiber spools. During this process, parameters such as heating temperature, extrusion temperature, extrusion speed, and winding speed can be adjusted to tune the properties of resultant fibers. As an industrial process, the spin rate of melt spinning is usually higher than other spinning methods (e.g., wet spinning and electrospinning), which enables the efficient production of fiber materials.⁴² To date, the PLA complex fiber is considered the representative ST-PCF prepared through melt spinning.^{49,50} PLA is a crystalline polyester, having the low biotoxicity of a natural material in addition to the easy machinability similar to synthetic materials.²⁶ While the melting temperature of pure PLA is around 180 °C, its stereocomplex has been found to exhibit a strikingly increased melting point of 230 °C, owing to the existence of stereocomplex crystals induced by the side-by-side aggregation of PLLA and PDLA with opposite helicity.⁴⁰ Thus, the stereocomplex crystals are understood to modulate fiber properties, and various work began to focus on improving the melting temperature and mechanical properties of PLA complex fibers by tuning the fraction of stereocomplex crystal. Takasaki et al. identified the crystalline states in the PLLA/PDLA stereocomplexes using X-ray diffraction and conformational energy analysis, finding that the formation of homo crystals and stereocomplex crystals within the materials was dependent on the ratio of PLLA/PDLA in the extrudate. In their work, the initial dope containing 16.4 wt % PDLA only possessed homo crystals and increasing the ratio of PLLA/PDLA to 1:1 led to both homo and stereocomplex crystals.⁴²

Further study revealed that the drawing and annealing temperatures can also influence the content of the stereocomplex crystals.^{41,43,45} Furuhashi reported that the PLLA/PDLA blend fibers drawn at a temperature close to the homo crystallization temperature consisted of homo crystals, while elevating the temperature resulted in the formation of both stereocomplex and homo crystals. Further, the differential scanning calorimeter (DSC) heating curves showed that the melting endotherm of stereocomplex crystal became sharper as that of the homo crystal became smaller and disappeared as the annealing temperature rose above 190 °C, indicating the effect of annealing temperature on tuning the crystalline structure of PLLA/PDLA ST-PCF.⁴⁹

3.2. Interfacial Drawing. Different from the melt spinning technique, interfacial drawing is designed and developed for PCF fabrication under mild conditions on a laboratory scale. In the interfacial drawing process, insoluble complexes are formed at the interface of polymer solutions, which are then drawn by tweezers or pipet tips to yield PCFs.¹⁸ Technically, this method is suitable to process polymer complex systems that could generate viscous coacervates, such as polyelectrolyte complexes, hydrogen-bonded complexes, or coordination complexes, yet most studies have used this method primarily to prepare PE-PCFs. For example, the first PE-PCF reported by Yamamoto et al. was fabricated using interfacial drawing. In their work, the polyelectrolyte complex thin film, formed at the interface by dropping gellan solution into CHI solution at pH 5, then withdrawing the product from the interface and draping over a glass rod.¹⁷ Different polyelectrolyte pairs (e.g., CHI/poly(α ,L-glutamic acid) and poly(L-lysine)/gellan) were utilized by Yamamoto group to construct PE-PCFs through the same method.^{55,56} Wan and co-workers later refined this technique, proposing the mechanism of fiber formation during interfacial drawing.^{18,65} The Wan group divides the fiber formation process into four steps (Figure 3a): (1) Formation of insoluble polyelectrolyte complex at the interface of two oppositely charged polyelectrolyte solutions; (2) Generation of “nuclear fibers” by drawing the interfacial complex vertically upward; (3) Growth of “nuclear fibers” by depleting the surrounding polyelectrolyte solution; (4) Formation of a thicker primary fiber by “nuclear fibers” coalescing. During interfacial drawing, the interface is continually consumed and replaced by fresh polyelectrolytes through diffusion, and thus a high concentration of polyelectrolyte solution is needed to stabilize the complex interface.¹⁸ In addition, the drawing rate

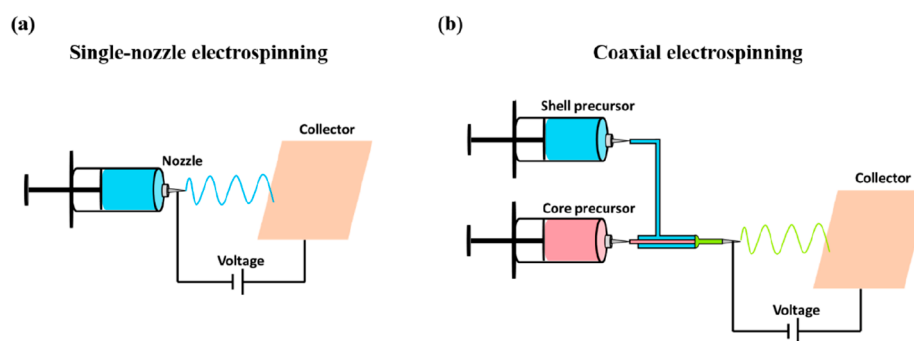


Figure 4. Schematic illustration of fabricating PCFs by (a) single-nozzle electrospinning; (b) coaxial electrospinning.

must be slow enough to allow the formation of fresh complexes. When the drawing rate was too high, the complex interface was consumed too quickly to draw continuously, and the beads would align along the fibers. In order to realize a hierarchical structure to enrich the functionalities, Wan et al. further developed the multi-interface drawing method for PCF fabrication.⁶⁵ Two interfaces can be created when a droplet of the oppositely charged polyelectrolyte; then fibers could be drawn and fused from the interfaces. By adjusting various configurations (Figure 3b), different number of interfaces can be constructed, with various components distributed parallel within the fiber, leading to a hierarchically complex structure incorporating multiple functionalities of PCFs. Apart from the ionizable polymers, charged colloids and small molecules can also be incorporated into PCFs.⁸⁶ In summary, interfacial drawing is a facile and powerful technique to fabricate micro-to-milli-sized PCFs having multifunctionalities and tunable structures. However, as the drawing process is based on manual preparation, the interfacial drawing is not currently suitable for mass production. Additionally, defects are inevitable for interfacially drawn fibers due to the polymer beads/droplets that form along fiber lines during the fabrication and influence the morphology, structure, and properties of the resulting fibers.

3.3. Electrospinning. Electrospinning is a cost-effective and well-established technique that utilizes electrical forces to prepare single-component or composite fibers with porosity and high surface-to-volume ratio.²⁰ Based on the design of nozzle used in preparation, electrospinning can be divided as single-nozzle and coaxial electrospinning,²¹ and recent progress has demonstrated that both electrospinning methods can be applied to produce PCFs. Compared with other methods, electrospinning is more complicated yet controllable because many parameters (e.g., solution properties and process parameters) must be considered and adjusted during the fiber fabrication. The effects of various parameters on the resultant fibers have been reviewed and discussed in detail by Rathore and Schiffman, and by Ewaldz and Brettmann.^{19–21} Herein, we will focus on discussing the features of PCF fabrication using electrospinning and how the key fabrication parameters affect the morphology of PCFs.

Figure 4a illustrates a typical process for PCF fabrication through single-nozzle spinning. In brief, the complementary polymer pairs are stored in the syringe as a precursor solution, which is then ejected through a charged needle toward a grounded collector, forming PCFs that are deposited onto the collector as solvent evaporates. For a successful electrospinning, the primary requirement of the precursor solution

is to have a suitable viscosity, because low viscosity results in the occurrence of electrospraying rather than electrospinning, while high viscosity will hinder the electrospinning process.²¹ Regarding PE-PCF preparation, one challenge is to obtain a homogeneous precursor solution with appropriate viscosity for spinning since the strong electrostatic interactions between polymer chains will cause solid precipitate to clog the spinneret. To overcome this challenge, Schiffman et al. used salts to adjust the molecular interactions of polyelectrolyte pairs. From the measurements of rheology, they found that the crossover point between G' and G'' shifted from 1 rad/s to 10 rad/s when NaCl concentration increased from 300 mM to 600 mM, indicating that the polymer complexes relaxed faster and behaved in a more liquid-like manner at 600 mM salt concentration. Thus, solid-like polymer complexes could be adjusted to behave as liquid-like complex coacervates being used as precursors for electrospinning by tuning the concentration of salts.⁷⁶ PSS and PDADMAC complexes modulated with potassium bromide (KBr) salt between 1.20 and 1.75 M formed a desired, flowable coacervate which could be electrospun into cylindrical fibers.⁸⁷ As salt concentration increased, electrostatic associations were gradually weakened alongside precursor viscosity, leading to the diameter decreasing in as-spun fibers. The Schiffman group further used the same strategy to fabricate the cargo-loaded PSS/PDADMAC fibers and CHI/hyaluronic acid (CHI/HA) biopolyelectrolyte nanofibers directly from aqueous solution, verifying the feasibility and universality of using complex coacervate for electrospinning, which demonstrates a facile and green processing method for PCF preparation.⁷⁵ Recently, they have also discovered that the complex coacervate facilitates electrospinning of PE-PCFs as it could eliminate the traditional requirements for polymer chain length and entanglement. In the traditional process, a precursor polymer solution should have sufficient chain entanglements to suppress chain rearrangement and capillary instabilities to facilitate successful fiber spinning.²¹ Thus, the molecular weight of polymers is usually above a critical entanglement weight (M_C , typically in the range of 10–20 kg/mol) to enable physical chain entanglements. The work by Schiffman, however, indicated that shorter polyelectrolytes ($10 < N < 60$, with N , representing the degree of polymerization) or even oligomers ($N < 10$) can be successfully electrospun into continuous cylindrical fibers owing to the electrostatic interactions within complex coacervates.⁷⁶ Their work has revealed that the associative interactions between polymers could slow the chain relaxation and eliminate the need for entanglements in electrospinning, extending its application into fiber preparations using low molecular weight “nonspinnable” polymers.

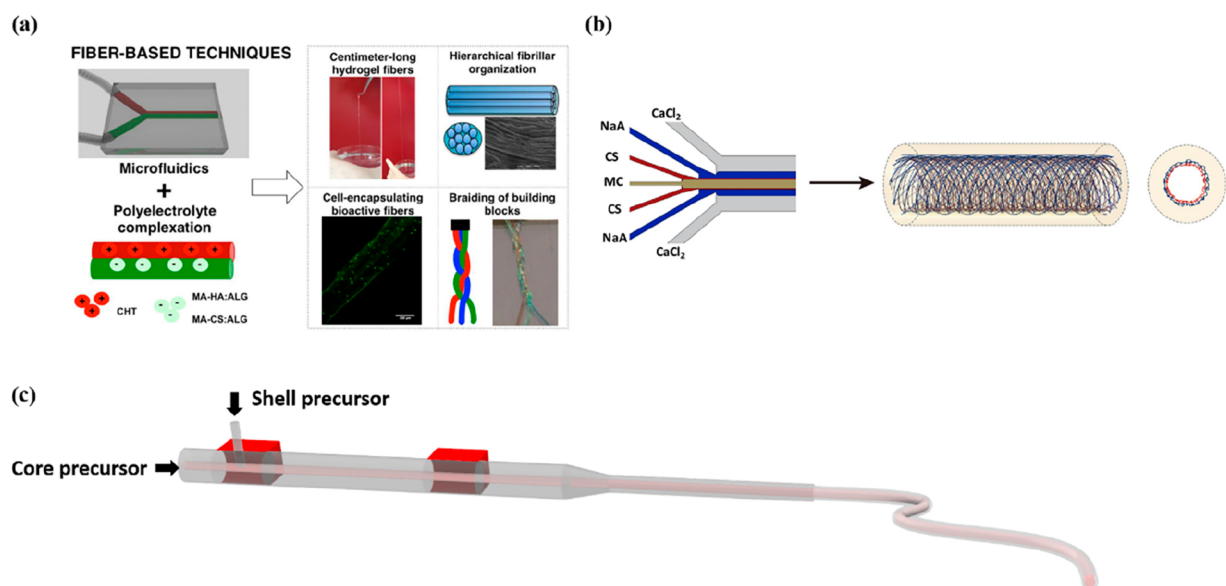


Figure 5. Schematic illustration of PCFs with controllable geometry configurations prepared through microfluidics: (a) side-by-side; (b) hollow structure; (c) core–shell. Redrawn and reprinted with permission from (a) ref 81 and (b) 92. Copyright (a) 2017 American Chemical Society and (b) 2019 John Wiley and Sons.

Another key parameter to influence the electrospinning of PCFs is the applied voltage used in the fiber formation. Generally, voltage is applied for charging the precursor solution and enabling the Coulombic forces to overcome the surface tension and viscosity to generate a stable jet. Increased Coulombic repulsion could disrupt the continuity of the jet if the voltage is far beyond the critical voltage.²¹ The effect of increasing applied voltage on single-nozzle spinning fiber is case-dependent, which is usually determined by whether the Coulombic repulsion or enhanced electric field dominates the fiber process. However, reports about electrospinning PCFs have demonstrated that increasing the applied voltage would decrease fiber diameters. For instance, PSS/PDADMAC PCFs exhibited a smaller average diameter owing to the coupling of increased applied voltage (6–16 kV) and spinneret-to-collector distance (10–20 cm), with diameter ranging from 7 to 2.4 μm .⁸⁷ The CHI/HA PCFs also presented decreasing diameter as the applied voltage elevated from 22 kV to 24 kV, with the spinneret-to-collector distance fixed. That phenomenon can be explained by jet stretching during spinning due to increased Coulombic repulsion between charges.⁷⁴ Besides PE-PCF, PLA ST-PCF prepared through single-nozzle electrospinning demonstrated a similar trend,^{47,48,51,88} in which the diameters of PLA PCFs were originally 800–1400 nm and reduced to a range of 400–970 nm when the absolute value of applied voltage was increased from 12 to 25 kV.⁴⁴ In addition, the study indicated the amount of crystals in ST-PCF could also be influenced by the applied voltage. In a PLLA/PDLA (1:1) blend fiber, the homo crystallites decreased from 5 to 1%, stereocomplex crystallites increased from 16 to 20% as the voltage was increased from 0 to 25 kV. The results revealed that high voltage could promote the growth of stereocomplex crystallites and suppress the formation of homocrystallites, which then affect the physical properties of the resulting complex fibers.⁴⁴

The coaxial electrospinning, using two nozzles during the process, has been developed to fabricate fibers with more complicated architectures, such as core–shell and multilayered

fibers.²⁰ The setup for coaxial electrospinning is shown in Figure 4b, in which the concentric spinneret is used and two different solutions are fed through the core and shell capillaries separately, which then combine at the orifice to form the jet under electrical field for fiber spinning. As more than one liquid is used in the process, coaxial electrospinning has increased complexity compared to the single-nozzle electrospinning. Yu et al. and Schiffman et al. have separately provide comprehensive overviews about how parameters that affect the surface tension, viscous stress and electrostatic force in the formation process are controlled to fulfill successful coaxial electrospinning and the resulting fibers can be tailored for developing applications in biomedical materials and electrical/electrochemical materials.^{21,89} Though considerable attention has been focused on coaxial electrospinning, the preparation and study of PCFs using this technique is still in its infancy, likely due to the intricacies which arise from the molecular interactions between polymeric complexes. For PCF fabrication, complementary polymeric solutions are introduced from inner and outer nozzles and mixed at the spinneret to form the charged droplets where the complexation occurs in situ at the core–shell interface. This coaxial electrospinning is unstable and fails to form fibers with core–shell structure if the complexation time is longer than the jet travel time, if the spinneret can be clogged due to the complexation time being too fast, or if the polymer interaction is strong enough to induce solid complexes.²¹ To date, PCF prepared through coaxial electrospinning is reported by the Yang group in which a proper solvent was chosen to inhibit strong complexation between PEO and PAA to generate a spinnable jet for fabrication of HB-PCF with a clear core–sheath structure.³⁴ Among the solvents used in the study, DMF has a lower boiling point than DMSO, which facilitates solvent evaporation during fiber formation. In addition, PEO/PAA has a weak interaction in DMF, enabling the hydrogen bonds of the complexes at the core–shell interface without blocking the nozzle orifice. In their work, Yang et al. also investigated the effect of injection rate on fiber formation, which indicated that

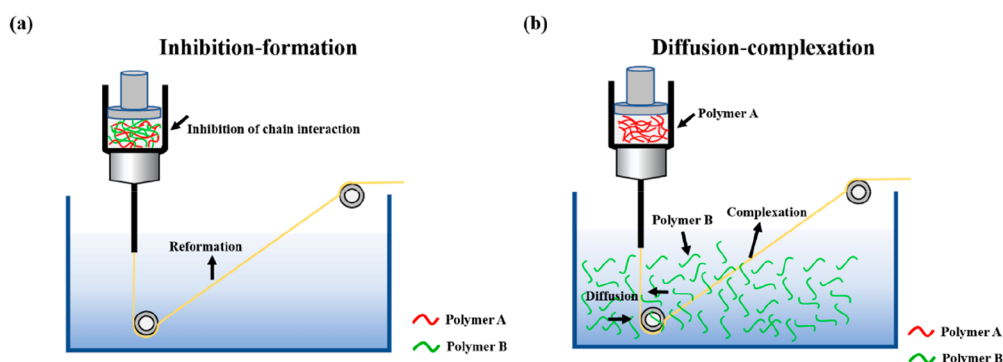


Figure 6. Schematic illustration of complexation-based wet spinning: (a) inhibition-formation: chain interactions between polymer A and polymer B are inhibited to generate a homogeneous spinning solution and are reformed in a coagulation bath to enable the PCF formation; (b) diffusion-complexation: the associated polymer pairs are used as spinning (polymer A) and coagulation solution (polymer B), respectively, and their complex forms in situ upon extruding polymer A into the polymer B solution, resulting in PCF fibers.

elevating the flow rate of the PEO precursor (core solution) could increase the core–shell interface and hence the hydrogen-bonding association to stabilize the as-prepared fibers.

3.4. Microfluidics. Microfluidic technologies, which feature energy-savings, rapid reaction time, precise control, and the capability to safely encapsulate bioentities, offer the manipulation of microscale fluids to prepare functional fiber materials with diverse complex structures for biomedical applications.^{90,91} Miniaturization and manipulation make microfluidics difficult to scale for manufacturing. Microfluidic spinning is initiated as the sample solutions are injected into separate microchannels, which then contact to form laminar flows that cured (e.g., photopolymerization, ionic, or chemical cross-linking reactions) to yield fibers.⁹¹ Microchannel design can allow micro/nanoscale fibers with controllable geometry configurations to be prepared. Common fiber morphologies are shown in Figure 5, where the Y-shaped microfluidic channels are applied to fabricate side-by-side fibers, and double- or triple-coaxial laminae are designed to obtain the core–shell and hollow structure, respectively.^{78,81,92}

The control of laminar flows and solidification modulation are essential for fiber formation and property. For PCFs, the complexation takes place immediately at the interfaces when the complementary components are met in the outlet microchannel which induces the gelation and/or solidification of laminar flows. To successfully prepare PCFs using microfluidic technology, the gelation/solidification process should meet two requirements: (1) solidification needs to take place fast to enable complete fiber solidification within microchannels; (2) solidification degree should be controlled to avoid high viscosities induced by the gelation to allow fiber extrusion without blocking the microchannel nozzle.⁹¹ Thus, the ALG-Ca system has been most often used in microfluidic spinning of PCFs because of its rapid gelation process, mechanical flexibility and ease of molding under the mild conditions.^{93–95} In the fabrication of the ALG-Ca fiber, the CaCl₂ solution used as a sheath flow can solidify the ALG core fluid through coordination complexation and act as lubricant to avoid clogging of solid fiber during extrusion.^{78,79} The gelation and solidification process of fibers has been found to be regulated by varying the flow rates and concentrations of fluids as these two parameters influence the degree of complexation through changing the residence time of fluids

in the microchannel and the concentration of diffused Ca ions.^{93,94,96} The gelling process can be estimated as follows:⁹⁴

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - \frac{\partial S}{\partial t} \quad (1)$$

where C is the concentration of Ca ions in sheath solution, D is the diffusion coefficient of ions, and S is the concentration of complexed ions. The introduction of buffer (e.g., NaCl) flow between the ALG and CaCl₂ solutions could also regulate the gelation process to facilitate flowability of the ALG complexes, and the addition of thickener (e.g., dextran) in the buffer or gelling solutions can enable the balance of laminar flows to allow control over widths of ALG flows during fiber preparation.⁹⁷

Besides coordination complexation, polyelectrolyte complexation is also an ionic cross-linking reaction to mediate gelation/solidification for PCF preparation. In the microfluidic process, two opposite charged water-soluble polymers become insoluble on meeting to generate the PCFs. Through careful exploitation of that rapid complexation process, such polyelectrolytes could be used to fabricate ultrathin microfibers.⁸² The introduction of other types of interactions further modulates the formation and property of PE-PCF. For example, the mechanical property of hollow fibers was found to be enhanced by generating a sacrificial layer outside the polyelectrolyte shell with the assistance of coordination complexation. The coordinate complex layer provides a stable and close environment to facilitate the complete development of ionic interaction between the polyelectrolytes.⁸² Chemical-cross-linking applied before extrusion could effectively improve the stability and handling of polyelectrolyte complexes, resulting in the strengthened fibers with diameter less than 1 μm and elastic modulus of ~1 MPa.⁸³

3.5. Complexation-Based Wet Spinning. Complexation-based wet spinning is a modified wet spinning technology dedicated for PCF fabrication. In traditional wet spinning, fiber formation is caused by nonsolvent-induced phase separation. Later techniques of complexation-based wet spinning introduce interchain complexation between complementary polymers which contributes to PCF solidification. For now, this method has been applied for PE-PCF and HB-PCF preparation.^{33,62,64,84} Based on the complexation course, two mechanisms have been proposed for fiber formation: inhibition-formation and diffusion-complexation (Figure 6).

Table 1. Summary of Fabrication Methods for PCFs

Fabrication methods	Application scenarios	Structure	Advantage	Disadvantage
melt spinning ^{42,43,49}	ST-PCF	homogeneous	high spinning rate, mass production	narrow application, severe pollution
interfacial drawing ^{65–71}	PE-PCF, HB-PCF	core–shell, side-by-side	simple operation, controllable multicomponent structures	beads and defects align along the fibers
electrospinning ^{44,72–77}	PE-PCF, HB-PCF, ST-PCF	core–shell, homogeneous	controllable diameter from nano to micro, mass production	high energy, severe pollution
microfluidics ^{78–83}	CO-PCF, PE-PCF	core–shell, side-by-side, hollow	energy savings, rapid formation, precise control	miniaturized preparation
complexation-based wet spinning ^{53,62,64,84}	PE-PCF, HB-PCF	homogeneous, core–shell	mass production, simple operation	low spinning rate

During the “inhibition-formation” mechanism, noncovalent interactions in the precursor are inhibited to obtain a homogeneous spinnable solution and then restored, leading to the double diffusion phenomenon in the coagulation bath. In this process the drawing speed should match the recovery rate of noncovalent interactions to stabilize the jets and enabling the formation of continuous PCFs after drying and drafting. According to the intrinsic character of complexation, the addition of salts or adjustment of pH can be used to regulate the associations of polymeric precursor. Yang et al. utilized various salts (e.g., KBr, NaBr, LiBr) to inhibit strong electrostatic interactions between ALG and PDADMA to obtain precursor fluid that solidified in the ethyl alcohol coagulation bath to form nascent fibers. For ALG/PDADMA spinning solution, the viscosity elevated with increasing salt concentration at low shear rate and the relaxation time of chains becomes longer. This phenomenon was different to many researches. In commonly, higher salt concentration could help to loosen the association of ion-pairs and free the chains in solution, resulting in a smaller viscosity. However, ALG chains have lots of hydrophilic groups that can bind with water molecules. When increasing the salt concentration, these combined water molecules are attracted by the small salt ions due to hydration, and thus the lubrication between polyelectrolyte chains is decreased, causing the increase in viscosity. Fiber prepared using KBr as an inhibition reagent exhibited an improved breaking strength and Young’s modulus after washing in water, resulting from the elimination of fiber defects and promotion of the recovery electrostatic interaction upon removal of redundant ions from nascent fibers. Using different salts for inhibition also led to the difference in mechanical characteristic of the resulting PE-PCF. Fibers prepared with LiBr as the inhibition reagent exhibited the highest breaking strength around 80 MPa. It is postulated that ions with smaller radius can be removed more easily and thoroughly from fibers, which strengthens the electrostatic interactions between oppositely charged polymers and enhances mechanical properties of the fiber.⁶² As for HB-PCFs, the environmental pH is crucial to control the polymer associations for precursor preparation and fiber formation. For example, the hydrogen bond between PAA and PEO could be inhibited by mixing PAA with PEO in alkaline solution and allowing noncovalent interactions to be reformed during fiber extrusion into an acid bath.³³

In “diffusion-complexation” wet spinning, the interactional polymer fluids are used as spinning solution (polymer A) and coagulation bath (polymer B), separately. The complex then forms in situ upon extruding polymer A into the polymer B solution. The obtained fibers can possess a core–shell structure with a polymer B shell and polymer A core. In this

fabrication technique, the concentration of spinning solution plays an important role to achieve PCFs and must be tuned on a case-by-case basis according to the participating polymers. The basic principle is to use spinning solutions having concentrations neither so high that the jet clogs the needle nor so small that the flow speed during the complexation step in the coagulation bath only leads to jet dispersion without maintaining continuity of the one-dimensional fluid. For example, within a system consisting of CHI and ALG, the ALG or CHI solution being spun should have a viscosity 10 times higher than that of the coagulation bath.⁸⁴ In addition, the complexation time should be taken into account for fiber formation; though complexation occurs instantly once spinning solution is injected into the coagulation solution, the nascent polymer complex fiber has to be kept in coagulation bath for a minimum time to complete complexation and yield a stable structure which allows for fiber handling. It is reported that prolonging the incubation time from 15 min to 24 h would permit more CHI to complex with ALG to form fibers with thicker shells, and the mechanical strength of the resulting fibers increased by 1.5 times.⁸⁴

Fabrication technologies can be applied to produce different PCFs based on the features of components and noncovalent interactions. Each technology has its own advantages and disadvantages and a scope which is determined by the end-use application (Table 1). Selecting an appropriate method will allow facile fiber preparation to achieve PCFs with improved performance and bespoke characteristics targeting behavior and properties suited to the targeted application.

4. PCF DESIGN AND PROPERTIES

The composition and structure of PCFs can be regulated by the molecular design and directing formation during the fiber preparation, which further influence the fiber properties and applications. In the previous section (Fabrication Technology), we have discussed the roles of method selection and control over processing parameters in modulating PCF structure (e.g., homogeneous, core–shell) and properties (e.g., mechanical properties and thermal stability). Here, we will introduce the designed composition of PCFs and fiber properties. The relationship between PCF composition and its properties is also detailed in this section.

4.1. PCF Design. **4.1.1. Polymer Selection.** Hitherto, various polymers have been discovered that can form PCFs, including natural polymers like polysaccharides and proteins, and synthetic polymers like synthetic polyanions, polycations, polyamides, polyesters, and others.^{44,87,65,17} Natural polymers usually possess ionizable groups (e.g., amino and carboxyl groups) and hence are used frequently to construct PE-PCF. In addition, the accessibility, nontoxicity, and rigid structure of

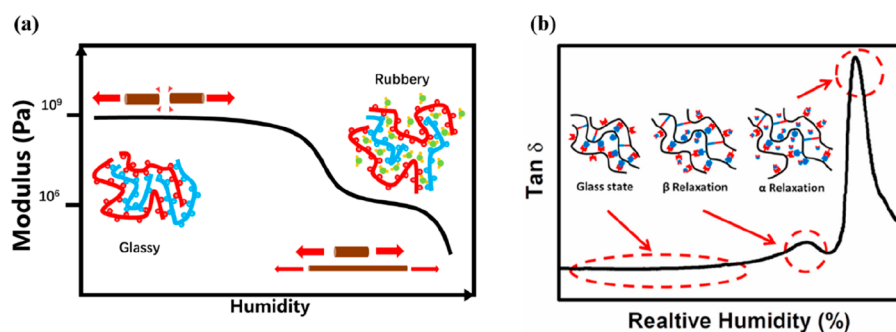


Figure 7. Humidity induced (a) plastic–rubber transition and (b) secondary relaxation of PCFs. Redrawn and reprinted with permission from (a) ref 105 and (b) 106. Copyright (a) 2020 American Chemical Society and (b) 2021 Elsevier.

natural polymers has spurred widely exploration in their use for biomedical materials with tunable mechanical properties and biocompatibility. Synthetic polymers exhibit better structural stability compared to natural polymers, demonstrating their potential to be processed and applied under harsh conditions, which expands the possibilities for both manufacturing and end-use environments. By varying the composition of polymer chains, synthetic polymers are able to constitute CO-PCF, ST-PCF, PE-PCF, and HB-PCF, facilitating widespread application of PCFs for daily life. Table S1 summarizes the currently applied natural and synthetic polymers for PCF fabrication.

4.1.2. Further Functionalization of PCFs. Further tuning the properties and enrich the functionalities of PCFs can be done through two strategies during fiber design: chemical modification of polymer chains and additive incorporation during fabrication.

Chemical Modification of Polymer Chains. Chemical modification can integrate functional units into polymer chains to realize the desired properties through tuning the physicochemical makeup. For example, poly(lactic acid)-*b*-poly(*N,N*-dimethylamino-2ethyl methacrylate) block copolymers synthesized by atom transfer radical polymerization (ATRP) was used for electrospinning ST-PCF, leading to the hemostatic and antibacterial properties in the resulting fibers.⁴⁶ Incorporating butylene succinate units resulted in modified PLA fibers found to be degradable by a greater variety of microorganisms.⁹⁸ In another case, azobenzene (Azo) was reported to be linked to PAA through amidation, and the functionalized PAA (PAA-Azo) was complexed with PEO to yield HB-PCF. As Azo has *cis*–*trans* isomerization upon light excitation, the as-prepared fibers exhibited a photoresponsive contraction ratio of 25% in response to UV irradiation, which served as a candidate to prepare photoactuator.⁹⁹

Additive Incorporation. Diverse substances including salts (ions), small molecules, polymers, nanoparticles, and nanosheets are able to be introduced into PCF networks to extend their properties. Ions can associate with polymer complex systems through coordination or electrostatic interaction. In addition, the migration of metal ions can endow PCFs with conductive behavior. For instance, extruding ALG into coagulate solution containing LiBr and CaCl₂ could form ALG/Ca/LiBr complex fiber. The strong ionic hydration effect between LiBr and water endowed the prepared fiber with antidrying property, and the associated water molecules could promote ion transfer and provide a robust pathway for conductivity.¹⁰⁰ The introduction of functional polymers could also bring new properties and functions for their PCFs. Zhu et al. have designed a core–shell fiber in which poly(ethylene

glycol diacrylate-*co*-acrylamide) was in situ synthesized through photoinitiated polymerization to serve as the core, while ALG interacts with Ca ions to form the polymer complex shell. The obtained fibers demonstrated an improved cell adhesion, flexibility, and stretchability.³⁷ The recent study utilized hydrophobic poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVDF-HFP) as the sheath solution to prepare an ALG complex fiber having a hydrophobic surface, enabling the fiber material to be used as packaging to keep food fresh.¹⁰¹ Further, nanoparticles and nanosheets can act as fillers to endow PCFs with hierarchical structure and increased performance. Liimatainen et al. prepared anionic polymer solution that consisted silver nanoparticles and anionic cellulose, which was then complexed with cationic cellulose to form PE-PCF. The resulting fiber showed desired antimicrobial property against *Staphylococcus aureus* and *Escherichia coli*.⁸⁶ Charged carbon-based nanomaterials (e.g., MXene nanosheet, graphene nanosheet and CNT) have abundant negatively charged groups which can be dispersed homogeneously in anionic polyelectrolyte solution and hence to interact with cationic polyelectrolytes to prepare PE-PCF with strengthened mechanical property and conductivity.⁸⁶

4.2. Properties. Differing from covalently cross-linked materials with permanent networks, PCFs possess dynamic noncovalent cross-links, which account for fiber formation and stabilization. Noncovalent interactions have an interaction energy 1–3 orders of magnitude lower in comparison to covalent interactions, which can be ruptured and restored upon stimulation or undergo reversible exchanges between the participating segments/components.¹⁰² Here, we have divided PCF properties into two categories: the intrinsic properties originating from the dynamic noncovalent interactions of PCFs, and the extrinsic properties related to fiber compositions. The representative intrinsic properties discovered for PCFs include inherent stimuli-response, shape memory, and self-healing, while properties like elasticity, conductivity, and bioproperty have been considered as extrinsic properties, and the corresponding work have been summarized in Table S1. To be noted, the functionalized components (e.g., azobenzene) could endow PCFs with stimuli-responsiveness (e.g., light sensitivity), which is out of the scope of inherent stimuli-responsive of PCFs as it is not related to the dynamic bonds that participate in the PCF network.

4.2.1. Stimuli Responsiveness. Materials with stimuli-responsive behaviors have been widely applied in drug delivery systems, sensors, actuators, soft robots, and adhesives.¹⁰³ For PCFs, the dynamic nature of noncovalent bonds enables their stimuli-responsiveness. The breakage and reformation of

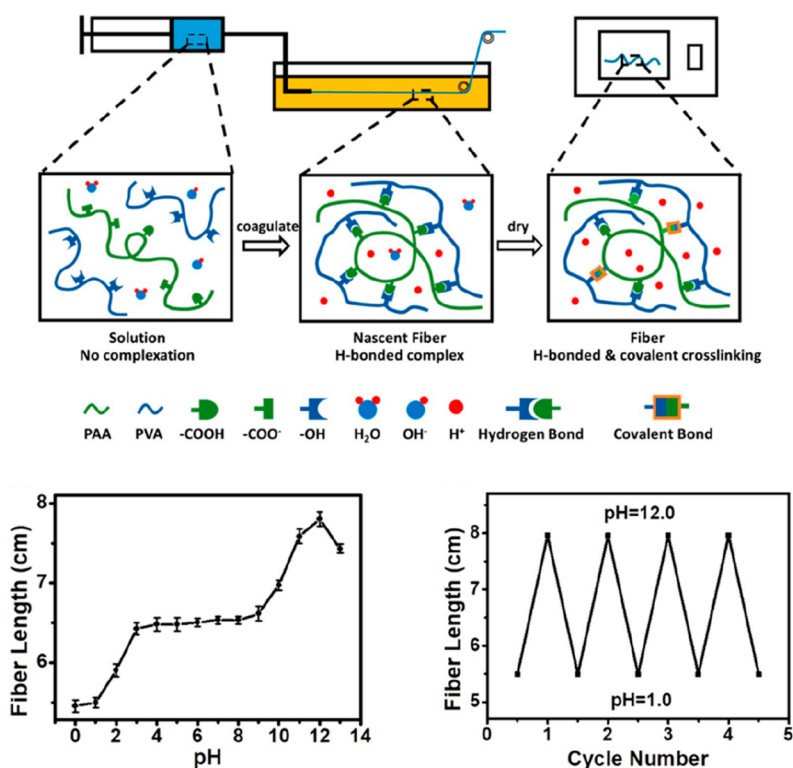


Figure 8. pH-induced fiber length change. Redrawn and reprinted with permission from ref 64. Copyright 2020 American Chemical Society.

noncovalent cross-linking upon environmental variation may alter the fiber structures and morphologies, which can further affect their other properties.

Humidity-Sensitivity. Hydrophilic PCFs can demonstrate humidity-responsive behavior due to the fact that water content within fibers may influence their dynamic cross-linking. Water molecules present affinity to hydrophilic segments of PCFs due to secondary bonding interactions (e.g., hydrogen bond and polar–polar interaction). The increase in humidity will increase the amount of adsorbed water in fibers, which lead to the augmentation of free volume to facilitate the movement of polymer chains and rearrangement of the network cross-links, and decrease the activation energy. Thus, water can serve as a plasticizer to relax polymer chains in hydrophilic polymer complex systems. In a pioneering study, Michaels discovered that the polyelectrolyte complex was brittle when dry and became either leathery or rubbery on hydrated.¹⁰⁴ Subsequently, the Yang group found that ALG/PDDA PE-PCF performed like a plastic material at a relative humidity below 65%, while it exhibited a rubber plateau and a plastic-rubber transition at relative humidity above 65% (Figure 7a).¹⁰⁵ Further, the humidity-sensitivity was reported for HB-PCF, where PVA/PAA fiber showed a humidity-triggered glass transition. Further introducing covalent interactions through esterification led to a doubly cross-linked network fiber, which presented both glass transition and secondary relaxation induced by humidity (Figure 7b).¹⁰⁶ Humidity-induced mechanical property transitions enable PCFs to have strong potential as materials for humidity sensors and actuators.

pH Sensitivity. PAA can be used to prepare PE-PCFs through electrostatic interactions with polycations or HB-PCFs via hydrogen bonds with hydrogen bond acceptors. As the

ionization degree of PAA is sensitive to the surrounding pH, pH can be varied to induce the generation/breakage of the noncovalent bonds in PCFs and tune their strength which endows the fibers with pH-responsiveness. Boas et al. has found that the swelling extent of PAH/PAA PE-PCF increased from 350% to 1225% by varying pH from 5.5 to 1.8, driven by the degree of ionization decreasing from 85% to 18% in PAA. Correspondingly, the fiber diameter at pH 1.8 was four times larger than that at pH 5.5. This pH-regulated swelling process was reversible and repeatable, rendering the fiber a good candidate as an active material.¹⁰⁷ Recently, it was shown that a chemically cross-linked PVA/PAA HB-PCF could contract and dilate upon pH variation due to covalent bonds acting as fixed sites and the dynamic bonds breaking and reforming at different pH to allow fluctuation in the fiber length. (Figure 8).⁶⁴

4.2.2. Shape Memory and Self-Healing. The property of shape memory is highly desired in the design and development of advanced materials for aviation, tissue engineering, and biomedicine. Material with shape memory ability can transform to the temporary shape and restore its original shape under stimuli variation.¹⁰⁸ Shape memory materials usually have permanent networks and reversible cross-links, in which the former can keep the structure integrity and prevent polymer chain slippage/creep while the latter can store and release the energy to enable the transition between temporary shape and original shape.^{109,110} Recent studies, however, have found that PCFs without permanent networks also exhibited shape memory behavior upon suitable excitation. PDADMAC/PSS fiber prepared by Schlenoff et al. was stretched in water at 80 °C to impose the temporary shape, which remained fixed after cooling to room temperature. The initial fiber shape could be recovered immediately (~5 s) when immersing the

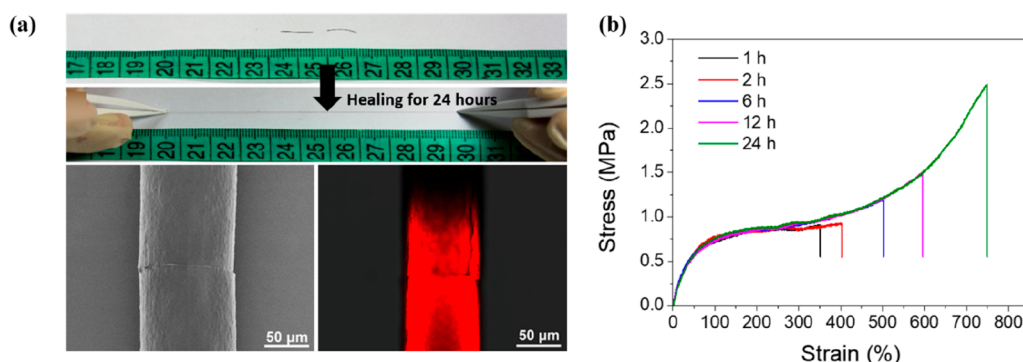


Figure 9. Schematic of fiber self-healing process and mechanical recovery. Redrawn and reprinted with permission from ref 113. Copyright 2019 Springer Nature.

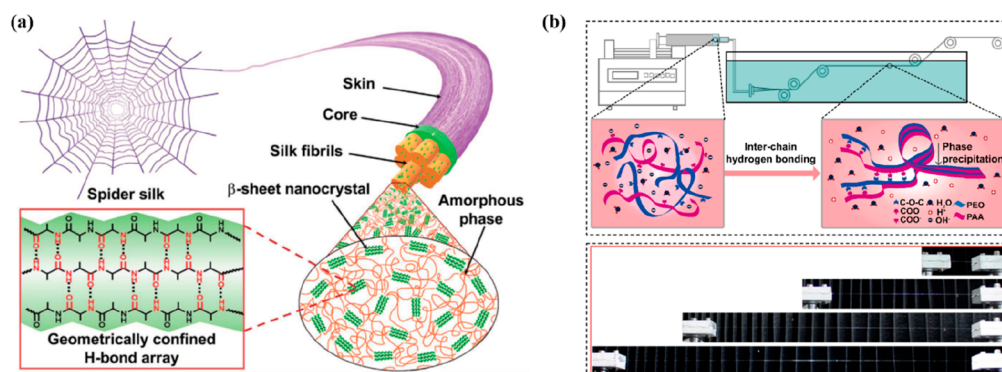


Figure 10. Schematic illustration of the hydrogen-bonding induced elastic behavior: (a) the spider silk; (b) PAA/PEO HB-PCF. Reprinted with permission from (a) refs 33 and (b) 117. Copyright (a) 2021 John Wiley and Sons and (b) 2016 American Chemical Society.

deformed fiber (in the hydrated state) in water at 80 °C, while a longer time (~10 min) was needed for the recovery of the dry counterpart, which was caused by the much faster relaxation speed at 80 °C.³⁰ In another study, the PVA/PAA/PEO three-component HB-PCF was found having shape memory behavior under humidity stimuli. The fiber had elasticity under high humidity condition and deformed upon stretching. During this process, the hydrogen bonds were broken and reformed to generate the new fiber network, which could maintain the deformed shape without external force upon drying at 60 °C. After putting the fiber back to the high humidity environment, it could transform to the initial shape.¹¹¹

Self-healing is a thrilling property to prolong the material lifetime and meet the demands of sustainable development. Besides using an embedded healing-agent, artificial self-healing materials can be obtained by constructing the dynamic networks with reversible noncovalent bonds in the systems.¹¹² The PAA/PEO HB-PCF was discovered to exhibit reparability under ambient condition and the healed fiber could be stretched to 5-fold longer to its initial length after 24 h healing. (Figure 9a). Further cross-linking fibers with polydopamine (DOPA) would improve their stability and self-healing property was maintained in alkaline solutions. Stress–strain curves revealed that both PAA/PEO and PAA/PEO/DOPA fibers possessed similar healing efficiency about 71% which caused by the reformation of the damaged hydrogen bonds (Figure 9b). More importantly, the healed fibers still preserved high extensibility and shape memory capability.¹¹³ The electrostatic interaction can also contribute to the self-healing

behavior of PCFs. The ALG/poly-L-ornithine (ALG/PLO) PE-PCF was reported being self-healed after treating with 2.5 M NaCl for 30 min followed by PBS washing. This self-healing performance was attributed to the ionic strength triggered rearrangement of ionic bonds between ALG/PLO, in which the high concentration salt decreased or broke the electrostatic interaction of polymers while the complexation was re-established in PBS to bridge the cut pieces and partially recovered the mechanical strength and elasticity for the fiber.¹¹⁴ In addition, metal–ligand coordination interaction can be brought in to enhance the self-healing property of PCFs, as the thermodynamic and kinetic parameters of coordination interactions can be tuned over a broad range.¹¹⁵ Wang et al. prepared a type of PCF which contained both dynamic ionic bonds and coordination bonds, wherein a damaged sample could be healed after immersion in dilute supernatant solution for 25 min at room temperature, evincing the disappearance of the scar and the 95% recovery of the storage modulus. Further applying force could bring the fragments close to each other and facilitate the migration of free ions across the notches to overcome the activation barriers, which promoted the reformation of the cross-linking and hence accelerated the self-healing process.¹¹⁶

4.2.3. Elasticity. Elastic materials of high strength integrate good elasticity and high toughness into a single network, which have received intensive attention in emerging fields such as soft robotics, flexible electronics, and stretchable optical devices. To achieve robust elasticity, the flexibility and mobility of polymer chains within the network should be achieved by using flexible polymers, weakening polymer crystallization, and

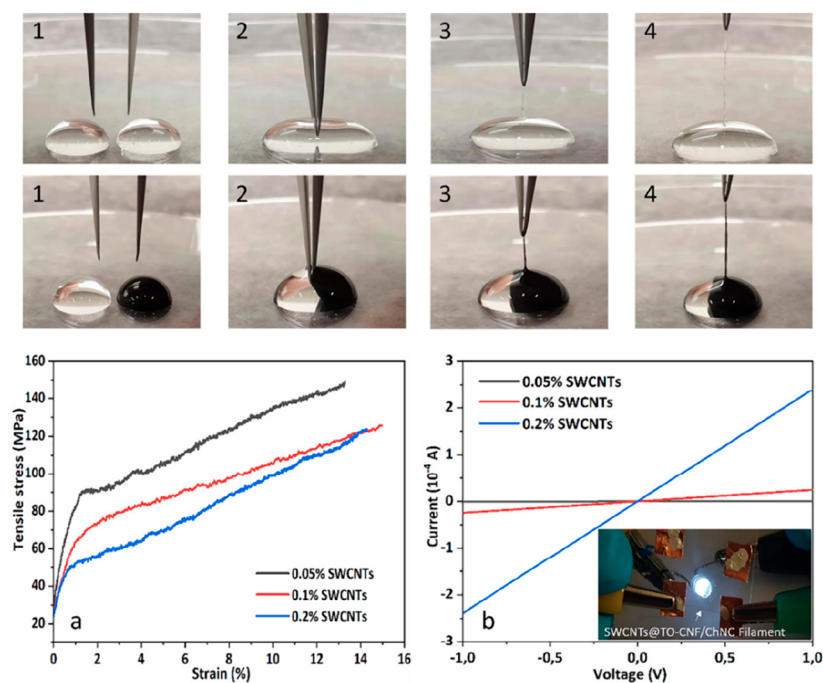


Figure 11. Spinning diagram of incorporating CNTs into PCFs and conductive behavior. Redrawn and reprinted with permission from ref 139. Copyright 2020 Elsevier.

decreasing the glass transition temperatures.³³ As a desired candidate to construct elastomers, PCFs combine polymers with different glass transition temperatures via noncovalent interactions to yield homogeneous behavior. Owing to the miscibility on molecular level, the resulting polymer complex system shows only one glass temperature, which can be tuned to meet the different requirement by simply varying the polymer content. Spider silk is a natural elastomer whose amorphous phase is self-assembled through hydrogen bonds (Figure 10a). The dense hydrogen-bonded cross-linking in spider silks can dissipate energy and enable the material with great toughness.^{117,118} Inspired by this, the hydrogen-bonded complexes have been developed to achieve high elasticity. The Yang group used PAA and PEO to construct elastic HB-PCF.³³ PAA is an amorphous polymer with a glass transition temperature around 100 °C and flexible PEO has crystallization ability and a relatively low glass transition temperature. Though neither PAA nor PEO was elastic under ambient conditions, their hydrogen-bonded complex showed excellent elastic behavior. The PAA/PEO fiber demonstrated an elongation up to 12 times (Figure 10b), which was attributed to the inhibition of PEO crystallization through hydrogen bonds and the low glass transition temperature of the fiber tuning to around room temperature. In addition, the brittle and stiff PCFs can gain elasticity by addition of a low glass transition temperature polymer during the fabrication. For example, the ALG/Ca fiber exhibited ultralow elongation because of the rigid structure of ALG and the “egg-box” structure of ALG/Ca complexes, and its elastic property can be improved using polyacrylamide as an additive.^{119–121} Wu et al. fabricated a high-performance ALG/Ca/polyacrylamide fiber with ultrastretchability. The incorporated polyacrylamide not only contributed to the high elasticity but also endowed the fiber with a double network and introduced effective energy dissipation, leading to a 1400% elongation of the fiber without breaking.¹⁰⁰

4.2.4. Conductivity. To date, PCFs with conductivity have been prepared by introducing the conductive additive during fiber formation process. CNT, graphene oxide (GO), and MXene have negative charges on the surface that can interact with polycations to fabricate PE-PCF (Figure 11). Ajayan et al. embedded CNTs into PDADMAC/PSS fiber through interfacial drawing of the complexes formed between CN-PSS dispersion and PDADMAC. The resulting composite fibers exhibited conductivity as 45 S/cm for single-walled CNTs and 90 S/cm for multiwalled CNTs, respectively. The same technique could also be applied to enhance the performance of conductive polymer-based PE-PCF, leading to an increase of 2 orders of magnitude in the conductivity after CNT incorporation.¹²² The Yang group has successfully assembled GO with PEO through hydrogen bonds to prepare fiber material as the abundant phenol and carboxylic acid groups existing on the GO surface. After chemical reduction, the GO could form conjugated network of graphene which endowed the fiber with excellent conductivity as high as 210 S/cm.¹²³ In a recent study, Taheri-Qazvini et al. reported a charge-driven complexation between MXene and PAH which resulted in electroconductive assemblies of 3D porous structures.¹²⁴ The conductivity of the material was increased from 11 to 25 S/cm as the PAH concentration increased from 3 wt % to 42 wt %, demonstrating a polycation-concentration-dependent manner, which could be explained by the more compact 3D porous structures as more PAH diffused into the MXene layer.

4.2.5. Bioproperties. PCFs that are constructed by assemblies of natural polymers or nontoxic synthetic polymers (e.g., CHI, ALG, PEO, and PLA) possess favorable biorelated properties that enable their applications as tissue engineering scaffolds, wound healing, and drug delivery. CHI, a type of biocompatible and biodegradable polysaccharide, can exert specific functions such as hemostasis, antibacterial behavior, and hygroscopicity.¹²⁵ The amino groups render CHI with

positive charges in acid solution that can interact with polyanions (e.g., ALG, PSS, gum, HA) to form PE-PCFs. For example, CHI/PSS core-shell PE-PCFs were prepared through a water-based wet-spinning process whose mechanical properties could be enhanced after adding PEO. The PEO-doped PE-PCFs presented excellent cell adhesive ability and low cytotoxicity in which considerable amount of metabolically active cells were sustained after 5 days of cultivation.¹²⁶ In another case, PE-PCF was prepared using CHI and heparin, which exhibited excellent biocompatibility and low immune responses, making it a good candidate for implantation without inflammation or other biorejection processes. The *in vivo* test also revealed the PE-PCF experienced a relatively slow degradation phase up to four months due to the stiffness of CHI in the fiber.¹²⁷ The anionic ALG can participate in electrostatic interaction or coordination with metal ions and provide additional cross-linking within the network. Owing to their nontoxicity, high water uptake, and degradability, the ALG-based PCFs are widely used to deliver drugs and construct platform for cell proliferation.⁷⁹ In addition, ALG/Ca fiber present good wound healing properties attributed to the exchange of Na ions from the wound and Ca ions in the fibers.¹²⁸ The ion exchange process would cause the calcium ALG to gradually convert to sodium ALG and absorb the water from wound surface to dry damaged area for wound healing. Through complexation with different metal ions or introduction of functional nanoparticles, the ALG-based fibers can be engineered to fulfill specific bioproperties such as antibacterial activity. Hussain et al. prepared zinc-containing fibers through coordination complexation between ALG and Zn²⁺ or doping the ZnO nanorods on the ALG/Ca fibers. The obtained fibers showed excellent resistance against bacterial growth which was caused by the antibacterial property of released zinc ions or the generation of reactive oxygen species induced by ZnO nanorods.¹²⁹

5. FUNCTIONALITY AND APPLICATIONS

Owing to noncovalent interaction and the basic physicochemical properties of substituent components, PCFs can display diverse structures and modulated properties. Various design strategies can be used to tune the functionalities, making PCFs outstanding candidates for a wide range of advanced applications. In this section, we focus on the applications of PCF functional systems in the field of energy storage and sensor, water treatment, biomedical materials, actuator, and biomimetic platform.

5.1. Energy Storage and Sensor. Supercapacitors are a type of attractive power sources that can store large amounts of energy, which have been developed rapidly in recent years with the merits of fast charge/discharge rates, long lifecycle, high dynamics of charge propagation, and environmentally friendly composition.¹³⁰ For some specific applications, the supercapacitor must be integrated into textiles with a tiny size and a variety of shapes, to be used as microelectronic devices. Traditional electrochemical supercapacitors are planar format with 2D or 3D structure and are hard to be made into miniaturized electronic devices or textile electronics.^{131–133} Thus, some attempts have been made to fabricate fiber-shaped supercapacitors, which have dual advantages of light weight and flexibility. The stored energy (E) in a supercapacitor is proportional to specific capacitance, the formula is as follows:¹³³

$$E = 1/2CV^2 \quad (2)$$

where C is the capacitance of the device and V is the operating voltage. To improve the energy storage ability of the fiber-shaped supercapacitor, some electrochemically active materials, such as metal oxides, CNT, graphene, and MXene, can be incorporated into fibers to modulate specific properties.^{134–137} Traditional fibers coated with these materials are prone to peel off, causing lesser cycling stability. PCFs with advantages of integrating various components into systems showed great potential to be used as fiber-shaped supercapacitors (Figure 11).^{28,138,139}

The Yang group utilized GO to make hydrogen-bond supercapacitor fibers with PEO that show high flexibility and long-term bending durability. GO contains hydrogen bond donor groups (phenol and carboxylic acid groups), which could form HB-PCF with PEO. After the chemical reduction of GO (rGO), the conjugated network of graphene will make the fiber conductive. Also, the obtained rGO/PEO fiber had better tensile strength than GO/PEO, improving from 145 to 476 MPa, because the rGO formed more complexation with PEO and completely inhibited the crystal formation of PEO. Three parallel rGO/PEO fibers covered with PVA/H₂SO₄ gel polyelectrolyte could be assembled into a capacitor. The typical rectangular shape of cyclic voltammetry and symmetrical triangle of galvanostatic charge-discharge measurements proved to have excellent electrochemical stability and high reversibility of the capacitor. After 4000 charge/discharge cycles, the capacitors showed a long cyclic stability with specific capacitance retention of 92% of its initial capacitance (50 F/g), capable of lighting a blue LED.¹²³

However, the stacked structure of graphene has limited the ion transfer and constrained the specific capacitance to some extent. In order to enhance the specific capacitance, lots of fillers such as CNT, MoS₂, MnO₂, and cellulose nanofibrils (CNF) acting as spacers have been incorporated into graphene fibers.^{140–142} Chen et al. added CNF into a GO-based complex fiber, making CNF/GO/CHI complex fibers by interfacial drawing. Compared to GO fibers, incorporating the CNF would decrease the electrical conductivity, while the mechanical strength and specific capacitance would increase. The reason is that aligned CNFs acting as reinforcing agent and spacer would reinforce the strength, increase the gap between GO, and accelerate the diffusion of ions while increasing internal resistance. Under optimal conditions, the specific capacitance was 182.6 F/g, which improved about three times in comparison to the GO fiber without spacer. After 1500 charge-discharge cycles, the fiber could still maintain 92% of the original capacitance value, showing the stable capacitance performance.¹³⁰

MXene is a kind of two-dimensional transition metal carbides, with homogeneous distribution of negatively charged groups on the surfaces and a smaller lateral size.¹⁴³ Compared to GO, it can assemble into 3D stacked structures based on 2D nanosheets without the assistance of spacers to enlarge the gap between nanosheets. Taheri-Qazvin found that charge-driven complexation of polyelectrolytes and MXene at the interface could help MXene assemble into 3D porous structures, permitting increased ion transfer and bringing new opportunities to fabricate energy storage materials (Figure 12a).¹²⁴

In addition, fiber is a flexible material used in clothing that can withstand certain deformations and sensitively respond to changes in shape. As conductive fibers are pulled along the

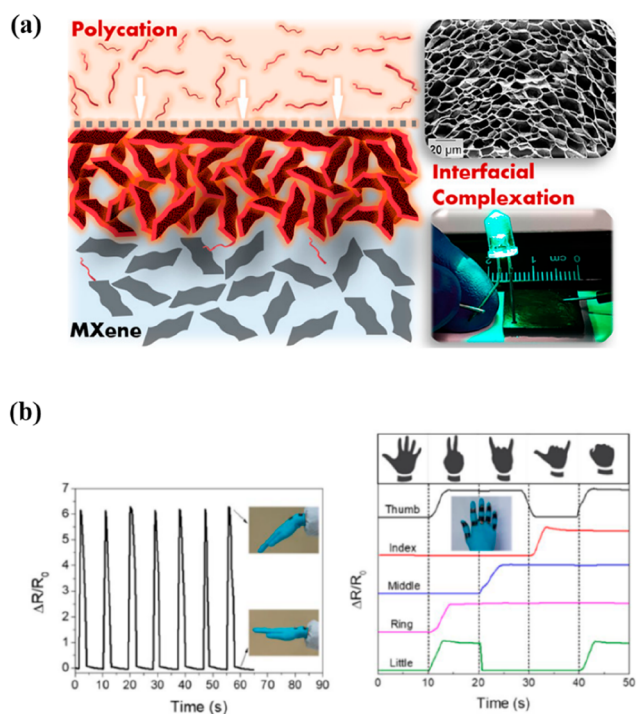


Figure 12. Conductive PCFs were used as (a) supercapacitors and (b) strain sensors. Redrawn and reprinted with permission from refs (a) 113 and (b) 124. Copyright (a) 2021 American Chemical Society and (b) 2019 Springer Nature.

direction of applied force, the fiber cannot maintain the original shape and suffers from deformation, causing a drastic decrease in the effective cross-sectional area and increasing the electrical resistance. When the applied force is removed, the fiber recovers to the initial shape as does the electrical resistance.¹⁴⁴ Hence, conductive fibers can be used as a strain sensor and attached at the target positions, having morphology that integrates seamlessly. The sensor would record changes in resistance as the strain continuously changes through cycles of bending and unbending (Figure 12b). To realize the mechanical response behavior, conductive fibers also should have a large range of elasticity to undergo a large deformation and recovery with no wastage. As described previously, PCFs can be endowed with excellent conductive and elastic properties. Based on this, many PCF-based strain sensors

have been developed to monitor the specific motions of fingers, wrists, and elbows.

Peng et al. prepared CNF/CHI-based PE-PCFs through interfacial spinning and the second network was formed after the in situ polymerization of acrylamide and acrylic acid within the CNF/CHI structure. Further adding Fe^{3+} could improve the fiber strength and toughness by introducing the metal coordination interactions with carboxylate groups. The highly oriented CNFs endowed fibers with a hierarchically muscle-like structure, which provided plenty of nanochannels for ion transport, and the system showed high ionic conductivity when LiCl was incorporated. The fiber was then encapsulated onto human skin, as a test of its application as a muscle-like sensor to monitor human motion. When the finger was straightened and bent repeatedly, the electrical resistance ($\Delta R/R_0$) fluctuated periodically, with stable amplitude and period, which provided a robust method to register the dynamics of finger motion and provided direct measurement of a muscle-like fiber.¹⁴⁵

5.2. Water Treatment. Clean water is known as one of the most essential resources for basic human life, as well as a primary vector for preventable disease caused by microbes and natural or manmade pollutants. Currently, methods of water purification are mainly based on procedures relying on filtration, sedimentation, centrifugation, flocculation, and anaerobic/aerobic digestions.¹⁴⁶ Among these techniques, filtration has the advantage of low energy consumption, nontoxicity, and high efficiency, arousing significant interest in both academia and industry.

Electrospun nanofibers have the advantages of remarkably high specific surface area, porosity, and as three-dimensional fibrous structure, which show excellent performance in water treatment (Figure 13a). Functional groups such as surface carboxylates allow polyelectrolyte based nanofibrous mats to demonstrate strong interactions with toxic metal ions and are investigated as water softening to remove mineral ions. Deb et al. use PVA and PAA to fabricate PVA/PAA nanofibrous mats. Due to the ionized carboxylic acid group of PAA and the high specific area of electrospinning nanofiber, nanofibrous mats could be formed through PAA– COOCa^{2+} complexation used as highly effective Ca(II) ions, which are the most common mineral ions found in domestic water. Removal of Ca^{2+} would reach equilibrium within 60 min. Mineral ions in solution with different charges, such as Mg^{2+} and Na^+ , showed an

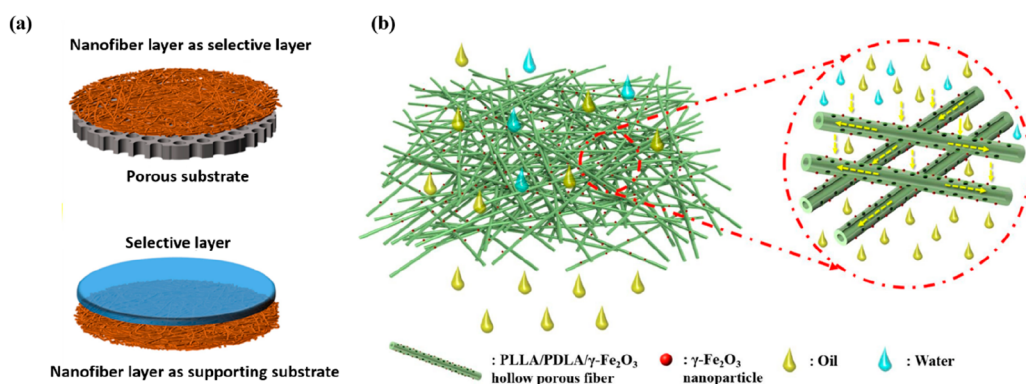


Figure 13. Fabrication of PCF systems used in water treatment including (a) electrospun nanofibrous mats used for multiple-ion removal and (b) PLA nanofibrous mats used for oil/water separation. Redrawn and reprinted with permission from refs (a) 146 and (b) 150. Copyright (a) 2022 AAAS and (b) 2021 Elsevier.

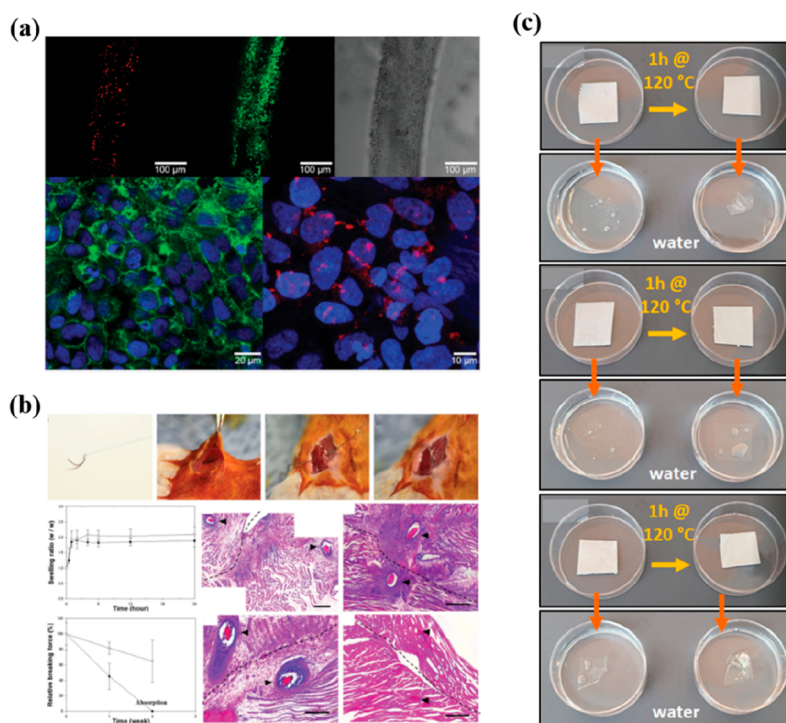


Figure 14. Biomedical applications of PCFs: (a) tissue engineering scaffolds; (b) wound healing; (c) delivery and release of curcumin. Redrawn and reprinted with permission from refs (a) 126, (b) 127, and (c) 166. Copyright (a) 2020 John Wiley and Sons, (b) 2017 John Wiley and Sons, and (c) 2022 American Chemical Society.

interferential effect on the removal of Ca^{2+} . Mg^{2+} competes with Ca^{2+} and decreased its adsorption capacity from 88.8% to 70% at low concentration (0.005 M). However, monovalent Na^+ showed a limited effect on adsorption capacity when competing with Ca^{2+} in solution.¹⁴⁷

Another method to improve the removal is to combine polyelectrolyte complex nanofibers with commercial membranes. Based on poly(ether sulfone) ultrafiltration (UF) membranes, a homogeneous solution of PAA and PAH were electrospun under a high electrostatic field. The obtained PAH/PAA-UF membrane had better hydrophilicity than the UF membrane due to the functional groups of PAH/PAA. Compared to the UF membrane, the PAA/PAH-UF membrane exhibited 38%, 49%, and 85% higher removal of Pb^{2+} , Cu^{2+} , and Cd^{2+} from DI water, respectively. These may contribute to the complexation of metal ions due to the carboxylic acid groups in PAA/PAH mats. The decreased removal of Pb^{2+} was due to the larger ionic radius, which resulted in less complexation of Pb^{2+} by $-\text{COO}^-$ groups.¹⁴⁸

Nevertheless, challenges remain despite promising results reported in previous studies. In particular, mats coated by PE-PCFs were easily fouled by landfill leachate compared to pure UF membranes. Further, removal can be affected by solution pH, with acidic solutions decreasing the negative charges on the membrane surface through decreased ionization of carboxylic acid groups.

In addition to the ion separation functions with PCF membranes, reports also demonstrate solvent/water separation using electrospun stereocomplex PLA fibers as water treatment, including *n*-hexane, tetrachloromethane, and chloroform (Figure 13b).^{149,150}

PLA stereocomplexes are hydrophobic, and chloroform is a good solvent for homo crystallites and can act as a model to

mimic hydrophobic pollutants which may affect water supplies, such as petroleum. However, chloroform cannot dissolve stereocomplex crystallites of PLA. Therefore, electrospinning membranes of PLA can theoretically be used to separate the chloroform/water mixture. However, the PLA stereocomplex membranes with no strong connections between individual stereocomplex crystallites can still be destroyed by chloroform. The Fu group utilized low-temperature sintering of annealed PLA stereocomplex membranes under 1 MPa pressure to increase the fraction of stereocomplex crystallites from 7.6% to 46.6% and improve interfiber adhesion. The obtained membranes maintained integrity in chloroform and would not be destroyed or swell under recycled flux. When pouring the chloroform/water mixture into a Büchner funnel having a filter of a PLA stereocomplex membrane, chloroform easily penetrated through to the funnel below while water remained within the Büchner funnel. Almost no water was observed in the collected chloroform.¹⁴⁹

5.3. Biomedical Materials. PCFs based on natural biomaterials have been developed for biomedical applications exploiting the advantages of aqueous compatibility, biocompatibility, robust mechanical properties, and dynamic response, including tissue engineering scaffolds,^{151–153} wound healing,^{119,127,154,155} and drug delivery and release (Figure 14).^{156–158}

Tissue engineering scaffolds are a promising strategy to achieve local regeneration of malfunctioning tissues and organs by culturing cells on biocompatible scaffolds.¹⁵⁹ Polysaccharide based PCFs have unique advantages over other materials, particularly high specific-surface area, adjustable mechanical strength, modulated flexibility, biocompatibility, controllable degradation rate, making them great candidates in tissue-engineering scaffolds. Their biocompatibility is defined by their

lack of immune response on introduction within the body or triggering foreign body reactions, such as tissue encapsulation.¹⁶⁰

Wessling et al. prepared core–shell PCFs scaffolds based on electrostatic interactions between CHI and PSS. In this work, the core–shell structure was constructed to endow the components with independent functionalities from each component, as CHI is a good cell culture substrate and PSS can be doped with PEO to enhance the mechanical properties. Following a four-day cultivation of human HeLa cells on CHI/PSS fibers, adhered cells were homogeneously distributed over the fiber surface and the cell viability was determined to be 81.49%, indicating the biocompatibility of the fibers and minimal cell death. Figure 14a shows the organization of the HeLa actin cytoskeleton on PE-PCF scaffolds. Spread of actin filaments indicates that cells had a high affinity to CHI/PSS scaffolds.¹²⁶ Nie et al. prepared the PCFs with the natural biopolymers CHI and HA, which are oppositely charged, by interfacial drawing. Sterilized fibers were placed in wells and cells were incubated for 24 h. For comparison, fresh culture medium was prepared under the same seeding conditions. There was no significant difference of cell activity between the PCF-modified group and the plain fresh culture medium. In-vitro cytocompatibility experiments showed a high cell density and the fiber surface showed homogeneous distribution of HEK293 cells. All cells retained a rounded morphology with spreading along the fiber scaffolds. These results suggest that CHI and HA complex fibers can be used as materials for bioscaffolding with good cytocompatibility and having advantages for cell adhesion and spreading.¹⁵²

Skin is the primary barrier protecting the body against pathogens, but it can lose its protective function as an organ through damage. While a slight wound heals naturally through tissue regeneration, damage extending through a large area of the epidermis is quite difficult to heal naturally, in part due to the flexibility and motion inherent to skin. Surgical sutures are likely the most widely used medical devices in biomedical applications for wound closure, though ease and ubiquity make that statistic difficult to measure.¹⁶¹ During their application, sutures may be exposed to many microorganisms' environment, leading to surgical site infections through their colonization along the surface of the suture. Also, the movement of skin is likely to re-crack the wound in more extensive injuries. These facts make it necessary to develop surgical sutures which can inhibit bacteria and possess excellent mechanical properties as a preventative for one of the most common causes of infection and increase the quality of medical outcomes.

Polysaccharide-based PCFs are bestowed with high mechanical strength due to the rigid molecular structure of polysaccharide, making them a robust material for surgical sutures which can improve wound healing. For example, CHI is a cationic polysaccharide with rigid structure and antibacterial property. Heparin is a natural anionic polymer which can bind with various proteins and other cationic biopolymers, including CHI. The tensile strength of a CHI/heparin suture formed of 64 CHI/heparin strands was 220 MPa, and sufficient for use under clinical conditions due to its mechanical strength. Sutures of CHI/heparin fibers were used to close a wound using a common suture needle under typical conditions. After a two-week implantation, the CHI/heparin fibers maintained 64% strength, while the surgical gut sutures (PLAIN GUT) were completely degraded. After four-week

implantation, the inflammatory cells had almost disappeared. The in vitro cytotoxicity data showed that cells exhibited high viability and normal adhesion-spreading morphology after a 7-day culture. Because of the stiffness of polysaccharide, the CHI/heparin fiber had an increased degradation time of about 12 weeks, which was longer than that of surgical gut sutures. However, its superior biocompatibility without causing severe immune responses or scar tissue formation, and the capability of binding AAV vectors, could provide the extended time for sustained gene expression at local incision sites for gene therapy.¹²⁷

Drug delivery refers to technologies, formulations, approaches, and systems for delivering pharmaceutical agents into human tissues to safely realize their expected therapeutic effect, often focusing on tumor tissue.¹⁶² While many strategies exist for the delivery and release of drugs, fibers provide mechanical support for a wide range of applications and a structure with high surface area for cell adhesion.¹⁶³ Depending on the application, fiber's size and orientation can be modified to optimize drug release. By incorporating different additives during fabrication, PCFs can be used as carriers to deliver drug and antimicrobial particles. In contrast to conventional polymeric vehicles, PCF carriers have the capability to undergo rapid changes in response to certain external pH stimulus, thereby enabling the controllable release of encapsulated drugs into the media.

Cellulose is an excellent candidate to construct PCF-based drug delivery systems owing to its remarkable physical properties, versatile surface chemistry, and excellent biological properties.^{164,165} Antitumor drug (doxorubicin hydrochloride, DOX) is a positively charged drug that can be incorporated into cationic cellulose nanocrystals (AH–CNC)/anionic cellulose nanofibers (TO–CNF) complex fibers with high loading efficiency (83%). By changing the pH of the medium, AH–CNC/TO–CNF fibers exhibited differential swelling abilities that can influence the release behavior. In PBS (pH 7.4, swelling ratio $81.9 \pm 8\%$), 80% of DOX was released within 3 h and 100% release of DOX was observed after 77 h. In ABS (pH 4, swelling ratio $20.3 \pm 6\%$), the AH–CNC/TO–CNF fibers released $\sim 25\%$ DOX within 1 h and continued to release for several hours.⁸⁶ Luyt et al. prepared ALG/CHI/AgNP nanofibers through electrospinning in which AgNPs were dispersed homogeneously using CHI as reducing and stabilizing agent and the mixed CHI/AgNPs could complex with ALG. To study the release and antibacterial property, the ALG/CHI/AgNP nanofiber membrane was placed inside glass tubes containing the bacterial solutions; water could immigrate through the membrane to promote AgNP release owing to the porous structure of membrane. The results showed that the membrane could release about 90% of AgNPs within 1 h and caused eradication of 72% of Gram-negative and 98% of Gram-positive bacteria. There was no growth of Gram-negative and Gram-positive bacteria observed after 24 h incubation.¹⁵⁸ Uyar et al. prepared CHI/pectin electrospinning fibers that could be used as a platform with pH responsive molecular release. Curcumin was chosen as the molecule to be delivered due to its beneficial bioactivity, and hydroxypropyl- γ -cyclodextrin (HP γ CD) was chosen as its carrier within the PCF due to their known compatibility. After encapsulating curcumin into HP γ CD, the HP γ CD–curcumin inclusion complexes were formed and then mixed into CHI/pectin electrospinning fibers with $\sim 89\%$ curcumin loading efficiency. The release test revealed that CHI/pectin fibers had a pH-dependent curcumin

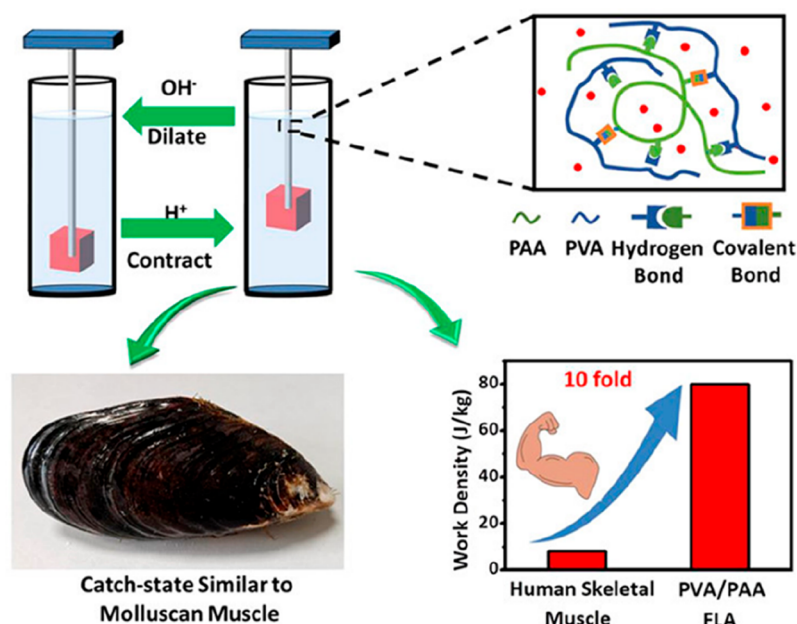


Figure 15. Schematic illustration of artificial actuator driven by pH. Reprinted with permission from ref 64. Copyright 2020 American Chemical Society.

release behavior, which was attributed to their different swelling ratio and integrity status at pH 5.4 and pH 7.4.¹⁶⁶

Myriad natural polymers have been designed for use as tissue engineering scaffolds, wounding healing, and drug delivery vehicles, and some meaningful achievements have been made. However, there is still a wide range of unexplored potential to extend the diversity of materials beyond the exploiting basic solution chemistry or mechanical triggers and instead devising platforms for PCFs designed for phototherapy and magnetotherapy. With emerging synthetic technologies coupled with recent developments in fabrication methods, increasing numbers of biodegradable and biocompatible PCFs having multiple functions will be designed and developed for diverse biomedical applications.

5.4. Actuator. Actuators are devices that can transform various input energies into mechanical energy for operation.^{167,168} For instance, steam engines, combustion engines, and electric motors are classical actuators that drove the industrial revolution and shaped modern society. Nowadays, much of chemistry and physics have been combined to realize miniaturized actuators at micro and nanoscale, essential for drug delivery and soft robotic systems. Many materials have been fabricated into actuators, including stimulus-responsive gels, liquid crystal elastomers, dielectric elastomers, shape memory polymers, conductive polymers, CNTs, graphene, and polymer/inorganic nanocomposites, with different forms such as bulky pieces (3D objects), films (quasi 2D objects), and fibers (quasi 1D objects).¹⁶⁹ Due to their flexibility and orientable structure, actuating fibers can provide contraction and dilation to mimic the form and function of muscles, which have a fibrous structure.¹⁷⁰

Polymer complex fibers are another potential class of candidates to build artificial actuators, due to their dynamic behavior and stimuli response. Yang's group developed a novel kind of pH-actuated fiber, formed by the assembly of PVA and PAA (Figure 15). Hydrogen-bonded complexes of PVA and PAA are well-known to form in acidic solution, and their complexes are stable even when immersed in low pH solutions.

When immersed into alkaline solution, however, the fiber would dissolve as hydrogen bonds break between PVA and PAA. Yang et al. improved the stability of nascent PVA/PAA fibers through chemically cross-linking through thermal treatment, during which covalent ester bonds formed between the carboxylic acid of PAA and the hydroxyl group of PVA. The cross-linked fibers become capable of swelling in alkaline solution without dissolution, while deswelling in acidic solution as the ionic charges dissipated in the presence of H^+ . In response to the stimulus of changes of environmental pH (pH 1–12), the fiber showed reversible contraction and dilation, which can be used for linear actuation. The fiber was easily capable of lifting cargo in excess of 1000 times of its own weight, with a contraction ratio up to 30% and output actuation stress up to 0.24 MPa. The sustainable work density of the fiber was ~ 80 J/kg, 10 times the typical value of the human skeletal muscle fiber. More importantly, in comparison to vertebrate skeletal muscles, the fiber shows a stable catch-state with no energy consumption.⁶⁴

Also, photothermal and moisture-responsive PCF actuators can be achieved through the swelling–deswelling action of hydrophilic polymers having a twisted or helical structure. GO is considered as an excellent material to construct fiber actuator due to its photothermal, hygroscopic, and mechanical properties. The GO/ALG fiber can be fabricated by mixing GO with ALG, followed by injecting the mixture into $CaCl_2$ coagulation bath to form ionic calcium cross-links between the two biopolymers and resulting in a fiber complex. The obtained GO/ALG fiber was then fixed on the twister apparatus to prepare the twisted GO/ALG actuator fiber. Through the cycling of infrared light irradiation, the GO/ALG fiber showed water molecular desorption/adsorption behavior. In response to infrared heating, the temperature at the fiber surface changed from 30 to 36 °C within a narrow range, triggering thermal actuation and generating a stress of 1.4 MPa. Moreover, when the GO/ALG fiber was stimulated by moisture, ALG quickly absorbed water and swelled, producing a swelling force which allowed rearrangement to relieve

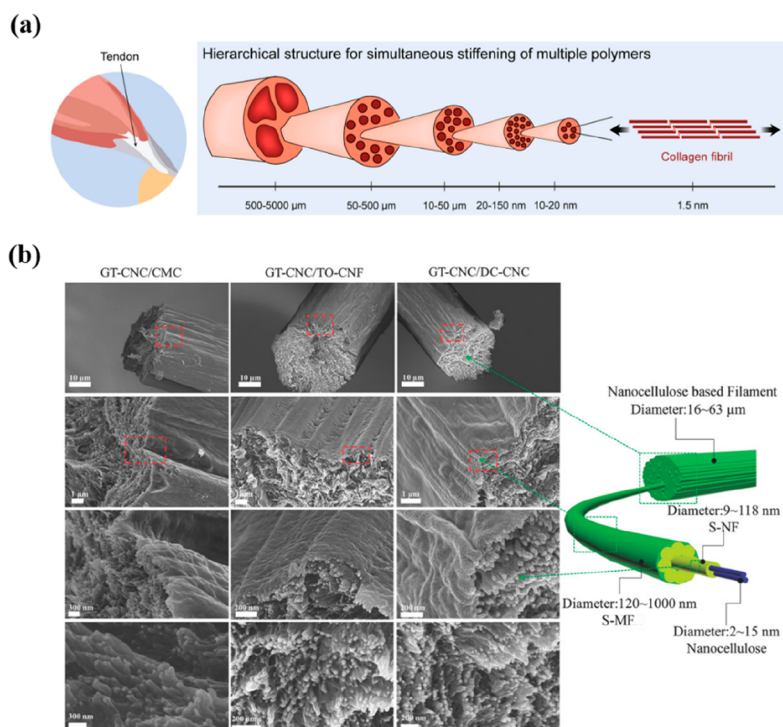


Figure 16. Schematic hierarchical structure of (a) natural tendon and (b) PE-PCF. Reprinted with permission from refs (a) 174 and (b) 179. Copyright (a) 2021 American Chemical Society and (b) 2018 John Wiley and Sons.

internal stress and entropy, resulting in the fiber to untwist from the imposed structure. As the moisture dropped, water in the fiber desorbed and generated deswelling force to recover the original state. Fast adsorption and desorption of water by GO and the swelling–deswelling behavior of ALG, the actuation behavior of the twisted GO/ALG fiber was robust and showed no attenuation after 100 actuation cycles, proving the system's excellent stability.¹⁷¹

Responsive groups can, moreover, be fabricated into PCFs by chemical modification to build stimulus-responsive actuators, such as light-responsive azobenzene,¹⁷² temperature-responsive poly(*N*-isopropylacrylamide), and magnetic-responsive nanoparticles.^{37,173}

5.5. Miscellaneous (Biomimetic Platforms). Natural tissues in the human body have various structural characteristics, among which anisotropic structural features are unique. Tendons and ligaments have similar structures showing anisotropic features linearly arranged collagen fibers with a hierarchy of bundles, with dimensions ranging from nano to macroscale (Figure 16a).¹⁷⁴ Tissues with anisotropic structure have high mechanical strength and constructing the materials with anisotropic and hierarchical structure is a proven and enticing pathway to develop next-generation soft materials for soft electronics and robotics.¹⁷⁵ Current fabrication methods such as wet-spinning, melt spinning, and drawing hydrogels have been applied to construct biomimetic platforms.¹⁷⁶ However, challenges still exist in the quest to fabricate artificial mimics of the hierarchically anisotropic structures and excellent mechanical properties present in natural tissues. This section will introduce the current progress of PCFs for construction of biomimetic platforms having hierarchical structure ranging from nano- to macroscale and their enhanced mechanical properties.

Gomes et al. used microfluidics technology to prepare ALG/CHI fiber mimicking the architecture of natural fibrous tissues.⁸¹ Photo-cross-linking of ALG/CHI fiber was performed by UV exposure and fibers were then extracted from the microfluidic reactor. Complexation resulted in the formation of thinner fibrils, and the fibers exhibited smaller fibrils aligned in parallel. However, this structure was still macroscale and failed to mimic the nano structure of natural tissues assembled through cellular action. Following this, further attempts were made in research on nanocellulose based PCFs with interfacial drawing.^{69,177,178} CNFs with nano structure have drawn much attention in recent years due to their attractive combination of high mechanical strength and biocompatibility. Gandini's group used anionic nanocellulose complexed with cationic CHI to fabricate microfibril (Figure 16b). The process involves the continuous pulling incorporating each polymer at their interface, inducing progressive alignment of the CNF and the CHI. Such fiber shows compact structure with some hierarchy, consisting of dense fibril bundles with continuous, folded layers. This morphology suggested that the CNFs, had been covered by CHI during the fiber formation due to ionic associations, giving rise to dimensions ranging from nano to macroscale in contrast to their diameter of 25 to 75 nm. The tensile modulus was ~22 GPa and the tensile strength was 220 MPa, exceeding natural tissues such as tendons or ligaments.¹⁷⁹ Combining such mechanical properties with biocompatibility shows potential to be used as artificial ligaments or tendons in biomaterials and soft robotics and may be able to match or surpass the function of normal human tissues.^{180,181}

6. CONCLUSION AND OUTLOOK

In this review, we provided a comprehensive summary and analysis of the current advances within PCF research. To date,

four kinds of PCFs have well-established bodies of work, namely coordination complex fiber (CO-PCF), stereocomplex fiber (ST-PCF), polyelectrolyte complex fiber (PE-PCF), and hydrogen-bonded complex fiber (HB-PCF), all of which have been developed and comprehensively studied with the possibility of further refinement. Based on the intrinsic features of polymer complex systems and the specific properties/applications that are being aimed for, different technologies can be selected for PCF fabrication, including melt spinning, interfacial drawing, electrospinning, microfluidics, and complexation-based wet spinning. We have summarized the respective characteristics and applicability of each fabrication method, and detailed effects of processing parameters on structure–property relationships of spun fibers, which we expect to provide a quick guideline and reference for researchers during PCF preparation. In addition, the diverse properties of PCFs are addressed, including the intrinsic properties (e.g., inherent stimuli responsiveness, shape memory, and self-healing) attributed to the dynamic nature of noncovalent interactions in PCFs, and the extrinsic properties (e.g., elasticity, conductivity and bioproperties) relying on the fiber composition. Owing to the structural versatility and tunable properties, PCFs hold great potential to promote the advancement of technology and human wellbeing in such diverse areas as energy storage and sensing, water treatment, biomedical materials, artificial actuator, and biomimetic platforms.

Along with the progress achieved in the fabrication and application of PCFs, there are still numerous opportunities of significance in the field. First, PCFs are considered excellent candidates for biomimetic systems for intelligent material construction, yet exiting PCFs cannot realize many of the fundamental characteristics of biological systems such as active adaptivity, communication, or computation. This is likely caused by the lack of multiple interactions and hierarchically complex structures required to facilitate intricate and simultaneous functionalities. Prepared PCFs usually have a single noncovalent interaction responsible for fiber formation, and few studies have introduced a secondary interaction with the intent of enhancing stability, mechanical properties, or stimuli-sensitivity. Future work can investigate rational integration of multiple interactions into the single fibers or fiber assemblies, as delicate regulation of these molecular interactions is imperative to evolve the interactivity of smart PCF materials. Second, although complex structure can be achieved using fabrication devices with delicate design and varying processing parameters, precise control over PCF structures with fine resolution at various scales is still challenging. In this regard, polymers with controlled molecular structures (e.g., linear, brush, star) prepared via precise synthetic methods (e.g., living polymerization, blocking-cyclization, biosynthesis, and click chemistry) can be applied to construct PCFs and achieve complex structures. Block copolymers can be introduced into the system to combine phase separation and polymer complexation to realize the multilevel structures of PCFs. Such PCFs can be further structured through knitting or weaving on demand to achieve fine macrostructures for the targeted applications. Third, as various strategies and techniques have been used to regulate fiber properties during initial fabrication, postfabrication modification is rarely explored, yet offers great potential value to improve the diversity of fiber structure and functionality. Surface modification is a common method for

postfabrication treatment in many physical and chemical systems. However, traditional surface modification methods like radiation, plasma treatment or electron beam irradiation may be incompatible, mainly damaging the structure and making them unsuitable as methods of PCF modification. Future work focusing on the development of new surface modification methods dedicated for PCFs may yield significant improvements and greatly expand the possibilities mentioned previously. Fourth, the rheological properties of polymer complexes have been widely studied. Numerous researchers have investigated the viscoelasticity of polymer complexes affected by temperature, water, salts and pH, and further established principles of Time–Temperature, Time–Water, Time–Salt superposition. Also, rheology plays an important role in spinning. By studying the fluidity of the spinning solution and adjusting the viscosity to improve spinnability, rheology can provide the important parameters to optimize production conditions. However, the more profound insights of analyzing the rheology of PCF spinning solution have been rarely reported. More research about the rheology-structure relationship of PCF materials should be established.

Finally, some applications of PCFs are not refined beyond proof-of-concept, and effort should be devoted to realize practical applications. For example, current studies of various biomimetic platforms focus on the implementation of structure and mechanical properties resembling natural tissues and may provide materials that surpass the original. However, investigation is still needed to prove the feasibility of these biomimetic platforms as artificial tendons or soft robotics, to realize the potential progress promised by these systems or establish the reasons behind their limitations. We believe, with the advances of theory and technique, PCFs with novel properties and multifunctionality can be designed and prepared to facilitate the development of next generation materials.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsami.2c19583>.

Summary of PCF composition and properties (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Gucht, J. V. D.; Spruijt, E.; Lemmers, M.; Cohen Stuart, M. A. Polyelectrolyte Complexes: Bulk Phases and Colloidal Systems. *J. Colloid Interface Sci.* **2011**, *361*, 407–422.
- (2) Srivastava, S.; Tirrell, M. V. Polyelectrolyte Complexation. *Adv. Chem. Phys.* **2016**, *161*, 499–544.
- (3) Rasmussen, S.; Chen, L. H.; Deamer, D.; Krakauer, D. C.; Packard, N. H.; Stadler, P. F.; Bedau, M. A. Transitions from Nonliving to Living Matter. *Science* **2004**, *303*, 963–965.
- (4) Muthukumar, M. 50th Anniversary Perspective: A Perspective on Polyelectrolyte Solutions. *Macromolecules* **2017**, *50*, 9528–9560.
- (5) Klosin, A.; Hyman, A. A. A Liquid Reservoir for Silent Chromatin. *Nature* **2017**, *547*, 168–170.
- (6) Kulkarni, A. D.; Vanjari, Y. H.; Sancheti, K. H.; Patel, H. M.; Belgamwar, V. S.; Surana, S. J.; Pardeshi, C. V. Polyelectrolyte Complexes: Mechanisms, Critical Experimental Aspects, and Applications. *Artif. Cell. Nanomed. B* **2016**, *44*, 1615–1625.
- (7) Schmitt, C.; Turgeon, S. L. Protein/Polysaccharide Complexes and Coacervates in Food Systems. *Adv. Colloid. Interfac.* **2011**, *167*, 63–70.
- (8) Voets, I. K.; de Keizer, A.; Cohen Stuart, M. A. Complex Coacervate Core Micelles. *Adv. Colloid. Interfac.* **2009**, *147*, 300–318.
- (9) Donald, A. M. Aggregation in beta-Lactoglobulin. *Soft Matter* **2008**, *4*, 1147–1150.
- (10) Khutoryanskiy, V. V. Hydrogen-Bonded Interpolymer Complexes as Materials for Pharmaceutical Applications. *Int. J. Pharmaceut.* **2007**, *334*, 15–26.
- (11) Berger, J.; Reist, M.; Mayer, J. M.; Felt, O.; Gurny, R. Structure and Interactions in Chitosan Hydrogels Formed by Complexation or Aggregation for Biomedical Applications. *Eur. J. Pharm. Biopharm.* **2004**, *57*, 35–52.
- (12) Zhang, X. Supramolecular Polymer Chemistry: Past, Present, and Future. *Chin. J. Polym. Sci.* **2022**, *40*, 541–542.
- (13) Liu, D. Z.; Li, J. F.; Huang, W. T.; Yang, S. G. Progress in Polymer Complex Fibers. *Acta. Polym. Sin.* **2018**, *4*, 445–455.
- (14) Imeson, A. P.; Ledward, D. A.; Mitchell, J. R. Effects of Calcium and pH on Spun Fibres Produced from Plasma-Alginate Mixtures. *Meat. Sci.* **1979**, *3*, 287–294.
- (15) Fraser, R.; Gilchrist, T. Sorbsan Calcium Alginate Fibre Dressings in Footcare. *Biomaterials* **1983**, *4*, 222–224.
- (16) Tsuji, H.; Ikada, Y.; Hyon, S. H.; Kimura, Y.; Kitao, T. Stereocomplex Formation between Enantiomeric Poly(lactic acid). VIII. Complex Fibers Spun from Mixed Solution of Poly(D-Lactic Acid) and Poly(L-Lactic Acid). *J. Appl. Polym. Sci.* **1994**, *51*, 337–344.
- (17) Amaike, M.; Senoo, Y.; Yamamoto, H. Sphere, Honeycomb, Regularly Spaced Droplet and Fiber Structures of Polyion Complexes of Chitosan and Gellan. *Macromol. Rapid Commun.* **1998**, *19*, 287–289.
- (18) Wan, A. C. A.; Cutiongco, M. F. A.; Tai, B. C. U.; Leong, M. F.; Lu, H. F.; Yim, E. K. F. Fibers by Interfacial Polyelectrolyte Complexation-Processes, Materials and Applications. *Mater. Today* **2016**, *19*, 437–450.
- (19) Ewaldz, E.; Brettmann, B. Molecular Interactions in Electrospinning: From Polymer Mixtures to Supramolecular Assemblies. *ACS Appl. Polym. Mater.* **2019**, *1*, 298–308.
- (20) Han, D.; Steckl, A. J. Coaxial Electrospinning Formation of Complex Polymer Fibers and Their Applications. *ChemPlusChem.* **2019**, *84*, 1453–1497.
- (21) Rathore, P.; Schiffman, J. D. Beyond the Single-Nozzle: Coaxial Electrospinning Enables Innovative Nanofiber Chemistries, Geometries, and Applications. *ACS Appl. Mater. Interfaces* **2021**, *13*, 48–66.
- (22) Li, Z.; Wang, J.; Li, X.; Wang, Y.; Fan, L. J.; Yang, S.; Guo, M.; Li, X.; Tu, Y. Supramolecular and Physically Double-Cross-Linked Network Strategy toward Strong and Tough Elastic Fibers. *ACS Macro Lett.* **2020**, *9*, 1655–1661.
- (23) Qin, Y. The Gel Swelling Properties of Alginate Fibers and Their Applications in Wound Management. *Polym. Adv. Technol.* **2008**, *19*, 6–14.
- (24) Crne, M.; Park, J. O.; Srinivasarao, M. Electrospinning Physical Gels: The Case of Stereocomplex PMMA. *Macromolecules* **2009**, *42*, 4353–4355.
- (25) Sharma, J.; Zhang, X.; Sarker, T.; Yan, X.; Washburn, L.; Qu, H.; Guo, Z.; Kucknoor, A.; Wei, S. Biocompatible Electrospun Tactic Poly(Methyl Methacrylate) Blend Fibers. *Polymer* **2014**, *55*, 3261–3269.
- (26) Agrawal, A. K.; Bhalla, R. Advances in the Production of Poly(Lactic Acid) Fibers. A Review. *J. Macromol. Sci.-Polym. R.* **2003**, *43*, 479–503.
- (27) Monticelli, O.; Putti, M.; Gardella, L.; Cavallo, D.; Basso, A.; Prato, M.; Nitti, S. New Stereocomplex PLA-Based Fibers: Effect of POSS on Polymer Functionalization and Properties. *Macromolecules* **2014**, *47*, 4718–4727.
- (28) Granero, A. J.; Razal, J. M.; Wallace, G. G.; in het Panhuis, M. Spinning Carbon Nanotube-Gel Fibers Using Polyelectrolyte Complexation. *Adv. Funct. Mater.* **2008**, *18*, 3759–3764.
- (29) Cutiongco, M. F. A.; Tan, M. H.; Ng, M. Y. K.; Le Visage, C.; Yim, E. K. F. Composite Pullulan-Dextran Polysaccharide Scaffold with Interfacial Polyelectrolyte Complexation Fibers: A Platform with Enhanced Cell Interaction and Spatial Distribution. *Acta Biomater* **2014**, *10*, 4410–4418.
- (30) Wang, Q.; Schlenoff, J. B. Tough Strained Fibers of a Polyelectrolyte Complex: Pretensioned Polymers. *RSC Adv.* **2014**, *4*, 46675–46679.
- (31) Boroudjerdi, H.; Naji, A.; Netz, R. R. Salt-Modulated Structure of Polyelectrolyte-Macroion Complex Fibers. *Eur. Phys. J. E* **2011**, *34*, 72.
- (32) Lee, T. W.; Han, M.; Lee, S. E.; Jeong, Y. G. Electrically Conductive and Strong Cellulose-Based Composite Fibers Reinforced

with Multiwalled Carbon Nanotube Containing Multiple Hydrogen Bonding Moiety. *Compos. Sci. Technol.* **2016**, *123*, 57–64.

(33) Li, J.; Wang, Z.; Wen, L.; Nie, J.; Yang, S.; Xu, J.; Cheng, S. Z. D. Highly Elastic Fibers Made from Hydrogen-Bonded Polymer Complex. *ACS Macro. Lett.* **2016**, *5*, 814–818.

(34) Nie, J.; Wang, Z. L.; Li, J. F.; Gong, Y.; Sun, J. X.; Yang, S. G. Interface Hydrogen-Bonded Core-Shell Nanofibers by Coaxial Electrospinning. *Chin. J. Polym. Sci.* **2017**, *35*, 1001–1008.

(35) Gaikwad, A.; Hlushko, H.; Karimineghlani, P.; Selin, V.; Sukhishvili, S. A. Hydrogen-Bonded, Mechanically Strong Nanofibers with Tunable Antioxidant Activity. *ACS Appl. Mater. Interfaces* **2020**, *12*, 11026–11035.

(36) Zheng, X.; Zhang, Y.; Wang, Z.; Wang, Y.; Zou, L.; Zhou, X.; Hong, S.; Yao, L.; Li, C. Highly Effective Antibacterial Zeolitic Imidazolate Framework-67/Alginate Fibers. *Nanotechnology* **2020**, *31*, 375707.

(37) Chen, G.; Wang, G.; Tan, X.; Hou, K.; Meng, Q.; Zhao, P.; Wang, S.; Zhang, J.; Zhou, Z.; Chen, T.; et al. Integrated Dynamic Wet Spinning of Core-Sheath Hydrogel Fibers for Optical-to-Brain/Tissue Communications. *Natl. Sci. Rev.* **2021**, *8*, 209.

(38) Xia, B.; Zhang, Y.; Zhu, Q.; Lin, X.; Wu, Q. Enzymatic Synthesis and Stereocomplex Formation of Chiral Polyester Containing Long-Chain Aliphatic Alcohol Backbone. *Biomacromolecules* **2019**, *20*, 3584–3591.

(39) Tonelli, A. E.; Flory, P. J. The Configurational Statistics of Random Poly(Lactic Acid) Chains. I. Experimental Results. *Macromolecules* **1969**, *2*, 225–227.

(40) Ikada, Y.; Jamshidi, K.; Tsuji, H.; Hyon, S. H. Stereocomplex Formation between Enantiomeric Poly(Lactides). *Macromolecules* **1987**, *20*, 904–906.

(41) Jun Jae, L.; Yamane, H. Role of the Stereocomplex Crystallites in the PLLA/PDLA Mixed Spinning Dope on the Stereocomplex Formation in the Wet-Spun Fibers. *Sen-I Gakkaishi* **2010**, *66*, 236–242.

(42) Takasaki, M.; Ito, H.; Kikutani, T. Development of Stereocomplex Crystal of Polylactide in High-Speed Melt Spinning and Subsequent Drawing and Annealing Processes. *J. Macromol. Sci.-Phys.* **2003**, *42*, 403–420.

(43) Furuhashi, Y.; Kimura, Y.; Yamane, H. Higher Order Structural Analysis of Stereocomplex-Type Poly(Lactic Acid) Melt-Spun Fibers. *J. Polym. Sci., Polym. Phys.* **2007**, *45*, 218–228.

(44) Tsuji, H.; Nakano, M.; Hashimoto, M.; Takashima, K.; Katsura, S.; Mizuno, A. Electrospinning of Poly(Lactic Acid) Stereocomplex Nanofibers. *Biomacromolecules* **2006**, *7*, 3316–3320.

(45) Jae Lee, J.; Lee, J.-C.; Yamane, H. Stereocomplexation in the Solution Spun PLLA/PDLA Blend Fibers. *Sen-I Gakkaishi* **2010**, *66*, 174–180.

(46) Spasova, M.; Manolova, N.; Paneva, D.; Mincheva, R.; Dubois, P.; Rashkov, I.; Maximova, V.; Danchev, D. Polylactide Stereocomplex-Based Electrospun Materials Possessing Surface with Antibacterial and Hemostatic Properties. *Biomacromolecules* **2010**, *11*, 151–159.

(47) Lv, R.; Tian, R.; Na, B.; Zhang, P.; Liu, Q. Strong Confinement Effects on Homocrystallization by Stereocomplex Crystals in Electrospun Polylactide Fibers. *J. Phys. Chem. B* **2015**, *119*, 15530–15535.

(48) Maleki, H.; Barani, H. Stereocomplex Electrospun Fibers from High Molecular Weight of Poly(L-Lactic Acid) and Poly(D-Lactic Acid). *J. Polym. Eng.* **2020**, *40*, 136–142.

(49) Furuhashi, Y.; Kimura, Y.; Yoshie, N.; Yamane, H. Higher-Order Structures and Mechanical Properties of Stereocomplex-Type Poly(Lactic Acid) Melt Spun Fibers. *Polymer* **2006**, *47*, 5965–5972.

(50) Shyr, T. W.; Ko, H. C.; Chen, H. L. Homocrystallization and Stereocomplex Crystallization Behaviors of As-Spun and Hot-Drawn Poly(L-Lactide)/Poly(D-Lactide) Blended Fibers during Heating. *Polymers* **2019**, *11*, 1502.

(51) Yamamoto, M.; Nishikawa, G.; Afifi, A. M.; Lee, J. C.; Yamane, H. Effect of the Take-Up Velocity on the Higher-Order Structure of

the Melt-Electrospun PLLA/PDLA Blend Fibers. *Sen-I Gakkaishi* **2015**, *71*, 127–133.

(52) Ohkawa, K.; Takahashi, Y.; Yamamoto, H. Self-Assembling Capsule and Fiber Formations of Polyion Complexes of Chitosan and Poly(Alpha, L-glutamic Acid). *Macromol. Rapid Commun.* **2000**, *21*, 223–225.

(53) Ohkawa, K.; Yamada, M.; Nishida, A.; Nishi, N.; Yamamoto, H. Biodegradation of Chitosan-Gellan and Poly(L-lysine)-Gellan Polyion Complex Fibers by Pure Cultures of Soil Filamentous Fungi. *J. Polym. Environ.* **2000**, *8*, 59–66.

(54) Yamamoto, H.; Senoo, Y. Polyion Complex Fiber and Capsule Formed by Self-Assembly of Chitosan and Gellan at Solution Interfaces. *Macromol. Chem. Phys.* **2000**, *201*, 84–92.

(55) Ohkawa, K.; Takahashi, Y.; Yamada, M.; Yamamoto, H. Polyion Complex Fiber and Capsule Formed by Self-Assembly of Chitosan and Poly(Alpha, L-Glutamic Acid) at Solution Interfaces. *Macromol. Mater. Eng.* **2001**, *286*, 168–175.

(56) Yamamoto, H.; Horita, C.; Senoo, Y.; Nishida, A.; Ohkawa, K. Polyion Complex Fiber and Capsule Formed by Self-Assembly of Poly-L-lysine and Gellan at Solution Interfaces. *J. Appl. Polym. Sci.* **2001**, *79*, 437–446.

(57) Yamamoto, H.; Ohkawa, K.; Nakamura, E.; Miyamoto, K.; Komai, T. Preparation of Polyion Complex Capsule and Fiber of Chitosan and Gellan-Sulfate at Aqueous Interface. *B. Chem. Soc. Jpn.* **2003**, *76*, 2053–2057.

(58) Fu, J.; Fares, H. M.; Schlenoff, J. B. Ion-Pairing Strength in Polyelectrolyte Complexes. *Macromolecules* **2017**, *50*, 1066–1074.

(59) Suarez-Martinez, P. C.; Batys, P.; Sammalkorpi, M.; Lutkenhaus, J. L. Time–Temperature and Time–Water Superposition Principles Applied to Poly(Allylamine)/Poly(Acrylic Acid) Complexes. *Macromolecules* **2019**, *52*, 3066–3074.

(60) Manoj Lalwani, S.; Eneh, C. I.; Lutkenhaus, J. L. Emerging Trends in the Dynamics of Polyelectrolyte Complexes. *Phys. Chem. Chem. Phys.: PCCP* **2020**, *22*, 24157–24177.

(61) Yang, M.; Digby, Z. A.; Schlenoff, J. B. Precision Doping of Polyelectrolyte Complexes: Insight on the Role of Ions. *Macromolecules* **2020**, *53*, 5465–5474.

(62) Huang, W.; Liu, D.; Zhu, L.; Yang, S. A Salt Controlled Scalable Approach for Formation of Polyelectrolyte Complex Fiber. *Chin. J. Chem.* **2020**, *38*, 465–470.

(63) Smith, K. L.; Winslow, A. E.; Petersen, D. E. Association Reactions for Poly(Alkylene Oxides) and Polymeric Poly(Carboxylic Acids). *Ind. Eng. Chem. Res.* **1959**, *51*, 1361–1364.

(64) Liu, D.; Zhu, L.; Huang, W.; Yue, K.; Yang, S. Polymer Complex Fiber for Linear Actuation with High Working Density and Stable Catch-State. *ACS Macro. Lett.* **2020**, *9*, 1507–1513.

(65) Wan, A. C. A.; Leong, M. F.; Toh, J. K. C.; Zheng, Y.; Ying, J. Y. Multicomponent Fibers by Multi-Interfacial Polyelectrolyte Complexation. *Adv. Healthc. Mater.* **2012**, *1*, 101–105.

(66) Zou, J.; Kim, F. Self-Assembly of Two-Dimensional Nanosheets Induced by Interfacial Polyionic Complexation. *ACS Nano* **2012**, *6*, 10606–10613.

(67) Wang, F.; Liu, Z.; Wang, B.; Feng, L.; Liu, L.; Lv, F.; Wang, Y.; Wang, S. Multi-Colored Fibers by Self-Assembly of DNA, Histone Proteins, and Cationic Conjugated Polymers. *Angew. Chem., Int. Ed.* **2014**, *53*, 424–428.

(68) Patel, A.; Sant, V.; Velankar, S.; Dutta, M.; Balasubramanian, V.; Sane, P.; Agrawal, V.; Wilson, J.; Rohan, L. C.; Sant, S. Self-Assembly of Multiscale Anisotropic Hydrogels Through Interfacial Polyionic Complexation. *J. Biomed. Mater. Res., Part A* **2020**, *108*, 2504–2518.

(69) Grande, R.; Trovatti, E.; Carvalho, A. J. F.; Gandini, A. Continuous Microfiber Drawing by Interfacial Charge Complexation between Anionic Cellulose Nanofibers and Cationic Chitosan. *J. Mater. Chem. A* **2017**, *5*, 13098–13103.

(70) Zhao, X.; Chen, F.; Li, Y.; Lu, H.; Zhang, N.; Ma, M. Bioinspired Ultra-Stretchable and Anti-Freezing Conductive Hydrogel Fibers with Ordered and Reversible Polymer Chain Alignment. *Nat. Commun.* **2018**, *9*, 3579.

- (71) Grande, R.; Bai, L.; Wang, L.; Xiang, W.; Ikkala, O.; Carvalho, A. J. F.; Rojas, O. J. Nanochitins of Varying Aspect Ratio and Properties of Microfibers Produced by Interfacial Complexation with Seaweed Alginate. *ACS Sustain. Chem. Eng.* **2020**, *8*, 1137–1145.
- (72) Chen, Z.; Mo, X.; He, C.; Wang, H. Intermolecular Interactions in Electrospun Collagen-Chitosan Complex Nanofibers. *Carbohydr. Polym.* **2008**, *72*, 410–418.
- (73) Penchev, H.; Paneva, D.; Manolova, N.; Rashkov, I. Novel Electrospun Nanofibers Composed of Polyelectrolyte Complexes. *Macromol. Rapid Commun.* **2008**, *29*, 677–681.
- (74) Jeong, S. I.; Krebs, M. D.; Bonino, C. A.; Samorezov, J. E.; Khan, S. A.; Alsborg, E. Electrospun Chitosan-Alginate Nanofibers with In Situ Polyelectrolyte Complexation for Use as Tissue Engineering Scaffolds. *Tissue Eng. Pt. A* **2011**, *17*, 59–70.
- (75) Meng, X.; Schiffman, J. D.; Perry, S. L. Electrospinning Cargo-Containing Polyelectrolyte Complex Fibers: Correlating Molecular Interactions to Complex Coacervate Phase Behavior and Fiber Formation. *Macromolecules* **2018**, *51*, 8821–8832.
- (76) Sun, J.; Perry, S. L.; Schiffman, J. D. Electrospinning Nanofibers from Chitosan/Hyaluronic Acid Complex Coacervates. *Biomacromolecules* **2019**, *20*, 4191–4198.
- (77) Meng, X.; Du, Y.; Liu, Y.; Coughlin, E. B.; Perry, S. L.; Schiffman, J. D. Electrospinning Fibers from Oligomeric Complex Coacervates: No Chain Entanglements Needed. *Macromolecules* **2021**, *54*, 5033–5042.
- (78) Onoe, H.; Okitsu, T.; Itou, A.; Kato-Negishi, M.; Gojo, R.; Kiriya, D.; Sato, K.; Miura, S.; Iwanaga, S.; Kuribayashi-Shigetomi, K.; Matsunaga, Y. T.; Shimoyama, Y.; Takeuchi, S. Metre-Long Cell-Laden Microfibres Exhibit Tissue Morphologies and Functions. *Nat. Mater.* **2013**, *12*, 584–590.
- (79) Yamada, M.; Utoh, R.; Ohashi, K.; Tatsumi, K.; Yamato, M.; Okano, T.; Seki, M. Controlled Formation of Heterotypic Hepatic Micro-Organoids in Anisotropic Hydrogel Microfibers for Long-Term Preservation of Liver-Specific Functions. *Biomaterials* **2012**, *33*, 8304–8315.
- (80) Bidarra, S. J.; Barrias, C. C.; Granja, P. L. Injectable Alginate Hydrogels for Cell Delivery in Tissue Engineering. *Acta Biomater.* **2014**, *10*, 1646–1662.
- (81) Costa-Almeida, R.; Gasperini, L.; Borges, J.; Babo, P. S.; Rodrigues, M. T.; Mano, J. F.; Reis, R. L.; Gomes, M. E. Microengineered Multicomponent Hydrogel Fibers: Combining Polyelectrolyte Complexation and Microfluidics. *ACS Biomater. Sci. Eng.* **2017**, *3*, 1322–1331.
- (82) Liu, H.; Wang, Y.; Chen, W.; Yu, Y.; Jiang, L.; Qin, J. A Microfluidic Strategy to Fabricate Ultra-Thin Polyelectrolyte Hollow Microfibers as 3D Cellular Carriers. *Mater. Sci. Eng. C-Mater.* **2019**, *104*, 109705.
- (83) Robinson, T. M.; Talebian, S.; Foroughi, J.; Yue, Z.; Fay, C. D.; Wallace, G. G. Fabrication of Aligned Biomimetic Gellan Gum-Chitosan Microstructures through 3D Printed Microfluidic Channels and Multiple In Situ Cross-Linking Mechanisms. *ACS Biomater. Sci. Eng.* **2020**, *6*, 3638–3648.
- (84) Huang, W.; Zhu, L.; Liu, D.; Li, J.; Yang, S. Fabrication of Alginate/Chitosan Complex Fibers via Diffusion Controlled In-Situ Polyelectrolyte Complexation. *Carbohydr. Polym. Technol. Appl.* **2021**, *2*, 100030.
- (85) Hufenus, R.; Yan, Y.; Dauner, M.; Kikutani, T. Melt-Spun Fibers for Textile Applications. *Materials* **2020**, *13*, 4298.
- (86) Zhang, K.; Hujaya, S. D.; Järvinen, T.; Li, P.; Kauhanen, T.; Tejesvi, M. V.; Kordas, K.; Liimatainen, H. Interfacial Nanoparticle Complexation of Oppositely Charged Nanocelluloses into Functional Filaments with Conductive, Drug Release, or Antimicrobial Property. *ACS Appl. Mater. Interfaces* **2020**, *12*, 1765–1774.
- (87) Meng, X.; Perry, S. L.; Schiffman, J. D. Complex Coacervation: Chemically Stable Fibers Electrospun from Aqueous Polyelectrolyte Solutions. *ACS Macro. Lett.* **2017**, *6*, 505–511.
- (88) Zhang, P.; Tian, R.; Na, B.; Lv, R.; Liu, Q. Intermolecular Ordering as the Precursor for Stereocomplex Formation in the Electrospun Poly(lactide) Fibers. *Polymer* **2015**, *60*, 221–227.
- (89) Yoon, J.; Yang, H. S.; Lee, B. S.; Yu, W. R. Recent Progress in Coaxial Electrospinning: New Parameters, Various Structures, and Wide Applications. *Adv. Mater.* **2018**, *30*, 1704765.
- (90) Squires, T. M.; Quake, S. R. Microfluidics: Fluid Physics at the Nanoliter Scale. *Rev. Mod. Phys.* **2005**, *77*, 977–1026.
- (91) Du, X. Y.; Li, Q.; Wu, G.; Chen, S. Multifunctional Micro/Nanoscale Fibers Based on Microfluidic Spinning Technology. *Adv. Mater.* **2019**, *31*, 1903733.
- (92) Liu, H.; Wang, Y. Q.; Yu, Y.; Chen, W. W.; Jiang, L.; Qin, J. H. Simple Fabrication of Inner Chitosan-Coated Alginate Hollow Microfiber with Higher Stability. *J. Biomed. Mater. Res. B* **2019**, *107*, 2527–2536.
- (93) Su, J.; Zheng, Y.; Wu, H. Generation of Alginate Microfibers with a Roller-Assisted Microfluidic System. *Lab Chip* **2009**, *9*, 996–1001.
- (94) Shin, S.; Park, J. Y.; Lee, J. Y.; Park, H.; Park, Y. D.; Lee, K. B.; Whang, C. M.; Lee, S. H. On the fly" Continuous Generation of Alginate Fibers Using a Microfluidic Device. *Langmuir* **2007**, *23*, 9104–9108.
- (95) Lee, K. Y.; Mooney, D. J. Alginate: Properties and Biomedical Applications. *Prog. Polym. Sci.* **2012**, *37*, 106–126.
- (96) Sugiura, S.; Oda, T.; Aoyagi, Y.; Satake, M.; Ohkohchi, N.; Nakajima, M. Tubular Gel Fabrication and Cell Encapsulation in Laminar Flow Stream Formed by Microfabricated Nozzle Array. *Lab Chip* **2008**, *8*, 1255–1257.
- (97) Du, X. Y.; Li, Q.; Wu, G.; Chen, S. Multifunctional Micro/Nanoscale Fibers Based on Microfluidic Spinning Technology. *Adv. Mater.* **2019**, *31*, 3122–3130.
- (98) Stoyanova, N.; Mincheva, R.; Paneva, D.; Manolova, N.; Dubois, P.; Rashkov, I. Electrospun Non-Woven Mats from Stereocomplex between High Molar Mass Poly(L-Lactide) and Poly(D-Lactide)-Block-Poly(Butylene Succinate) Copoly(Ester Urethane)s. *Eur. Polym. J.* **2012**, *48*, 1965–1975.
- (99) Zhu, M.; Wang, W.; Zhang, C.; Zhu, L.; Yang, S. Photo-Responsive Behaviors of Hydrogen-Bonded Polymer Complex Fibers Containing Azobenzene Functional Groups. *Adv. Fiber Mater.* **2021**, *3*, 172–179.
- (100) Ding, H.; Wu, Z.; Wang, H.; Zhou, Z.; Wei, Y.; Tao, K.; Xie, X.; Wu, J. An Ultrasretchable, High-Performance, and Crosstalk-Free Proximity and Pressure Bimodal Sensor Based on Ionic Hydrogel Fibers for Human-Machine Interfaces. *Mater. Horiz.* **2022**, *9*, 1935–1946.
- (101) Xiao, Y.; Xie, F.; Luo, H.; Tang, R.; Hou, J. Electrospinning SA@PVDF-HFP Core-Shell Nanofibers Based on a Visual Light Transmission Response to Alcohol for Intelligent Packaging. *ACS Appl. Mater. Interfaces* **2022**, *14*, 8437–8447.
- (102) Wemyss, A. M.; Bowen, C.; Plesse, C.; Vancaeyzeele, C.; Nguyen, G. T. M.; Vidal, F.; Wan, C. Dynamic Crosslinked Rubbers for a Green Future: A Material Perspective. *Mater. Sci. Eng. R.* **2020**, *141*, 100561.
- (103) Stuart, M. A. C.; Huck, W. T. S.; Genzer, J.; Mueller, M.; Ober, C.; Stamm, M.; Sukhorukov, G. B.; Szleifer, I.; Tsukruk, V. V.; Urban, M.; Winnik, F.; Zauscher, S.; Luzinov, I.; Minko, S. Emerging Applications of Stimuli-Responsive Polymer Materials. *Nat. Mater.* **2010**, *9*, 101–113.
- (104) Michaels, A. S. Polyelectrolyte Complexes. *Ind. Eng. Chem.* **1965**, *57*, 32–40.
- (105) Huang, W.; Li, J.; Liu, D.; Tan, S.; Zhang, P.; Zhu, L.; Yang, S. Polyelectrolyte Complex Fiber of Alginate and Poly-(Diallyldimethylammonium Chloride): Humidity-Induced Shape Memory and Mechanical Transition. *ACS Appl. Polym. Mater.* **2020**, *2*, 2119–2125.
- (106) Liu, D.; Zhu, L.; Huang, W.; Yang, S. Humidity Induced Relaxation Transition of Hydrogen-Bonded Complex Fibers. *Polymer* **2021**, *225*, 123794.
- (107) Boas, M.; Gradys, A.; Vasilyev, G.; Burman, M.; Zussman, E. Electrospinning Polyelectrolyte Complexes: pH-Responsive Fibers. *Soft Matter* **2015**, *11*, 1739–1747.

- (108) Huang, W. M.; Ding, Z.; Wang, C. C.; Wei, J.; Zhao, Y.; Purnawali, H. Shape Memory Materials. *Mater. Today* **2010**, *13*, 54–61.
- (109) Lendlein, A.; Jiang, H. Y.; Junger, O.; Langer, R. Light-Induced Shape-Memory Polymers. *Nature* **2005**, *434*, 879–882.
- (110) Liu, C.; Qin, H.; Mather, P. T. Review of Progress in Shape-Memory Polymers. *J. Mater. Chem.* **2007**, *17*, 1543–1558.
- (111) Liu, D. Z.; Yang, S. G. Preparation and Properties Modulation of Multi-Component Polymer Complex Fibers. *Acta. Polym. Sin.* **2021**, *52*, 1353–1360.
- (112) Taylor, D. L.; in het Panhuis, M. Self-Healing Hydrogels. *Adv. Mater.* **2016**, *28*, 9060–9093.
- (113) Li, J.; Sun, J.; Wu, D.; Huang, W.; Zhu, M.; Reichmanis, E.; Yang, S. Functionalization-Directed Stabilization of Hydrogen-Bonded Polymer Complex Fibers: Elasticity and Conductivity. *Adv. Fiber Mater.* **2019**, *1*, 71–81.
- (114) Xue, W.; Liu, B.; Zhang, H.; Ryu, S.; Kuss, M.; Shukla, D.; Hu, G.; Shi, W.; Jiang, X.; Lei, Y.; Duan, B. Controllable Fabrication of Alginate/Poly-L-Ornithine Polyelectrolyte Complex Hydrogel Networks as Therapeutic Drug and Cell Carriers. *Acta Biomater* **2022**, *138*, 182–192.
- (115) Mozhdzhi, D.; Ayala, S.; Cromwell, O. R.; Guan, Z. Self-Healing Multiphase Polymers via Dynamic Metal-Ligand Interactions. *J. Am. Chem. Soc.* **2014**, *136*, 16128–16131.
- (116) Wang, J.; Sun, S.; Wu, B.; Hou, L.; Ding, P.; Guo, X.; Cohen Stuart, M. A.; Wang, J. Processable and Luminescent Supramolecular Hydrogels from Complex Coacervation of Polycations with Lanthanide Coordination Polyanions. *Macromolecules* **2019**, *52*, 8643–8650.
- (117) Li, Z.; Zhu, Y. L.; Niu, W.; Yang, X.; Jiang, Z.; Lu, Z. Y.; Liu, X.; Sun, J. Healable and Recyclable Elastomers with Record-High Mechanical Robustness, Unprecedented Crack Tolerance, and Superhigh Elastic Restorability. *Adv. Mater.* **2021**, *33*, 2101498.
- (118) Li, J.; Li, S.; Huang, J.; Khan, A. Q.; An, B.; Zhou, X.; Liu, Z.; Zhu, M. Spider Silk-Inspired Artificial Fibers. *Adv. Sci.* **2022**, *9*, 2103965.
- (119) Ma, W.; Ling, S.; Zhang, J.; Chen, Z.; Xu, J. Microfluidic Fabrication of Calcium Alginate Helical Microfibers for Highly Stretchable Wound Dressing. *J. Polym. Sci.* **2022**, *60*, 1741–1749.
- (120) Xiao, L.; Ou, C.; Zhang, D.; Ma, Y.; Xu, Z.; Zhou, Y.; Jiang, H. Strong Tough Poly Acrylic-Co-Acrylamide Hydrogels via a Synergistic Effect of Fiber and Metal-Ligand Bonds as Flexible Strain Sensors. *Macromol. Mater. Eng.* **2022**, *307*, 2200389.
- (121) Park, S.; Yuk, H.; Zhao, R.; Yim, Y. S.; Woldegebriel, E. W.; Kang, J.; Canales, A.; Fink, Y.; Choi, G. B.; Zhao, X.; Anikeeva, P. Adaptive and Multifunctional Hydrogel Hybrid Probes for Long-Term Sensing and Modulation of Neural Activity. *Nat. Commun.* **2021**, *12*, 3435.
- (122) Razdan, S.; Patra, P. K.; Kar, S.; Ci, L.; Vajtai, R.; Kucovecz, A.; Konya, Z.; Kiricsi, I.; Ajayan, P. M. Ionically Self-Assembled Polyelectrolyte-Based Carbon Nanotube Fibers. *Chem. Mater.* **2009**, *21*, 3062–3071.
- (123) Li, J.; Huang, W.; Liu, D.; Sun, J.; Zhu, L.; Wang, Y.; Yang, S. Formation and Reduction of Hydrogen-Bonded Graphene Oxide-Poly(Ethylene Oxide) Complex Fiber. *Mater. Today Commun.* **2019**, *19*, 425–432.
- (124) Gholamirad, F.; Taheri-Qazvini, N. Three-Dimensional Porous $Ti_3C_2T_x$ MXene-Based Hybrids Formed by Charge-Driven Assembly. *Chem. Mater.* **2021**, *33*, 9560–9570.
- (125) Nasrollahzadeh, M.; Sajjadi, M.; Iravani, S.; Varma, R. S. Starch, Cellulose, Pectin, Gum, Alginate, Chitin and Chitosan Derived (Nano) Materials for Sustainable Water Treatment: A Review. *Carbohydr. Polym.* **2021**, *251*, 116986.
- (126) Cui, Q.; Bell, D. J.; Rauer, S. B.; Wessling, M. Wet-Spinning of Biocompatible Core-Shell Polyelectrolyte Complex Fibers for Tissue Engineering. *Adv. Mater. Interfaces.* **2020**, *7*, 2000849.
- (127) Do, M.; Im, B. G.; Park, J. P.; Jang, J. H.; Lee, H. Functional Polysaccharide Sutures Prepared by Wet Fusion of Interfacial Polyelectrolyte Complexation Fibers. *Adv. Funct. Mater.* **2017**, *27*, 1702017.
- (128) Chen, Z.; Song, J.; Xia, Y.; Jiang, Y.; Murillo, L. L.; Tsigkou, O.; Wang, T.; Li, Y. High Strength and Strain Alginate Fibers by a Novel Wheel Spinning Technique for Knitting Stretchable and Biocompatible Wound-Care Materials. *Mater. Sci. Eng. C-Mater.* **2021**, *127*, 112204.
- (129) Riaz, S.; Rehman, A.; Ashraf, M.; Hussain, T.; Hussain, M. T. Development of Functional Alginate Fibers for Medical Applications. *J. Text. I.* **2017**, *108*, 2197–2204.
- (130) Lin, Y.; Wen, S.; Peng, X.; Cai, Y.; Geng, L.; Chen, B. Interfacial Polyelectrolyte Complexation Spinning of Graphene/Cellulose Nanofibrils for Fiber-Shaped Electrodes. *J. Mater. Res.* **2020**, *35*, 122–131.
- (131) Yang, Z.; Deng, J.; Chen, X.; Ren, J.; Peng, H. A Highly Stretchable, Fiber-Shaped Supercapacitor. *Angew. Chem., Int. Ed.* **2013**, *52*, 13453–13457.
- (132) Gao, L.; Surjadi, J. U.; Cao, K.; Zhang, H.; Li, P.; Xu, S.; Jiang, C.; Song, J.; Sun, D.; Lu, Y. Flexible Fiber-Shaped Supercapacitor Based on Nickel Cobalt Double Hydroxide and Pen Ink Electrodes on Metallized Carbon Fiber. *ACS Appl. Mater. Inter.* **2017**, *9*, 5409–5418.
- (133) Yu, J.; Lu, W.; Smith, J. P.; Booksh, K. S.; Meng, L.; Huang, Y.; Li, Q.; Byun, J. H.; Oh, Y.; Yan, Y.; Chou, T. W. A High Performance Stretchable Asymmetric Fiber-Shaped Supercapacitor with a Core-Sheath Helical Structure. *Adv. Energy Mater.* **2017**, *7*, 1600976.
- (134) Pu, X.; Li, L.; Liu, M.; Jiang, C.; Du, C.; Zhao, Z.; Hu, W.; Wang, Z. L. Wearable Self-Charging Power Textile Based on Flexible Yarn Supercapacitors and Fabric Nanogenerators. *Adv. Mater.* **2016**, *28*, 98–105.
- (135) Qu, G.; Cheng, J.; Li, X.; Yuan, D.; Chen, P.; Chen, X.; Wang, B.; Peng, H. A Fiber Supercapacitor with High Energy Density Based on Hollow Graphene/Conducting Polymer Fiber Electrode. *Adv. Mater.* **2016**, *28*, 3646–3652.
- (136) Xu, P.; Kang, J.; Choi, J. B.; Suhr, J.; Yu, J.; Li, F.; Byun, J. H.; Kim, B. S.; Chou, T. W. Laminated Ultrathin Chemical Vapor Deposition Graphene Films Based Stretchable and Transparent High-Rate Supercapacitor. *ACS Nano* **2014**, *8*, 9437–9445.
- (137) Wu, J. K.; Ye, C. C.; Liu, T.; An, Q. F.; Song, Y. H.; Lee, K. R.; Hung, W. S.; Gao, C. J. Synergistic Effects of CNT and GO on Enhancing Mechanical Properties and Separation Performance of Polyelectrolyte Complex Membranes. *Mater. Design* **2017**, *119*, 38–46.
- (138) Geng, L.; Lin, Y.; Chen, S.; Shi, S.; Cai, Y.; Li, L.; Peng, X. Superior Strength and Toughness of Graphene/Chitosan Fibers Reinforced by Interfacial Complexation. *Compos. Sci. Technol.* **2020**, *194*, 108174.
- (139) Zhang, K.; Ketterle, L.; Jarvinen, T.; Hong, S.; Liimatainen, H. Conductive Hybrid Filaments of Carbon Nanotubes, Chitin Nanocrystals and Cellulose Nanofibers Formed by Interfacial Nanoparticle Complexation. *Mater. Design.* **2020**, *191*, 108594.
- (140) Yu, G.; Hu, L.; Vosgueritchian, M.; Wang, H.; Xie, X.; McDonough, J. R.; Cui, X.; Cui, Y.; Bao, Z. Solution-Processed Graphene/MnO₂ Nanostructured Textiles for High-Performance Electrochemical Capacitors. *Nano Lett.* **2011**, *11*, 2905–2911.
- (141) Kou, L.; Huang, T.; Zheng, B.; Han, Y.; Zhao, X.; Gopalsamy, K.; Sun, H.; Gao, C. Coaxial Wet-Spun Yarn Supercapacitors for High-Energy Density and Safe Wearable Electronics. *Nat. Commun.* **2014**, *5*, 3754.
- (142) Sun, G.; Liu, J.; Zhang, X.; Wang, X.; Li, H.; Yu, Y.; Huang, W.; Zhang, H.; Chen, P. Fabrication of Ultralong Hybrid Microfibers from Nanosheets of Reduced Graphene Oxide and Transition-Metal Dichalcogenides and their Application as Supercapacitors. *Angew. Chem., Int. Ed.* **2014**, *53*, 12576–12580.
- (143) Zhang, X.; Zhang, Z.; Zhou, Z. MXene-Based Materials for Electrochemical Energy Storage. *J. Energy Chem.* **2018**, *27*, 73–85.

- (144) Amjadi, M.; Kyung, K. U.; Park, I.; Sitti, M. Stretchable, Skin-Mountable, and Wearable Strain Sensors and Their Potential Applications: A Review. *Adv. Funct. Mater.* **2016**, *26*, 1678–1698.
- (145) Geng, L.; Hu, S.; Cui, M.; Wu, J.; Huang, A.; Shi, S.; Peng, X. Muscle-Inspired Double-Network Hydrogels with Robust Mechanical Property, Biocompatibility and Ionic Conductivity. *Carbohydr. Polym.* **2021**, *262*, 117936.
- (146) Tang, Y.; Cai, Z.; Sun, X.; Chong, C.; Yan, X.; Li, M.; Xu, J. Electrospun Nanofiber-Based Membranes for Water Treatment. *Polymers* **2022**, *14*, 105355.
- (147) Xiao, S.; Luo, X.; Peng, Q.; Deb, H. Effective Removal of Calcium Ions from Simulated Hard Water Using Electrospun Polyelectrolyte Nanofibrous Mats. *Fiber Polym.* **2016**, *17*, 1428–1437.
- (148) Esfahani, A. R.; Zhai, L.; Sadmani, A. H. M. A. Removing Heavy Metals from Landfill Leachate Using Electrospun Polyelectrolyte Fiber Mat-Laminated Ultrafiltration Membrane. *J. Environ. Chem. Eng.* **2021**, *9*, 105355.
- (149) Jing, Y.; Zhang, L.; Huang, R.; Bai, D.; Bai, H.; Zhang, Q.; Fu, Q. Ultrahigh-Performance Electrospun Polylactide Membranes with Excellent Oil/Water Separation Ability via Interfacial Stereocomplex Crystallization. *J. Mater. Chem. A* **2017**, *5*, 19729–19737.
- (150) Deng, Y. F.; Zhang, N.; Huang, T.; Lei, Y. Z.; Wang, Y. Constructing Tubular/Porous Structures toward Highly Efficient Oil/Water Separation in Electrospun Stereocomplex Polylactide Fibers via Coaxial Electrospinning Technology. *Appl. Surf. Sci.* **2022**, *573*, 151619.
- (151) Cutiongco, M. F. A.; Choo, R. K. T.; Shen, N. J. X.; Chua, B. M. X.; Sju, E.; Choo, A. W. L.; Le Visage, C.; Yim, E. K. F. Composite Scaffold of Poly(Vinyl Alcohol) and Interfacial Polyelectrolyte Complexation Fibers for Controlled Biomolecule Delivery. *Front. Bioeng. Biotechnol.* **2015**, *3*, 33.
- (152) Ma, G.; Wang, Z.; Chen, J.; Yin, R.; Chen, B.; Nie, J. Freeze-Dried Chitosan-Sodium Hyaluronate Polyelectrolyte Complex Fibers as Tissue Engineering Scaffolds. *New J. Chem.* **2014**, *38*, 1211–1217.
- (153) Wan, A. C. A.; Tai, B. C. U.; Leck, K. J.; Ying, J. Y. Silica-Incorporated Polyelectrolyte-Complex Fibers as Tissue-Engineering Scaffolds. *Adv. Mater.* **2006**, *18*, 641–644.
- (154) Gao, H.; Zhong, Z.; Xia, H.; Hu, Q.; Ye, Q.; Wang, Y.; Chen, L.; Du, Y.; Shi, X.; Zhang, L. Construction of Cellulose Nanofibers/Quaternized Chitin/Organic Rectorite Composites and Their Application as Wound Dressing Materials. *Biomater. Sci.* **2019**, *7*, 2571–2581.
- (155) Lv, X.; Liu, Y.; Song, S.; Tong, C.; Shi, X.; Zhao, Y.; Zhang, J.; Hou, M. Influence of Chitosan Oligosaccharide on the Gelling and Wound Healing Properties of Injectable Hydrogels Based on Carboxymethyl Chitosan/Alginate Polyelectrolyte Complexes. *Carbohydr. Polym.* **2019**, *205*, 312–321.
- (156) Liao, I. C.; Wan, A. C. A.; Yim, E. K. F.; Leong, K. W. Controlled Release from Fibers of Polyelectrolyte Complexes. *J. Controlled Release* **2005**, *104*, 347–358.
- (157) Utagawa, Y.; Ino, K.; Kumagai, T.; Hiramoto, K.; Takinoue, M.; Nashimoto, Y.; Shiku, H. Electrochemical Glue for Binding Chitosan-Alginate Hydrogel Fibers for Cell Culture. *Micromachines* **2022**, *13*, 420.
- (158) Mokhena, T. C.; Luyt, A. S. Electrospun Alginate Nanofibres Impregnated with Silver Nanoparticles: Preparation, Morphology and Antibacterial Properties. *Carbohydr. Polym.* **2017**, *165*, 304–312.
- (159) Elkhoury, K.; Morsink, M.; Sanchez-Gonzalez, L.; Kahn, C.; Tamayol, A.; Arab-Tehrany, E. Biofabrication of Natural Hydrogels for Cardiac, Neural, and Bone Tissue Engineering Applications. *Bioact. Mater.* **2021**, *6*, 3904–3923.
- (160) Sun, Y.; Zhang, Z.; Cheng, L.; Zhang, X.; Liu, Y.; Zhang, R.; Weng, P.; Wu, Z. Polysaccharides Confer Benefits in Immune Regulation and Multiple Sclerosis by Interacting with Gut Microbiota. *Food Res. Int.* **2021**, *149*, 110675.
- (161) Tummalapalli, M.; Anjum, S.; Kumari, S.; Gupta, B. Antimicrobial Surgical Sutures: Recent Developments and Strategies. *Polym. Rev.* **2016**, *56*, 607–630.
- (162) Goh, Y. F.; Shakir, I.; Hussain, R. Electrospun Fibers for Tissue Engineering, Drug Delivery, and Wound Dressing. *J. Mater. Sci.* **2013**, *48*, 3027–3054.
- (163) Lu, Y.; Huang, J.; Yu, G.; Cardenas, R.; Wei, S.; Wujcik, E. K.; Guo, Z. Coaxial Electrospun Fibers: Applications in Drug Delivery and Tissue Engineering. *Wires. Nanomed. Nanobi.* **2016**, *8*, 654–677.
- (164) Li, J.; Cha, R.; Mou, K.; Zhao, X.; Long, K.; Luo, H.; Zhou, F.; Jiang, X. Nanocellulose-Based Antibacterial Materials. *Adv. Healthc. Mater.* **2018**, *7*, 1800334.
- (165) Gao, P.; Cha, R.; Luo, H.; Xu, Y.; Zhang, P.; Han, L.; Wang, X.; Zhang, Z.; Jiang, X. Development of Antimicrobial Oxidized Cellulose Film for Active Food Packaging. *Carbohydr. Polym.* **2022**, *278*, 118922.
- (166) Celebioglu, A.; Saporito, A. F.; Uyar, T. Green Electrospinning of Chitosan/Pectin Nanofibrous Films by the Incorporation of Cyclodextrin/Curcumin Inclusion Complexes: pH-Responsive Release and Hydrogel Features. *ACS Sustain. Chem. Eng.* **2022**, *10*, 4758–4769.
- (167) Yuan, J.; Neri, W.; Zakri, C.; Merzeau, P.; Kratz, K.; Lendlein, A.; Poulin, P. Shape Memory Nanocomposite Fibers for Untethered High-Energy Microengines. *Science* **2019**, *365*, 155–158.
- (168) Wang, W.; Xu, X.; Zhang, C.; Huang, H.; Zhu, L.; Yue, K.; Zhu, M.; Yang, S. Skeletal Muscle Fibers Inspired Polymeric Actuator by Assembly of Triblock Polymers. *Adv. Sci.* **2022**, *9*, 2105764.
- (169) Apsite, I.; Salehi, S.; Ionov, L. Materials for Smart Soft Actuator Systems. *Chem. Rev.* **2022**, *122*, 1349–1415.
- (170) Stoychev, G. V.; Ionov, L. Actuating Fibers: Design and Applications. *ACS Appl. Mater. Interfaces* **2016**, *8*, 24281–24294.
- (171) An, Y.; Gao, L.; Wang, T. Graphene Oxide/Alginate Hydrogel Fibers with Hierarchically Arranged Helical Structures for Soft Actuator Application. *ACS Appl. Nano Mater.* **2020**, *3*, 5079–5087.
- (172) Zhu, M.; Wang, W.; Zhang, C.; Zhu, L.; Yang, S. Photo-Responsive Behaviors of Hydrogen-Bonded Polymer Complex Fibers Containing Azobenzene Functional Groups. *Adv. Fiber Mater.* **2021**, *3*, 172–179.
- (173) Tang, J.; Yin, Q.; Qiao, Y.; Wang, T. Shape Morphing of Hydrogels in Alternating Magnetic Field. *ACS Appl. Mater. Interfaces* **2019**, *11*, 21194–21200.
- (174) Zhao, X.; Chen, X.; Yuk, H.; Lin, S.; Liu, X.; Parada, G. Soft Materials by Design: Unconventional Polymer Networks Give Extreme Properties. *Chem. Rev.* **2021**, *121*, 4309–4372.
- (175) Choi, S.; Choi, Y.; Kim, J. Anisotropic Hybrid Hydrogels with Superior Mechanical Properties Reminiscent of Tendons or Ligaments. *Adv. Funct. Mater.* **2019**, *29*, 1904342.
- (176) Mredha, M. T. I.; Guo, Y. Z.; Nonoyama, T.; Nakajima, T.; Kurokawa, T.; Gong, J. P. A Facile Method to Fabricate Anisotropic Hydrogels with Perfectly Aligned Hierarchical Fibrous Structures. *Adv. Mater.* **2018**, *30*, 1704937.
- (177) Toivonen, M. S.; Kurki-Suonio, S.; Wagermaier, W.; Hynninen, V.; Hietala, S.; Ikkala, O. Interfacial Polyelectrolyte Complex Spinning of Cellulose Nanofibrils for Advanced Bicomponent Fibers. *Biomacromolecules* **2017**, *18*, 1293–1301.
- (178) Cai, Y.; Geng, L.; Chen, S.; Shi, S.; Hsiao, B. S.; Peng, X. Hierarchical Assembly of Nanocellulose into Filaments by Flow-Assisted Alignment and Interfacial Complexation: Conquering the Conflicts between Strength and Toughness. *ACS Appl. Mater. Inter.* **2020**, *12*, 32090–32098.
- (179) Zhang, K.; Liimatainen, H. Hierarchical Assembly of Nanocellulose-Based Filaments by Interfacial Complexation. *Small* **2018**, *14*, 1801937.
- (180) Bach, J. S.; Detrez, F.; Cherkaoui, M.; Cantournet, S.; Ku, D. N.; Corté, L. Hydrogel Fibers for ACL Prosthesis: Design and Mechanical Evaluation of PVA and PVA/UHMWPE Fiber Constructs. *J. Biomech.* **2013**, *46*, 1463–1470.
- (181) Chae, S. K.; Kang, E.; Khademhosseini, A.; Lee, S. H. Micro/Nanometer-Scale Fiber with Highly Ordered Structures by Mimicking the Spinning Process of Silkworm. *Adv. Mater.* **2013**, *25*, 3071–3078.