Natural Biopolymers for Flexible Sensing and Energy Devices

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Abstract  Natural biopolymers feature natural abundance, diverse chemical compositions, tunable properties, easy processability, excellent biocompatibility and biodegradability, as well as nontoxicity, providing new opportunities for the development of flexible sensing and energy devices. Generally, biopolymers are utilized as the passive and active building blocks to endow the flexible devices with mechanical robustness and good biocompatibility. This review aims to provide a comprehensive review on natural biopolymer-based sensing and energy devices. The diverse structures and fabrication processes of three typical biopolymers, including silk, cellulose, and chitin/chitosan, are presented. We review their utilities as the supporting substrates/matrix, active middle layers, separators, electrolytes, and active components of flexible sensing devices (sensors, actuators, transistors) and energy devices (batteries, supercapacitors, triboelectric nanogenerators). Finally, the remaining challenges and future research opportunities are discussed.

Keywords  Biopolymers; Silk; Cellulose; Electronics; Energy devices

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INTRODUCTION

In recent years, flexible sensing devices have attracted extensive attention, which contribute to the rapid development of wearable sensors, smart textiles, flexible displays, electronic skins, and medical devices [1–4]. For example, wearable sensor systems have been explored widely for continuous, noninvasive, long-term and accurate monitoring of human motions and physiological signals, providing clinical information for diagnosis and prevention of diseases, as well as rehabilitation therapy [5–9]. Typically, electronic devices are composed of flexible substrates, which are dominated by the traditional petro-materials-derived polymers, and active materials, including carbon materials [4,10,11], metals and metal oxides [12–14], semiconductors [15], and conducting polymers [16]. It is undeniable that these materials have significantly advanced the development of flexible devices. However, they are inevitably suffering from the high-cost, nonrenewable nature, and potential environmental pollution, impeding the further application of flexible sensing devices to some extent. Thus, harnessing and designing suitable materials as the key components of electronic devices is beneficial to simplifying the fabrication processes, reducing the cost, and improving the performance of electronics.

Consequently, there is an urgent need for the development of flexible energy devices, such as batteries, supercapacitors, and solar cells, which can power the electronic devices, and are capable of accommodating the deformation as their performances retain [17]. Conventional energy conversion and storage devices, including lithium-ion batteries (LIBs) and supercapacitors, are stiff and rigid because of their used materials, configurations and fabrication processes, which do not meet the new demand of flexible electronics. To fabricate flexible energy devices, all of the key components, including electrodes and separator/electrolyte, should have good mechanical flexibility. Currently, flexible polymers [18,19], carbon materials [20–24], metal-based materials [25], and other functional components [26–29] have found wide applications in designing and constructing flexible energy devices. Similarly, there still exists essential needs for energy devices that are low-cost, light-weight, naturally biocompatible, easy fabrication, high-performance and environmentally friendly. Hence, it is indispensable to rationally design and optimize the selected materials, as well as the device structures, to endow the energy devices with high performance.

Biopolymers, known as bio-based materials, are generally produced from raw materials through biosynthesis, bioprocessing, and chemical processes. Biopolymers include natural biopolymers and synthetic biopolymers. The biopolymers introduced in this review refer to natural biopolymers, especially silks, cellulose and chitin/chitosan. These natural biopolymers are chain-like molecules produced from the natur-
ally renewable resources, which generally contain repetitive units, such as proteins (silks), polysaccharides (cellulose and chitin), nucleic acids, and so on. Biopolymers are known for their natural abundance, unique structures, good mechanical properties, renewability, excellent biocompatibility and biodegradability, low cost, light weight and nontoxicity. Additionally, varieties of chemical compositions and reactive groups offer great opportunities to elaborately tailor the structures and functionalities. Furthermore, due to the good water solubility, biopolymers can be available processed into various formats (e.g. particles, nanofibers, films, foams, hydrogels, and aerogels) and further integrated with diverse functional materials, providing reliable building blocks for the production of multifunctional materials. Recently, a facile and scalable pyrolysis strategy has been demonstrated to prepare conductive carbon materials with intrinsically hierarchical structures, which is opening up a promising route for the fabrication of sensing and energy devices. Based on these unique structures and biological properties, biopolymers have been used as the flexible molds, substrates, separators, electrolytes, active materials for the wide application of medical devices, flexible sensing and energy devices. Due to the soaring interest in biopolymers, several reviews have been reported to present the progress of natural and synthetic biopolymers for applications in sensors, electronics, medical applications and energy devices. For example, Sun et al. reviewed the recent progress of flexible sensors based on natural and chemical-synthesized biomaterials. By contrast, we are aiming to provide a comprehensive review on the unique structures and properties of typical natural biopolymers, and the corresponding diverse applications in flexible devices, such as sensors, actuators, transistors, optical devices, batteries, supercapacitors and triboelectric nanogenerators. We first introduce the development of flexible sensing and energy devices, as well as the properties and applications of biopolymers. Then, three typical kinds of biopolymers (silks, cellulose, and chitin/chitosan) are highlighted. Their structures, properties and preparation strategies are briefly reviewed. Third, a detailed review of flexible sensing and energy devices based on biopolymers, where the biopolymers act as the flexible templates, substrates or packaging materials, separators/electrolytes, and active components, is presented. Finally, we proposed and discussed the remaining challenges and opportunities in this field.

### STRUCTURES AND PROPERTIES OF BIOPOLYMERS

Natural biopolymers are chain-like polymeric materials composed of different repetitive units, including amino acids, glucose and its derivatives. Biopolymers are famous for their unique structures and appealing properties, such as natural abundance, renewability, good biocompatibility and biodegradability, excellent processability, nontoxicity, etc. Additionally, the robust hierarchical structures endow biopolymers with superior mechanical properties and specialized functions. More importantly, natural biomaterials are generally capable of being modified and functionalized through various strategies because of their diverse chemical compositions, multiple reactive sites and unique structural features. Consequently, modification of biopolymers offers a promising chance to design and alter the structures and functionalities for the specialized applications. Therefore, natural biopolymers have greatly promoted the development of drug delivery system, tissue engineering, medical implants, biosensors, wound healing, wearable electronics, and flexible energy devices. In this part, we highlight three representative kinds of biopolymers, including silk, cellulose and chitin/chitosan, to briefly summarize their structures and fabrication processes.

### Silk

Natural silks, mainly spun by spiders, silkworms, and some other insects, are unique fibrous proteins containing highly repetitive amino acid sequences, which are further assembled by noncovalent interactions. Among the diversity of silks, spider dragline silks and silkworm silks are the most intensively studied silk materials, which are renowned for their unrivaled mechanical properties with an extraordinary integration of strength, elongation and toughness, exceeding most of biomaterials and engineering materials. Furthermore, silkworm silks produced by the domesticated *Bombyx mori* have continuously attracted extensive interests in unraveling the fundamental structure-property relationships and exploring the potential applications due to their mass-production, exceptional mechanical properties, biocompatibility and biodegradability.

Generally, the exceptional mechanical properties of silk fibers are considered to benefit from the hierarchical structures derived from the multiscale and highly ordered self-assembly of repetitive core sequences. Normally, as shown in Fig. 1(a), silkworm silks, which are separated from the cocoons, consist of two parallely aligned fibroin fibers and a layer of glue-like sericin coating on the surface of fibroins. Sericin is a kind of water-soluble protein and usually removed through a degumming process to obtain the shiny and resilient silk fibroin fibers. Fibroin fibers, constituting 70%–80% weight of silks, consist of a great deal of polymer-like nanofibrils. These nanofibrils, containing β-sheet crystalites, random coils and α-helices, are assembled by the repetitive sequences of amino acids with the assistance of hydrogen bonds, hydrophobic interactions, and van der Waals forces. Notably, the nanocrystals are confined to a few nanometers, and are highly aligned along the fiber axis, rendering the fascinating mechanical properties of silk fibers. In addition to the intriguing mechanical properties, silk fibers are widely admired for the ideally biocompatible and biodegradable features, and the degradation time of regenerated silk material can be altered, which ranges from several minutes to many years, enabling the development of transient electronics, biomedical and implantable devices. Natural fiber spinning is a miracle to generate silk fibers with exceptional properties under ambient conditions. With the advance in in-depth understanding of spinning mechanisms and structure-property relationships, bioinspired spinning methods, including wet or dry spinning techniques and electrostatic spinning approach, have been designed to produce regenerated silk fibers and composite fibers. Aside from the regenerated fibers, the solution of silk fibrins can serve as the building blocks to be feasibly processed into...
Silkworm cocoon
Cocoon silk
Bundle of silk microfibers
Silk microfibers
Silk nanofiber
Silk nanoribbon
β-crystalline and amorphous structure
Single β-sheet
Fibroin
Serciin

Fig. 1 Structure of natural silk fibers and various formats of silk materials. (a) Hierarchical structure of silk (Reproduced with permission from Ref. [48]; Copyright (2018) American Chemical Society); (b) Scanning electron microscopy (SEM) image of silk particles (Reproduced with permission from Ref. [58]; Copyright (2010) Elsevier); (c) Atomic force microscopy (AFM) image of silk nanofibrils with a height of 3–4 nm (Reproduced with permission from Ref. [59]; Copyright (2014) Wiley); (d) SEM image of electrospun silk fibroin nanofibers (Reproduced with permission from Ref. [55]; Copyright (2016) Springer); (e) Regenerated silk fibers with false color produced by a bioinspired spinning strategy, Scale: 20 μm (Reproduced with permission from Ref. [60]; Copyright (2017) Nature); (f) A free-standing silk nanoﬁber ﬁlm with a thickness about 520 nm (Reproduced with permission from Ref. [61]; Copyright (2016) American Chemical Society); (g) Highly elastic silk hydrogel (Reproduced with permission from Ref. [62]; Copyright (2014) Wiley).

Various material formats, such as micro/nanoparticles, nanofibers, films, foams, hydrogels, aerogels (Figs. 1b–1g). [58–63] Also, the impressive processability of fibroin is opening up new prospects for fabrication of multifunctional silk-based materials through combining fibroin solution with functional nanomaterials, leading to the further extension of their potential applications. Alternatively, the elaborate modification of original silk fibroin fibers can enhance the intrinsic properties or confer new functionalities to fibers. Surface modification is a simple and feasible approach to introducing functional materials onto the silk fibers, including nanoparticles (NPs), [64] carbon nanomaterials, [65,66] and conducting polymers, [67] providing good electrical conductivity, thermal conductivity, antibacterial property, or ﬂuorescence. Besides, due to the existing bioactive sites on the side chains of amino acid, the chemical modiﬁcation of silk proteins, such as the coupling reaction and grafting reaction, provides a promising avenue to prepare the optimized silk-based materials. [68]

Recently, the strategy of feeding silkworms with functional diets becomes fascinating because of its in situ functionalization and large-scale production. These materials, including organic dyes, [69] NPs, [70,71] carbon nanotubes (CNTs), [72,73] and graphene, [73] have served as the special diets to feed silkworms and produce colorful or structurally and functionally optimized fibers. In addition to the above modiﬁcation strategies, carbonization process of silk proteins contributes to the formation of poly-hexagonal carbon structures and endows silks with good conductivity. [74] Hence, the emergence of various fabrication strategies provides an opportunity to tailor the structures and optimize the performances of silk-based materials.

Actually, in ancient times, silk fibers were used as the textiles benefiting from their lustrous appearance, ﬂexible and comfortable traits, and light weight. By virtue of its mechanical robustness and biocompatibility, silk ﬁber has emerged as the sutures for many years. [75] More importantly, the inspiring progresses in modiﬁcation and fabrication strategies pave the way to develop functional silk composites and explore the promising applications. Therefore, with the charming features of mass-production, outstanding biocompatibility, solution-processability, as well as controllable and programable degradation, silk has been playing crucial roles in designing and fabricating electronics, optical devices, and energy devices, which will ﬁnd tremendous application in various ﬁelds. [38,63,76]

Cellulose

Cellulose, as the most abundant and ubiquitous polymeric raw material on earth, is an important green and renewable resource with appealing properties, which is widely isolated and extracted from the plants on a large scale, such as wood, cotton, cereal, or generated from bacteria. Normally, natural cotton ﬁbers contain as much as 98% of cellulose, and wood may have various contents of cellulose ranging from 10% to more than 90%, which depend on the types of wood and parts of material. [77,78] Actually, cellulose has been used as the fuels, building materials, ﬁbers for textile and papers since ancient times, [79] which has signiﬁcantly facilitated the development of human civilization. Nowadays, commercial cellulose, mainly derived from wood pulp, serves as the building block to produce regenerated ﬁbers and ﬁlms, and is of paramount signiﬁcance to the production of cellulose derivatives, high-value-added chemicals and fuels on an industrial scale. [80]

Cellulose is a linear polysaccharide material consisting of repetitive β-(1,4)-linked D-glucose units. [33] The hydroxyl groups in D-glucose can interact through intrachain and inter-
terchain hydrogen bonds, which promote the formation of linear chains and facilitate the ordered stacking of adjacent chains to form the crystalline regions, respectively.[81] The crystalline regions confer high stiffness to cellulose materials, and are connected by the amorphous-like regions, forming the cellulose chains. These chains assemble into nanofibers (< 35 nm), which are further aligned and bonded together into fibrils (< 1 μm) and fibers (10–50 μm), showing a hierarchical structure (Fig. 2a).[78] Notably, acid hydrolysis of cellulose structure is a feasible route to break the linkages between the disordered regions and crystalline areas, resulting in the liberation of rod-like cellulose nanocrystals (CNCs),[82] as demonstrated in Fig. 2(b). CNCs generally have an acceptable aspect ratio, which is with a length ranging from 50 nm to 500 nm and a width varying from 3 nm to 50 nm,[81,83] as well as a high crystallinity and superior mechanical strength. As another type of common cellulose nanomaterials, cellulose nanofibers (CNFs) are prepared by the strategy of combining mechanical nanofibrillation and chemical modification.[35,41] CNFs can also be produced from the cellulose solution by bottom-up techniques, such as electrospinning method. Compared with CNCs, CNFs containing amorphous and crystalline regions are frequently longer with a length of 50–3000 nm (Fig. 2c),[84] and lower in crystallinity. Alternatively, several bacteria are capable of synthesizing cellulose, which is called bacterial cellulose. Bacterial cellulose is the longest and more chemically pure, and features high crystallinity, along with excellent biocompatibility.[35]

As a renewable and sustainable resource, cellulose has advantages of excellent mechanical property, thermal and structural stability, easy modification, good biocompatibility and biodegradability, and industrial accessibility on a large scale. Besides, to satisfy the needs of diverse applications, cellulose nanomaterials can be used to construct specifically structural materials with different forms, such as fibers, films, papers, aerogels and hydrogels (Figs. 2b–2e).[85–89] Various material formats of cellulose enable the fabrication of flexible electronics and optical devices, which basically serve as the substrates or skeleton supporting materials. In addition, cellulose-based functional composites can be obtained by integrating the cellulose with different functional materials, including metal or metal oxide nanomaterials,[90] carbon nanomaterials,[91] and conducting polymers.[92] The above strategies endow the composites with specific functionalities and make the fabrication of flexible sensors and energy devices possible.[92,93,94] Thus, in terms of its unique structures and excellent properties, cellulose is gaining highly attractive attention to being applied in flexible and wearable electronic devices.

**Chitin/Chitosan**

Chitin is the second most abundant biopolymers after cellulose on earth, serving as the ubiquitous structural components in the exoskeletons of crustaceans or the cell walls of certain fungi.[95] Chitin exists naturally along with proteins and minerals in crustacean shells, and thus the processes involving deproteination, demineralization and decoloration are normally adopted to produce the commercial chitin.[96,97] Alternatively, ionic liquid extraction technique enables the isolation of chitin with high yields, high purity and a high degree of crystallinity.[98] Chitin is also a renewable natural polymer with the extraordinary combination of abundance, excellent biocompatible, admirable biodegradable, and non-toxicity. However, considering the highly crystalline structure, chitin is insoluble in almost all of common solvents,[99] which may hinder the fabrication of

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**Fig. 2** Hierarchical structure, nanomaterials and devise assemblies of cellulose. (a) Structure of wood-derived cellulose (Reprinted with permission from Ref. [78]; Copyright (2013) American Chemical Society); (b) Transmission electron microscopy (TEM) image of cellulose nanocrystals (CNCs) with the width of 10 ± 5 nm (Reprinted with permission from Ref. [82]; Copyright (2016) American Chemical Society); (c) TEM image of cellulose nanofibers (CNFs) showing the width of 2–6 nm (Reprinted with permission from Ref. [84]; Copyright (2014) Wiley); (d) Transparent CNF paper (Reprinted with permission from Ref. [85]; Copyright (2009) Wiley); (e) Ultra-lightweight and highly porous CNC aerogel (Reprinted with permission from Ref. [86]; Copyright (2014) American Chemical Society).
functional materials and the appropriate applications to some extent. Chitosan, as the deacetylated derivative of chitin, not only possesses the favorable biological properties but presents the better solubility, available processability, pH-sensitive feature and highly sophisticated functionality, rendering a wide variety of emerging applications in environmental, biomedical and electrical fields.\textsuperscript{[31,100]}

As a long-chain polysaccharide, chitin consists of the repeated N-acetyl glucosamine units, and contains 6\%—7\% nitrogen.\textsuperscript{[101]} Based on the orientation and stacking of molecular chains, chitin is commonly divided into α-, β- and γ-chitin. The α-chitin, widely found in crab and shrimp shells, arranges in an alternating antiparallel form, while β-chitin, mainly existing in mollusks, has parallel chains.\textsuperscript{[102]} Notably, the antiparallel arrangement in α-chitin endows the chitin with more outstanding stability than β-chitin.\textsuperscript{[103]} Besides, γ-chitin, containing both an antiparallel and parallel structure, can be converted to the stable α-chitin. The above polymorphs can respectively assemble into chitin nanofibers with a diameter of 2—5 nm and a length of about 300 nm, which are wrapped with proteins to further arrange in aligned microfiber bundles.\textsuperscript{[102]} The bundles consequently form into chitin fibers with the hierarchical structure (Fig. 3a).\textsuperscript{[104]} Similar to the strategies of preparing cellulose nanofibers, isolation of chitin nanofibers can be achieved through the mechanical treatment and chemical modification (Fig. 3b).\textsuperscript{[33,102,105]} In addition, strong acid hydrolysis of chitin is able to remove the amorphous regions and release the chitin nanocrystals with high crystallinity and excellent mechanical properties.

By virtue of the reactive groups, chitosan is conferred distinctive features and can act as a specific platform for elaboration modification to impart special properties. In particular, physical modification and chemical grafting of chitosan offer an opportunity to fabricate chitosan materials with specific functionalities.\textsuperscript{[100]} Furthermore, its good aqueous-processability provides a promising avenue to tailor and optimize chitosan materials with desired structures and properties (Fig. 3c).\textsuperscript{[106]} In particular, chitin can be dissolved in several solvents, including ionic liquids, 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), and alkali/urea solvent systems,\textsuperscript{[35]} which offer opportunities to prepare chitin-based materials. For example, Fig. 3(d) shows the transparent and flexible chitin film, which is prepared through a centrifugally casting process of chitin/HFIP solution.\textsuperscript{[107]} Nowadays, various forms of chitin/chitosan-based materials, including nanoparticles, microspheres, membranes, hydrogels, aerogels, and numerous composites, have been prepared to pave the way for the desirable applications (Fig. 3e).\textsuperscript{[108]} Therefore, owing to their abundance, low-cost and versatile biological properties, chitin and chitosan materials are becoming an indispensable natural biopolymer for the fabrication of flexible electronics and other devices.

**BIOPOLYMERS FOR FLEXIBLE SENSING DEVICES**

Electronic devices based on inorganic materials are ubiquitous in a variety of modern technology and have contributed much convenience to our daily life. However, the wide application of electronics is suffering from the generation of electronic waste along with toxic, non-degradable materials. In addition, the novel electronics with flexibility, mechanical robustness and biocompatibility can accommodate the arbitrary surfaces or interfaces with soft biological tissues/organs conformably, making the electronics applicable in human activity monitoring, human-machine interfaces, biomedical diagnosis and therapy.\textsuperscript{[45,38]} Natural biopolymers, including silks, cellulose and chitin/chitosan, have been gradually becoming the attractive building blocks for the fabrication of the next-generation renewable, flexible and biocompatible sensing electronics, such as flexible and wearable sensors, thin film transistors, optoelectronics, due to their earth-abundance, biocompatibility, biodegradability, nontoxicity and light weight.\textsuperscript{[31,35,109—111]} Based on their various structures and appealing properties, biopolymers can generally serve as the flexible structural templates, substrates, active middle layers and functional components of flexible sensing devices. In this section, we mainly pay close attention to the utilization of silks (fibers, films, fabrics, etc.), cellulose (fibers, films, cotton, paper, fabrics, aerogels, wood, etc.), chitin/chitosan (fibers, films, hydrogels, etc.) for flexible sensors, transistors and optical devices. Besides, the common fabrication processes, performances and applications are briefly introduced and summarized.

**Flexible Molds**

Biopolymers have undergone the evolution and optimization over millions of years, which realize the ideal combination of unique structures, specific compositions and functionalities. For example, wood from trees is a natural biopolymer composite, and possesses structural complexity and hierarchy, which endow it with distinct mechanical and functional properties.\textsuperscript{[109]} The 3D architecture and these hierarchical surface inspire researchers to design and prepare the unusual nanomaterials with specific structures and performances, as well as the patterned flexible substrates for sensing devices.\textsuperscript{[31]}

Particularly, the hierarchical micro/nanostructures of plant leaves and flowers make them applicable to act as the structural molds or templates for the preparation of well-ordered substrates. For instance, as shown in Figs. 4(a) and 4(b), Su et al. used mimosa leaves as the molds to produce the flexible polydimethylsiloxane (PDMS) substrates with perpetrator microdomains.\textsuperscript{[112]} The obtained microdomains had the average diameter of 18.4 ± 6.1 μm and average height of 16.1 ± 3.7 μm (Fig. 4b). The substrates were coated with conducting gold layers, and then employed to fabricate the flexible pressure sensors. The external pressure could induce the change of contact spots between top and bottom surfaces, and accordingly contribute to the variation of electrical signals (Fig. 4c). Thus the pressure could be detected by this flexible sensor with high sensitivity. Fig. 4(d) exhibits the sensitivity of pressure sensor within 1.5 kPa, which is 50.17 kPa\textsuperscript{-1} in the low pressure region. However, the workable sensing range was limited. Jian et al. obtained the microstructured PDMS films by directly duplicating plant leaves (Figs. 4e and 4f), and prepared aligned CNFs/graphene hybrid films serving as the electrodes of flexible pressure sensor.\textsuperscript{[113]} As shown in Fig. 4(g), CNFs and graphene form a coalescent network, which has good structural integrity and high conductivity. Besides, the hybrid film could be conformably coated on the PDMS films with uniform hierarchical microstructures. Based on the hybrid films-coating PDMS substrates, flexible pressure sensor could be elegantly designed...
and fabricated. The sensor presented high sensitivity (Fig. 4h), low detection limit, fast respond time and surprising long-term stability, enabling the detection of human movements and acoustic vibrations, and the wide application in future wearable electronics. Xia et al. transferred the fingerprint-like patterned graphene film onto the similar flexible substrates and fabricated high-performance pressure sensors (Fig. 4i). The hierarchically structured PDMS films and patterned graphene films afforded the high sensitivity (130 kPa⁻¹ within 0–0.2 kPa) and wide sensing range (up to 75 kPa) (Fig. 4j). In addition, the sensor could be applied in detecting tiny pressures and human physiological signals (Fig. 4k), demonstrating its great prospects in health monitoring and human/machine interfaces.

Moreover, lotus leaves, banana leaves, and petals of rose have also been chosen as the molds for the preparation of flexible microstructured films, which impart high sensitivity to the sensors. In addition to the plant materials, silk textiles with microstructured surface provide an applicable mold to create the thin micropatterned films, which further serve as the substrate of flexible sensor. It is clearly observed that the strategy of molding the specific structures of biological...
materials is simple, cost-effective and easy for large-scale production of patterned substrates. However, the obtained films are commonly limited by the small sizes and inferior structural uniformity depending heavily on the natural molds, which impedes the mass production and practical application of flexible sensors.

**Flexible Substrates and Packages**

Typically, substrates are the indispensable part of electronic devices, including sensors, displays, transistors, which support functional materials and isolate the adjacent devices. Traditionally, bulk materials such as silicon, sapphire, silicon oxide, germanium, and other rigid materials have served as the substrates for decades. Then flexible polymers and rubbers, including PDMS, polyurethane (PU), poly(ethylene terephthalate) (PET), polyimide (PI), and rubber, have been widely used as the substrates because of their excellent flexibility, acceptable thermal and chemical stability.\[8\] However, these common materials derived from traditional petro-materials are non-biodegradable, nonrenewable, and low biocompatible, which inevitably generate some environmental pollution. As concerns about the electronic waste increase, ideal materials with desirable flexibility, excellent biodegradability and biocompatibility are prevalently regarded as the appropriate candidates to be used as the substrates or packaging materials of novel electronic devices. Apparently, biological polymers are known for their abundance, superior biological properties and versatile functionalization, and have been intensively applied as the biodegradable substrate of electronics, which must play a critical role in reducing the electronic waste and consequent environmental pollution.

Notably, the original biopolymers and their simple products have been used as the flexible substrates to act as the foundation on various functional materials for fabricating high-performance sensing devices. Generally, conductive materials such as CNTs,\[66\] graphene,\[119–121\] other carbon allotropes (including graphite, carbon black),\[122\] conducting polymers,\[123\] metal NPs or nanowires (NWs),\[124\] and their hybrid materials\[125\] have been transferred or deposited onto the surface of biopolymer materials to confer good conductivity and further form flexible sensors, transistors and displays. As mentioned above, silk fibers have found wide ap-
plication in the textile industry for thousand years, which can be woven into diverse fibrous structures, including yarns and fabrics. This has great prospects for manufacturing fiber and textile electronics with traits of flexibility, breathability, comfort and washability. For example, as shown in Fig. 5(a), single silk fiber can be fabricated into a fiber-shaped strain sensor by a facile rod-coating process to coat ultrathin graphite flakes onto the surface of silk fiber. The sensor showed high sensitivity with a gauge factor (GF) of 14.5 within 15% strain (Fig. 5b), and could detect human motions (Fig. 5c). Silk fibers can be easily assembled into yarns, which are mechanically flexible and robust to be further woven into fabrics and textiles. Similarly, silk yarns and textiles are common to combine with conductive components for the fabrication of wearable electronics. Lund and co-workers reported a continuous dyeing process to convert a commercial silk yarn into the conductive one with a high conductivity of 70 S·cm⁻¹.[126,129] The silk yarn was modified by the aqueous ink of conducting polymer, poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS), and was further used to prepare the electronic textiles through textile processes. Alternatively, electronic textiles can be directly obtained by coating or printing functional materials on the surface of silk fabrics.[121,127]

Natural cotton fibers are mainly composed of cellulose, and not only are the important raw materials for textile industry, but play a significant role in everyday life and national economy. Similar to silk fibers, cotton fibers can be processed into yarns, fabrics and textiles, which are the promising building blocks to integrate with active components for the preparation of fiber and textile electronics. Afroj et al. demonstrated a high-speed and highly scalable dyeing technique to modify cotton yarns with graphene-based ink.[119] The electrically conductive yarns had excellent flexibility, and could keep a stable conductivity after cyclic bending and compression, showing great promise for next-generation wearable electronics. In addition, cotton textile was dip-coated with CNTs and then stacked on the patterned Ni-coated fabric to form textile pressure sensor.[128] The hierarchical, porous structure of fabrics offered large surface area, plenty roughness and elasticity to endow the sensor with remarkable sensitivity of 14.4 kPa⁻¹ for pressure below 3.5 kPa. The textile pressure sensors with the good mechanical and cycling stability, fast response, as well as low power consumption, could be able to detect human motions, monitor physiological data, and further fabricate large-scale sensor arrays to spatially map the tactile stimuli.

Paper, made from wood-derived cellulose, is a ubiquitous material and shows easy availability, cost effectiveness, biodegradability, environmental friendliness and light weight, which has been intensively investigated to be used as the flexible support material of electronic devices. Normally, it is essential to convert the insulating paper into conductive substrate with the assistance of various conductive materials. A large variety of modification strategies, such as vacuum filtration, printing (e.g., inkjet printing, screen printing,[129] coating (e.g., dip-coating, spray coating, rod-coating),[120,130] pen-writing,[131] in situ growth and polymerization[132,133] have been proposed to integrate paper with functional materials. Paper has the unique porous structure and distinctive properties (e.g., hydrophilicity, capillary channel and permeability), which make the deposition and immobilization of active components effective, and facilitate the aqueous solutions diffuse without the help of external forces.[132,133] Interestingly, a simple and facile pen-drawing strategy can be used to con-

![Fig. 5 Biopolymers as the substrate of flexible sensing devices.](https://example.com/fig5.png)

- (a) Illustration showing the fabrication process of strain sensors based on the silk fibers and graphite; (b) Relative change in resistance versus strain of the strain sensor, showing the gauge factor of 14.5 within 15% strain; (c) Strain sensor for detecting the joint movements (Reprinted with permission from Ref. [65]; Copyright (2016) American Chemical Society); (d) Schematic illustration for the fabrication of paper sensors with printing carbon ink (Reprinted with permission from Ref. [129]; Copyright (2016) Wiley); (e) Graphene-based pressure sensor based on cellulose paper substrate at different pressures; (f) Pressure sensor for monitoring respiration before and after exercise (Reprinted with permission from Ref. [120]; Copyright (2017) American Chemical Society).
struct highly sensitive strain sensors based on the printing papers.\textsuperscript{[131]} In addition, as exhibited in Fig. 5(d), graphite inks can be directly printed and patterned on the paper, which is used as the moisture sensor on the basis of the hygroscopic character of paper.\textsuperscript{[128]} The flexible sensor was capable of measuring the respiration based on monitoring the change of conductivities induced by the humidity difference between inhalation and exhalation. Various coating techniques have been developed to combine the active materials with papers. Tao and co-workers proposed a paper-based pressure sensor, which was prepared through mixing the paper with graphene oxide (GO) solution and then reducing GO by heating.\textsuperscript{[129]} This flexible sensor presented the optimization of sensitivity and working range, as well as the good stability under different pressures (Fig. 5e), realizing the measurement of human physiological activities, such as the human respiration (Fig. 5f) and motions. In addition to the flexible sensors, flexible light-emitting devices are also constructed on the paper substrates.\textsuperscript{[134]} It is notable that all of the functional layers are successively spray-coated on the papers, endowing the device with high flexibility and light weight. The top-emitting devices feature uniform light emission and good current conversion efficacy. Owing to the hierarchical porous architecture of papers, \textit{in situ} functionalization techniques can bring expanded functionalities to paper substrates, which can be further developed to fabricate paper electronics.\textsuperscript{[133]} To date, Au NPs\textsuperscript{[135]} Ag NPs\textsuperscript{[136]} and ZnO nanorods\textsuperscript{[137]} are respectively prepared on the surface of cellulose fibers, and utilized to realize the fabrication of electrochemiluminescence devices and light-emitting diodes. Thus, with the excellent biological properties, easy availability, low cost, and hierarchical structures, the ubiquitous paper can be integrated with active components with the aid of simple and effective modification techniques, holding a tremendous prospect for the design and fabrication of flexible electronics.

In addition to the natural fibers and their existing products, biopolymers can be processed into regenerated films, which are mainly composed of nanofibers and feature excellent transparency, mechanical robustness, flexibility and thermal stability. The unique biological properties confer these films to be used as the scaffold of implantable devices. For instance, regenerated silk films have been proven to act as the biocompatible and biodegradable substrates or packages for flexible sensing devices, which offer the conformal contact with curved surfaces and biological tissues/organisms for good fidelity, such as skin,\textsuperscript{[138,139]} brain,\textsuperscript{[140,141]} and tooth.\textsuperscript{[142]} Rogers’ group reported the transient electronics containing resistive microheaters and inductive coils, which were supported by the dissolvable silk substrates and were sealed with silk packages.\textsuperscript{[141]} As a consequence, the electronics could offer thermal therapy to serve as a programmable non-antibiotic bactericide. Similarly, transient electronic systems including sensors, actuators, and power supply units can be realized based on the manufacturing strategies. Besides, the regenerated films usually possess good transparency, which contributes to the realization of transparent electronics, such as light-emitting devices. Jin \textit{et al.} introduced a method for producing the chitin nanofiber transparent paper, which was prepared by centrifugal casting of a chitin solution.\textsuperscript{[143]} The chitin-based paper had an excellent optical transparency (91.7% at 550 nm) (Fig. 6a), and served as the biodegradable substrate for flexible organic light-emitting diodes (OLEDs) (Figs. 6b and 6c). Fig. 6(d) shows the current and power efficiency of OLEDs based on chitin nanofiber paper, which are equivalent to those of the counterparts, showing the desirable performance. Moreover, a hybrid material consisting of nanofibrous chitin and silk fibroin was produced by Hong and co-workers.\textsuperscript{[144]} Chitin and silk fibroin were respectively dissolved in the HFIP, and blended with varying compositions. A simple solvent casting of mixed solution could yield transparent and free-standing films. As shown in Fig. 6(e), the hybrid films have high optical transparency (> 90% at 550 nm) and a low haze level (< 1.5%). Benefiting from the excellent biocompatibility, optical transparency and mechanical robustness, the films were demonstrated to be utilized as the contact-lens-based wireless sensor for glucose-monitoring (Fig. 6f), wireless wearable heater and transparent display cover window with superior tribological property, showing the great prospects to serve as the structural platform for advanced electronics.

Cellulose nanofiber papers, namely cellulose nanopaper, also feature fascinating biodegradability, desirable flexibility and good optical transparency, which are made from wood-derived materials.\textsuperscript{[145,146]} Jung and co-workers produced the transparent cellulose nanopapers on the basis of the nanofibers abstracted from wood.\textsuperscript{[147]} Then electronic elements, such as gallium arsenide microwave devices and Si-based digital electronics, were transfer-printed onto the surface of nanopapers. The performance of electronics was comparable to their rigid counterparts, revealing the great potential in large scale integrated circuits with the cellulose nanopapers. High thermal durability is a representative property of nanopapers, which is helpful to obtain high-performance organic thin-film transistors (OTFTs).\textsuperscript{[148]} Importantly, the cellulose nanopapers exhibit much more superior surface morphologies and lower surface roughness than the aforementioned fabrics and papers, which are beneficial to avoiding the unwanted diffusion of deposited molecules. Fujisaki \textit{et al.} reported that the cellulose nanopapers had thermal stability (> 180 °C), and a low coefficient of thermal expansion that was much lower than common plastics.\textsuperscript{[149]} Then, the authors integrated the OTFTs on the cellulose nanopapers, which showed high mobility of about 1 cm\textsuperscript{2}.V\textsuperscript{−1}.s\textsuperscript{−1}, favorable operational and mechanical stability.

Regenerated fibers are the other promising candidate to fabricate fiber-shaped devices and intelligent textiles. Ling \textit{et al.} partially dissolved silk fibers into microfibris to form highly viscous and stable solution, which was then spun into polymorphic silk fibers by a direct extrusion technique.\textsuperscript{[60]} The regenerated silk fibers presented the hierarchical architecture and good mechanical properties. Furthermore, the silks could be coated with CNTs to produce conductive fibers, rendering the application in sensing humidity and temperature. Moreover, electrospinning approach is widely used to prepare nanopapers. As shown in Fig. 6(g), Yin \textit{et al.} proposed an innovative strategy to wrap the electrospun silk nanofiber films around CNTs yarns, which enables the production of silk-sheathed CNT (CNT@Silk) wires.\textsuperscript{[149]} Consequently, the in-
Regenerated biopolymer materials as the supporting materials of flexible devices. (a) Digital photograph of as-casted transparent chitin nanofiber paper (5 inches); (b) Illustration showing the device structure of OLED fabricated on chitin nanofiber paper; (c) OLED based on chitin nanofiber paper showing good flexibility; (d) Current and power efficiency of the flexible OLED supported by a chitin nanofiber paper and a polyethylene naphthalate (PEN) film (Reprinted with permission from Ref. [143]; Copyright (2016) Wiley). (e) As-casted chitin/silk fibroin hybrid film; (f) Schematic illustration of the chitin/silk fibroin hybrid-based contact lens sensor device structure and the glucose sensing mechanism (Reprinted with permission from Ref. [144]; Copyright (2017) Wiley); (g) Schematic illustration demonstrating the fabrication of CNT@Silk wires for wearable textile electronics; (h) Resistance variation of CNT@Silk wire under cyclic bending; (i) CNT@Silk wires for wireless charging in smart clothes (Reprinted with permission from Ref. [149]; Copyright (2018) American Chemical Society).

By virtue of their numerous superiorities, especially the mechanical flexibility and biodegradability, biopolymers have been the common matrix and packaging materials of flexible electronics, including sensors, transistors, actuators, optical devices, intelligent textiles, and so on. In particular, regenerated biopolymer films generally feature high optical transparency, admirable mechanical robustness, favorable surface roughness and small thermal expansion coefficients, thereby facilitating the application in transparent electronics, such as OLEDs, transparent heaters and integrated circuits.

Flexible Active Middle Layers
As an important component of the transistor, the insulating dielectric layer enables the separation of gate electrode and the semiconductor materials, and generates the polarization under an external electrical field. The properties of dielectric material and the interfaces between dielectric layer and active layer play critical roles in the resulting performance of transistors, including the mobility, operating voltage and current leakage. Generally, SiO$_2$ and Al$_2$O$_3$ are the commonly used dielectric materials in transistor due to their cost effect.
iveness and the capacity of improving the mobility and stability of devices. With the advancement of flexible devices, polymeric materials are regarded as the applicable gate dielectric materials because of the preferable flexibility, solution-processability, easy availability, light weight and low cost. Furthermore, given the outstanding biodegradability and biocompatibility, biological materials, such as silk fibroin, cellulose[153] and chitosan,[154] have been processed into the dielectric materials, providing new possibilities for the flexible transistors.

Silk fibroin film with a low surface roughness of 0.3 nm had been used as the gate dielectric and enhanced the performance of pentacene OTFTs.[152] The device displayed very high saturation mobility of 23.2 cm²·V⁻¹·s⁻¹ and low operating voltage of −3 V. The good performance was attributed to the increase of pentacene orthorhombic phase on silk fibroin thin film. Thus silk materials not only enable the flexibility and degradability, but improve the performance of device owing to the unique structure. Moreover, Cunha et al. demonstrated the utilization of cellulose-based hydrogel in electrolyte-gated transistors (EGTs).[153] The cellulose-based hydrogel electrolyte was prepared by dissolving the microcrystalline cellulose in aqueous LiOH/urea solvent systems containing different amounts of carboxymethyl cellulose, serving as the gate dielectric in EGTs. The hydrogel electrolyte showed high specific capacitance and superior ionic conductivity in the range of about 10⁻³ S·cm⁻¹. The flexible transistor based on the paper substrates presented favorable mobility and low operating voltage. Similarly, as demonstrated in Fig. 7(a), chitosan can act as the flexible support material and as the gate dielectric in synaptic transistors.[154] The field-effect mobility of synaptic transistors was estimated to be 13.6 cm²·V⁻¹·s⁻¹, and the good linear output characteristics indicated the formation of ohmic contact between the electrodes and metal probes (Fig. 7b). With the existence of protons in chitosan membrane, an ionic excitatory postsynaptic current could be triggered when a presynaptic spike was applied, demonstrating the similar process in the biological excitatory synapse. Besides, devices with multiple presynaptic inputs were constructed to realize the spiking logic function (Figs. 7c and 7d). The combination of flexible substrates and dielectric materials definitely suggests that the natural biopolymers have vast application prospects in flexible transistors, which enables the excellent biodegradability and the affordable enhancement of performance.

In addition to the transistors, resistive switching memory devices have been gaining great attention on the prospects in high-performance nonvolatile data memory. In principle, a typical resistive switching memory device consists of an active layer sandwiched between two conductive electrodes.[155] With applying an electrical field on the electrodes, the device exhibits the switch between a high resistance state (HRS or OFF-state) and a low resistance state (LRS or ON-state).[156,76] This switching behavior is mainly ascribed to the formation and fracture of conductive filaments, charge transfer, or trap charging and discharging in the middle active layer, and so on.[156,157] Typically, the selection and design of active layers are vital to fabricate high-performance resistive switching memory devices. Natural biopolymers are opening up new routes for the production of structurally flexible and biocompatible resistive-switching memory devices.

Silk fibroin film possesses good mechanical properties and excellent optical transparency, and has bipolar resistive switching behavior.[158] The type of resistive switching devices based on silk fibroin films can be precisely controlled by tailoring the compliance currents, and the memory resistive switching devices and threshold counterparts can be respect-

Fig. 7  Biopolymer materials as the active middle layers in flexible devices. (a) Chitosan membrane supporting the active components and acting as the gate dielectrics for flexible synaptic transistors; (b) Typical output characteristics of free-standing synaptic transistors; (c) Schematic diagram of the artificial synaptic network based on the flexible chitosan membrane; (d) Input-output characteristics of the logic operation (Reprinted with permission from Ref. [154]; Copyright (2015) Wiley); (e) Silk fibroin-based resistive switching memory device sustained by a human hair; (f) Weight of memory devices based on different substrates, and silk memory device showing the ultra-lightweight feature; (g) Typical current versus voltage curve of the silk memory device at ambient condition; (h) Retention characteristics of high and low resistance states (HRS and LRS) under a continuous 100 mV readout voltage (Reprinted with permission from Ref. [160]; Copyright (2016) Wiley).
ively triggered by a higher compliance current and a lower one.\textsuperscript{159} Furthermore, Wang et al. reported the ultra-lightweight resistive switching memory devices, in which the silk protein films served as the support materials and the functional layers.\textsuperscript{160} Benefiting from the light weight and outstanding properties of silks, the device was only 0.4 mg·cm\(^{-2}\), and displayed good mechanical flexibility, high resistance OFF/ON ratio (about 10\(^5\)), and long retention time (more than 10\(^3\) s), showing the prospective application in wearable communication systems, implantable electronics, etc. (Figs. 7e–7h). Cellulose nanopapers and chitosan membranes have also found application in the memory resistive switching devices, which reveal the excellent memory characteristics and other appealing performance.\textsuperscript{161} Hence, considering the superior mechanical and biological properties, natural biopolymers serving as the active middle layers have performed important roles in flexible transistors, resistive switching devices and other devices.

**Flexible Active Materials**

It is noteworthy that the selection and design of substrates, active materials and device structures are vital to develop high-performance flexible sensing devices.\textsuperscript{162} Among them, active materials are the core components of devices, which should be equipped with certain functionalities. For example, the sensing materials are essential to the flexible sensors, which play crucial roles in sensing and transducing the stimuli to detectable signals. To date, various conductive materials, semiconductors, piezoelectric materials and other functional materials have been emerging as the active components of flexible sensing devices.\textsuperscript{163–166} In addition, natural biopolymers are also offering new opportunities to develop naturally functional materials for high-performance devices. The unique chemical compositions of biopolymers enable them to directly serve as the active components. Also, on the basis of diverse active sites and solution processing, biopolymers are able to mix with a variety of functional materials to endow the inherent insulating materials with conductivity, which greatly motivates the exploration and application in flexible electronics. Alternatively, some facile techniques have been proposed to convert biopolymers into conductive materials, such as pyrolysis process and laser irradiation method, which offer the simple and effective routes to fabricate electronics on a large scale.

Natural biopolymers generally possess good hygroscopicity, resulting in the volume change during the water absorption and desorption. For instance, the diameter of silk fibers can increase by about 15\% as the maximum water is absorbed.\textsuperscript{167} This merit enables biopolymers to be a promising candidate for soft actuators. Very recently, Jia et al. demonstrated that water fog and humidity could generate the torsional and tensile actuation of different silk materials, including silk fibers and weave silk textiles (Fig. 8a).\textsuperscript{167} As the water fog was introduced, the silk fiber could produce a fully reversible torsional stroke of 547 (°)·mm\(^{-1}\), while the coiled-and-thermoset silk fibers provided an apparent contraction (Fig. 8b). Detailed characterization and simulation confirmed that the reduction of hydrogen bonds in the silk protein and the structural transformation accounted for the excellent actuation behavior of silk materials. The remarkable properties would open up novel possibilities in smart textiles and soft robotics. In addition, spider silk fibers, aligned CNFs and wet-spin chitosan fibers have been employed to develop the high-performance soft actuators, showing the potential application in novel sensors, smart textiles and green energy devices.\textsuperscript{168–170}

Natural biopolymers are insulating, but can be integrated with ions or conductive materials to confer electrical conductivity.\textsuperscript{171–174} Tong et al. reported a cellulose ionic hydrogel with high stretchability of about 126\% strain and compressibility.\textsuperscript{175} Cellulose was dissolved in NaOH/urea aqueous solution to prepare the allyl cellulose, which then underwent the free radical polymerization to form chemically cross-linked cellulose hydrogel. The ionic hydrogel had good transparency and ionic conductivity of 0.16 mS·cm\(^{-1}\) ascribed to the presence of Na\(^+\) and OH\(^{-}\). Consequently, the hydrogel could be used as reliable and stable strain sensors for the detection of human activities. More importantly, the integration of biopolymers and conductive materials is a general strategy to fabricate functional composites. Due to the feasible aqueous processing, Wang et al. incorporated graphene into silk/Ca\(^{2+}\) solution to produce the self-healable and functional electronic tattoos (Fig. 8c).\textsuperscript{176} As shown in Figs. 8(d) and 8(e), the composites have remarkable self-healing property due to the presence of dynamic hydrogen bonds and coordination bonds. Graphene in the silk matrix provided the conductive paths to sense the strain, humidity, and temperature with high sensitivity, which could be applied in monitoring various physiological signals, such as electrocardiogram (ECG) (Fig. 8f), breathing, and temperature. In addition to carbon nanomaterials, conducting polymers are the other common components to blend with biopolymers for the conductive composites.\textsuperscript{175,176} Han et al. prepared the aerogels consisting of PEDOT:PSS, crosslinking agent and CNFs.\textsuperscript{176} PEDOT: PSS offered the conductivity and thermoelectric property, and the CNFs provided the mechanical strength. Based on the different sensing mechanisms, the aerogels showed the decoupled pressure, temperature gradient and humidity sensing capacity. The pressure was measured by the resistance change, and the temperature could be obtained by the steady thermovoltage because of the electrically conducting PEDOT, and the humidity was detected by the thermovoltage peak ascribed to ionic conducting polymer PSS. Thus the aerogels realized the independent measurement of pressure, temperature gradient and humidity.

In addition to the aforementioned strategies, some facile techniques have been explored to convert biopolymers into conductive carbon materials, such as the pyrolysis process\textsuperscript{177–180} and laser-induced graphitization.\textsuperscript{181–184} Zhang’s group have done leading research on pyrolysis treatment of biopolymers acting as the active components for flexible sensors.\textsuperscript{185–192} For example, as exhibited in Fig. 9(a), the carbonized silk fabric (CSF) with hierarchical structures are used to fabricate the stretchable and highly sensitive strain sensors.\textsuperscript{187} The CSF strain sensor presented excellent mechanical robustness and flexibility (Fig. 9b). Besides, Fig. 9(c) shows the relative resistance change versus the applied strain of CSF strain sensors, and the GF is 9.6 within 250\% strain and 37.5 in the strain range of 250\%–500\%, indicating the strain sensors have high sensitivity in a large sensing range. The CSF
strain sensors could be applicable to be attached on human body for detecting both large and subtle human motions with high sensitivity, such as motion of fingers, motion of knee joint, pulse, respiration, tiny muscle movement and phonation (Fig. 9d). Notably, it is the first time to utilize the carbonized silk fabrics for the construction of high-performance strain sensors, and this strategy can be extended to cotton fabrics,\[190\] modal,\[186, 188\] and silk georgette,\[191\] providing a simple and scalable approach for the production of flexible sensors. In addition, electrospun silk nanofiber membranes have also been processed by the carbonization treatment to impart good conductivity, which have found application in electronic skin (Fig. 9e).\[189\] The carbonized silk nanofiber membranes pressure sensors were prepared based on the silk fibroin-derived active materials, which exhibited light weight, good transparency, unrivaled sensitivity (34.47 kPa\(^{-1}\) within 0.4 kPa), ultralow detection limit (0.8 Pa), fast respond time and excellent durability. Owing to the superior performances, the sensors could measure the human physiological signals, such as wrist pulses, respirations and phonations, motion of fingers (Fig. 9f) and spatial distribution of pressures, holding great potentials in developing cost-effective electronic skins and wearable sensors. The above results reveal the promising prospects of natural biopolymer derived carbon for high-performance flexible sensors.

Moreover, laser irradiation have been reported to convert the polymers and biopolymers into porous patterned graphene, which is known as laser-induced graphene (LIG).\[193\]
Wood and cotton paper with additional fire-retardant treatment can be converted to conductive graphene materials under ambient conditions.\(^1\) Besides, the ultrafast high-photon-energy laser pulses were employed to process natural woods and leaves into the highly conductive graphene in ambient air (Fig. 9g).\(^{184,194}\) By altering the laser powers and writing speeds, the sheet resistances of graphene material were tunable, and the lowest sheet resistance was 10 $\Omega\cdot$sq\(^{-1}\). Furthermore, the simple and scalable process enabled patterned graphene materials to construct electronic components and flexible temperature sensors (Fig. 9h).

Based on the unique compositions and properties, natural biopolymers can be directly used as the active materials for the fabrication of water-driven flexible actuators. Besides, the...
integration of conductive materials endows the biopolymers with good conductivity, which provides more possibilities to construct high-performance electronics. Benefiting from the easy solution-processing and the variety of conductive materials, this is the frequently-used strategy to endow the biopolymers with novel functionalities, which provides great opportunities to produce different types of flexible electronic and realize the utilization in various fields. Alternatively, the simple pyrolysis treatment and laser irradiation process are suitable for the utilization in large-scale fabrication of flexible sensing devices with low cost and eco-friendliness, paving the way for the practical applications.

In summary, because of their abundance, cost effectiveness, aqueous-processability, superior mechanical and biological properties, natural biopolymers have been generating wide interest in the fabrication of flexible devices, such as flexible sensors, actuators, transistors, optical devices, and so on. Notably, biopolymers and their composites can serve as the templates, substrates, active middle layers and/or active materials in various electronics, endowing the devices with high performance. As a consequence, with the burgeoning advancements, the biopolymer-based sensing devices will pave the way for the practical application in wearable sensors, electronic skins and biomedical diagnosis.

**BIOPOLYMERS FOR FLEXIBLE ENERGY DEVICES**

As mentioned above, natural biopolymers have been contributing to the rapid development of flexible electronics, which may accelerate the production of portable, attachable, lightweight and wearable electronic products. Obviously, power supply devices are an indispensable component to provide the energy for these electronics. However, the traditional energy devices, such as LIBs and supercapacitors, are too stiff and bulky to satisfy the new and special demands of flexible electronics. Hence, increasing demands have attracted tremendous scientific and commercial attention to developing the state-of-the-art energy devices with mechanical flexibility, good performance, light weight, low cost, and environmental friendliness. To date, numerous materials have served as the important parts of energy conversion and storage devices. Among them, natural biopolymers have been playing noticeable roles in the fabrication of flexible energy devices, providing novel and effective strategies to endow devices with mechanical robustness, high performance, biocompatibility, sustainability, cost effectiveness, and production on a large scale. Because of the various structures and properties, biopolymers are capable of acting as the substrates, electrolytes, separators and electrodes of energy devices. In this part, we review the recent progresses of biopolymer-based energy devices, such as electrochemical batteries, supercapacitors, solar cells and nanogenerators.

**Flexible Substrates**

Similar to the role of substrates for sensing devices, various flexible materials have served as the substrates of energy devices generally to provide the mechanical robustness and support the active components. In term of the diverse structures and superior biological properties, both untreated biopolymers and regenerated materials can be utilized as the scaffolds to integrate with active materials for energy devices.

The existing biopolymer fibers, yarns and textiles are easily available in our everyday life and have excellent mechanical flexibility, light weight and high surface area, providing economical and effective strategies for the large-scale production of energy conversion and storage systems. Generally, carbon materials, conducting polymers, metallic materials and other functional materials have physically or chemically modified the surface of fibers, yarns or textiles, especially silk, cotton and paper, making them suitable for the utilization in energy devices, such as supercapacitors and batteries. The common modification techniques include dip-coating, rod or blade coating, spray coating, screen printing, vacuum filtration, in situ growth and polymerization, and so on. Besides, a polymer-assisted metal deposition (PAMD) strategy has been proposed to realize the solution-based metal deposition, which enables the formation of different metal-modified yarns or fabrics.

Fiber-shaped energy devices have aroused soaring interest due to their intrinsic flexibility and knittability, showing the great potentials in wearable electronic systems. Supercapacitor is one of the important energy storage devices and has advantages of high charge-discharge rate, high power density, and long cycling stability. Based on the energy storage mechanism, they are typically divided into electric double layer capacitors (EDLC) containing carbon-based material electrodes, and pseudocapacitors, which realize the energy storage by the surface redox reaction of active materials, such as oxides and conducting polymers. Fiber-based supercapacitors can be fabricated successfully by coating silk or cellulose fibers/yarns with the active components. Jost et al. adopted cellulose yarns welding process to coat yarns with carbon materials, which further served as the conductive electrodes of supercapacitors. This process contributed to high carbon mass loadings of 0.62 mg·cm⁻¹, leading to high capacitance of 37 mF·cm⁻¹ at 2 mV·s⁻¹. In addition, some yarns can be knitted into fabric devices, demonstrating the approach is viable to weave textile electronic systems.

Film-shaped energy devices based on fabrics, papers, and membranes are also gaining great attention. Cotton fabrics are the generally-used scaffolds to support active materials for the construction of energy devices due to their low cost, easy availability, good flexibility, and highly porous structures. Yang et al. first coated cotton fabric with Ni via the PAMD method, and then used the Ni-coated fabric as a filtering membrane to vacuum filtrate the CNTs and reduced GO (rGO) solution. The alternating filtration process could increase the mass loading of active materials, which accounted for the excellent electrochemical performances. Ultimately, the mass loading was up to 23.7 mg·cm⁻² and did not observably influence the porosity, which resulted in an unrivaled areal capacitance of 6.2 F·cm⁻² at 20 mA·cm⁻², exceeding the performance of most reported EDLC electrodes. Besides, different types of papers have been incorporated with active components, such as filter paper, bacterial cellulose paper, printing paper, air-laid paper etc. Because of the large surface area and strong capillary force, paper allows the active materials to be easily absorbed and generate the conformal coating. Zhang et al. fabricated a flexible asymmet-
rical all-solid-state supercapacitor, in which Ni/MnO$_2$-filter paper prepared by electroless plating and electrodeposition served as the positive electrode and Ni/active carbon (AC)-filter paper prepared by electroless plating and electrodeposition served as the negative electrode (Fig. 10a). The electrodes showed excellent areal specific capacitance of 1900 mF·cm$^{-2}$ at 5 mV·s$^{-1}$ and superior cycling performance. Moreover, the paper-based supercapacitor exhibited good flexibility, and the electrochemical performance remained stable and outstanding under various bending situations (Figs. 10b and 10c). In addition, Fig. 10(d) displays the flexible supercapacitor with a large volume energy density of 0.78 mWh·cm$^{-3}$, which can power a LED (3 V) (Fig. 10e).

Similarly, these planar substrates have also found application in batteries, which are the other important energy storage device. Differing from supercapacitors, batteries exhibit high energy density and working voltage. LIBs are commercially available and widely used as the power supply of current electronics, which are an appropriate power source for the flexible electronics. To further explore high performance batteries and meet the special needs, some innovative batteries have been deeply investigated, such as Li-O$_2$, Na-ion, Li-sulfur (Li-S), Li-CO$_2$, and Zn-ion and so on. Particularly, biopolymer materials are opening up new application in the above batteries. Besides, Li-O$_2$ batteries can deliver higher energy density in comparison with LIBs, rendering them to emerge as a promising energy storage device.

Fig. 10 Biopolymers as the substrate of flexible energy devices. (a) Schematic illustration showing the fabrication of Ni/MnO$_2$-filter paper (FP) electrode; (b) All-solid-state supercapacitor with FP-based electrode in a bending state; (c) Cyclic voltammetry (CV) curves of supercapacitor at different bending angles; (d) Relationship between energy density and power density of FP-based supercapacitor; (e) Two supercapacitors in series powering the LED indicator (3 V) (Reprinted with permission from Ref. [207]; Copyright (2016) American Chemical Society). (f) A tri-pathway structural design based on the chemically treated natural wood and CNT/Ru to enable the noncompetitive transport of Li$^+$ ions, electrons and oxygen gas; (g) Photographs of flexible wood coated with CNT; (h) Discharge curves of the initial cycle for different electrode structures (Reprinted with permission from Ref. [208]; Copyright (2019) Wiley).
spired by the efficient transport system in natural tree, Chen et al. produced a flexible wood-based electrode for Li-O₂ batteries. Natural balsa wood was chemically treated to remove the lignin and hemicellulose and the intrinsic channels enabled O₂ gas transport. Then CNTs and Ru NPs were sequentially loaded on the flexible wood, and ensured the continuous electron transport and enhanced redox reactions within the cathode, respectively, which realized the noncompetitive triphase transport of O₂ gas, electrons and Li⁺ ions (Fig. 10f). Besides, the chemical treatment endowed the wood with good flexibility (Fig. 10g). Benefiting from the abundant porous structures, the CNT/Ru-coated wood served as the cathode of Li-O₂ cell, which delivered the high initial capacity (Fig. 10h), low overpotential (0.85 V at 100 mA·g⁻¹), record-high areal capacity of 67.2 mAh·cm⁻², excellent electrochemical and cyclic stability. Compared with LiBs, Na-ion batteries (SIBs) have advantages of source abundance, easy availability and low cost, which are considered as the applicable candidate to replace the Li-related energy storage systems. Zhu et al. employed the cotton textile to reclaim Ni from the electroless plating wastewater, and coated Prussian blue graphene composites on the textile. The modified textile had excellent flexibility, and further was used as the electrode of SIBs, showing the superior electrochemical performance.

Besides the pristine biopolymers, regenerated films derived from silk, cellulose or chitin generally present excellent optical transparency, low roughness, mechanical flexibility and stability, and can be used as the flexible support constituent of energy devices. In principle, the substrate with high optical transparency is desirable for solar cells. The biopolymer nanofiber-based films are transparent and mechanically flexible, which are the ideal materials for supporting the active components of solar cells. Cheng et al. mixed the etching of cellulose with cellulose nanocrystals to yield transparent nanopaper with smooth surface and good mechanical properties. Tin-doped indium oxide was then deposited on the nanopaper, which served as the electrode of flexible polymer solar cell. The power conversion efficiency of solar cell was 4.98%, suggesting the promising application as biodegradable and wearable electronic systems. Jia et al. prepared the silk fibroin film by a simple drop-casting method from the silk fibroin solution, and then coated a polypyrrole (PPy) layer on the silk fibroin film, which showed a conductivity of 1.1 S·cm⁻¹ and good catalytic activity. Then the silk fibroin-PPy film acted as the cathode material of Mg-air battery, forming a biocompatible and biodegradable battery.

Moreover, 3D lightweight aerogels can act as substrates for various materials by incorporating the active components during the aerogel assembly or through the subsequent coating process. Yang et al. proposed a delicate strategy to in situ incorporate functional nanomaterials into the CNC network during assembly. The capacitive NPs, such as PPy nanofibers, PPy-coated CNTs, and manganese dioxide NPs, were respectively blended with functionalized CNCs, and interacted with the CNCs based on hydrogen bonds and nonpolar interactions. After a freeze-drying process, the highly porous aerogels were prepared, and served as the electrodes for symmetric supercapacitors. The supercapacitors exhibited excellent capacitive behavior, which was attributed to the rapid diffusion and transportation of electrolyte ions.

Therefore, the existing biopolymers, such as silk fibers, cotton fibers, yarns, fabrics, and wood, are easily available to be integrated with active materials with the assistance of various coating or deposition techniques, which have played extraordinary roles in the fabrication of high-performance energy devices. In addition, their easy processing facilitates the production of regenerated materials, endowing the energy devices with mechanical robustness and good transparency. Briefly, biopolymers have widely served as the substrates for energy systems, which is opening up a new avenue to fabricate energy device with excellent mechanical flexibility, desired environmental friendliness, light weight, low cost and mass production.

Flexible Separators

Separator is a key component of energy storage systems, such as LiBs, which prevents the physical contact between the anode and cathode and ensures the effective ion transport. Currently, polyolefin separators, such as polyethylene (PE) and polypropylene (PP) based porous separators, are dominant in commercial energy devices owing to their inherent insulating properties and good electrochemical stability. Nevertheless, the polyolefin separators are limited by the poor thermal stability and inferior electrolyte wettability, and are not environmentally friendly and sustainable. Thus, various polymer materials have been explored as the alternatives for polyolefin separators, including the natural biopolymers. As previously mentioned, biopolymers have appealing merits of abundance, cost effectiveness, high thermal stability, good electrolyte wettability and unique biological properties, and have gained considerable attention as an alternative separator for energy systems.

The inner and outer of raw silk cocoons contain silk fibers with a random distribution to form multilayer structure, which offer a facile and environmental friendly separator for safe and sustainable LiBs. Besides, silk nanofibers derived from the scalable liquid exfoliation method can be assembled into porous membranes and serve as the separator of supercapacitors and batteries. Tan et al. reported a liquid exfoliation strategy to directly extract silk nanofibers with the diameters of 20–100 nm and lengths ranging from 0.3 μm to 10 μm. Then silk nanofiber membranes were prepared by the vacuum filtration of dispersions, which featured excellent mechanical properties, porous structures, and good thermal and chemical stability. The membranes served as the sustainable separators of supercapacitor and endowed the device with favorable electrochemical performances. In addition, silk membranes, which are produced by the electrospinning process, and silk sponges obtained by a freeze-drying method have been used as the appropriate separators for LiBs. The silk materials show the highly interconnected porous structures and ensure the high uptake of electrolyte, providing the good electrochemical results.

The commercial paper can be directly used as a green separator for energy devices. Commercial rice papers consist of the interpenetrating cellulose microfibers to form a highly porous structure, which are utilized as separators for LiBs for the first time. The paper separators demonstrate a lower resistance than the commercial counterparts, and deliver excellent electrochemical performances. Li-S battery has a high-
er theoretical energy density than LiBs, and sulfur is abundant, making this novel battery attractive. Yu et al. chose a porous cellulose-based separator for Li-S battery.\textsuperscript{[223]} The cellulose-based separators with a pore size between 50 and 100 nm could store more electrolyte and have much better thermal stability than the commercial counterparts do. Intriguingly, the cellulose-based separator was wet by the solid lithium metal and suppressed the formation of dendrite effectively, as well as blocked the polysulfides largely (Figs. 11a and 11b). Pan et al. proposed a sandwich-structured separator composed of two cellulose nanofiber surface layers and an intermediate glass microfiber/cellulose nanofiber composite layer for lithium metal batteries (LMBs).\textsuperscript{[224]} The cellulose nanofiber membranes offered the uniform distribution of nanopores, which contributed to the realization of a homogenous current distribution at electrodes. Besides, the existing macropores in the composite layer facilitated the ionic transport. Importantly, by virtue of the excellent hydrophilic trait and thermal stability of cellulose and glass microfiber, the separator showed the more superior electrolyte wettability, thermal stability and higher ionic conductivity than the commercial ones, resulting in the enhancement in the capacities and stabilities of LMBs. Cellulose-based materials have been made into soft separators, whereas the whole batteries still lacked flexibility. Zolin et al. fabricated an all-paper LiBs consisting of a stacking paper separator, a graphite-based paper anode, along with a LiFePO$_4$-based paper cathode.\textsuperscript{[225]} This provided a rapid, low-cost, scalable and eco-compatible technique to fabricate flexible LiBs on the basis of cellulose papers.

Furthermore, chitin nanofibers are sufficient and suitable as the separators for energy storage systems. Zhang et al. confirmed that the cyanoethyl-chitin nanofiber separators could exhibit higher ionic conductivity and more remarkable mechanical strength than the unmodified chitin nanofiber separators.\textsuperscript{[226]} Also, the LiBs with cyanoethyl-chitin nanofiber separators delivered superior rate capability and excellent capacity retention (Figs. 11c and 11d), showing the chemical modification of biopolymer nanofibers would provide a new avenue to fabricate sustainable and renewable separators for high-performance energy systems. Zhang et al. developed a green and sustainable separator based on chitin nanofibers derived from prawn shells.\textsuperscript{[227]} The pore sizes of chitin nanofiber membranes could be designed and tuned by altering the amounts of pore generation agent, which was conducive to the optimization of electrolyte uptake capabilities and ionic conductivities. The Li/Na-ion batteries with chitin nanofiber separators showed comparable or even better performance than the ones based on commercial PP separators, paving the way for development of renewable energy storage systems. Similarly, Kim et al. prepared the regenerated chitin fibers via a centrifugal jet-spinning technique, and used the unwoven fibers as the separator for Li-O$_2$ and Na-O$_2$ batteries.\textsuperscript{[228]} The unwoven chitin fibers were composed of hierarchically aligned self-assembled nanofibers, and exhibited excellent electrolyte uptake property. Attractively, the chitin-based separator was capable of effectively mitigating Li dendrites and greatly improving the Coulombic efficiency.

Flexible separators based on natural biopolymers have been broadly applied in the fabrication of sustainable energy systems due to their natural abundance, low cost, easy fabrication, excellent electrolyte wettability and uptake property, mechanical flexibility and robustness, and improvement in ion transport. Although biopolymers impart the energy devices with outstanding performances, some issues, such as the hygroscopic nature, thermal shutdown, mechanical properties and large scale manufacturing process,\textsuperscript{[216]} should be addressed elaborately to facilitate the practical application of residential energy storage in the near future.

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**Fig. 11** Biopolymers as the separator of flexible energy devices. (a) SEM image of cellulose-based porous membrane, which serves as the separator of Li-S cell; (b) Comparison of cycle performance and Coulomb efficiency of the cell with the Celgard 2500 or cellulose membranes as separators (Reprinted with permission from Ref. [223]; Copyright (2016) American Chemical Society). (c) Characterizations of cyanoethyl-modified chitin nanofiber separators for LiBs. Scale bar: 1 μm; (d) Rate performance comparison of the LiBs with commercial PP and cyanoethyl chitin nanofiber separators (Reprinted with permission from Ref. [226]; Copyright (2019) Wiley).
sustainable and flexible energy devices.

**Flexible Electrolytes**

Traditionally, liquid electrolytes are commonly used in energy generation and storage devices, such as batteries, solar cells and supercapacitors. Such electrolytes have raised safety concerns because of their volatility, leakage, corrosion and flammability. Polymer electrolytes, composed of polymers and organic or inorganic salts, have emerged as an ideal alternative to fabricate safe and flexible energy devices. Polymer matrix trapping the liquid electrolytes prevents the leakage and corrosion, and endows the devices with light weight, design flexibility, and good processability. Among them, biopolymer electrolytes generally have high ionic conductivity and good electrochemical stability, and feature mechanical flexibility, low cost and light weight, which may replace synthetic polymers for utilization in energy systems.\(^{[22]}\) Typically, polysaccharides, including cellulose and derivatives, chitosan, have been extensively investigated to serve as the polymer host for ionic conduction due to their naturally abundance, cost effectiveness and eco-friendliness.

Biopolymers have directly acted as the filler materials to reinforce polymer electrolytes. Willgert et al. utilized stiff CNCs to reinforce poly(ethylene glycol) (PEG) matrix and produced polymer electrolytes.\(^{[23]}\) Acrylate and alkyl groups were introduced on the surface of CNCs through an acid chloride reaction, which could react with the PEG-methacrylate oligomers to form covalent bonds between cellulose and PEG, and improve the mechanical strength of electrolyte. As the composite was swelled with a liquid electrolyte, the ionic conductivity was enhanced and came up to \(5 \times 10^{-5} \text{ S} \cdot \text{cm}^{-1}\). Zhao et al. introduced bacterial cellulose microfibers to poly(vinyl alcohol) (PVA) matrix for preparing the hydrogel electrolytes (Fig. 12a).\(^{[23]}\) Given the hydrogen bonds between cellulose and PVA, the mechanical strength of composite was increased 9 time. Besides, composite displayed an extremely high ionic conductivities of 80.8 mS \cdot \text{cm}^{-1}. Furthermore, flexible Zn-air battery with this composite electrolyte showed excellent cycling stability and flexibility, which provided a new possibility for the development of flexible and rechargeable Zn-air battery (Figs. 12b and 12c). Furthermore, blending chitosan and poly(ethylene oxide) (PEO) was expected to offer more sites for the ions and improve the ionic conductivity.\(^{[23]}\) This composite electrolyte was applied in the fabrication of dye sensitized solar cells (DSSCs), leading to the enhanced performance of DSSCs.

Alternatively, biopolymers can assemble into polymer matrix to incorporate with the organic or inorganic salts and form the polymer electrolytes. Zhao et al. developed a simple and scalable solution-phase inversion process to prepare flexible and transparent mesoporous cellulose membranes (mCel-membrane).\(^{[23]}\) The mCel-membrane was highly transparent, flexible and could be folded into various forms (Fig. 12d). The KOH-saturated cellulose membranes showed high electrolyte retention (451.2 wt%), ultrahigh ionic conductivity (0.325 S \cdot \text{cm}^{-1}), and excellent mechanical robustness. The cellulose electrolyte-based EDLC had high capacitance and long cyclic life (Fig. 12e). Furthermore, planar-type micro-supercapacitors could be fabricated by directly coating active materials on the polymer electrolyte, which delivered high areal capacitance (153.34 mF \cdot \text{cm}^{-2}), volumetric capacitance (191.66 F \cdot \text{cm}^{-3} at 10 mV \cdot \text{s}^{-1}), and desired volumetric energy density (6.655 mWh \cdot \text{cm}^{-3} at a power density of 0.2395 W \cdot \text{cm}^{-3}) (Fig. 12f). Jia et al. combined silk fibroin and ionic liquid to form a biode-

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Fig. 12  Biopolymers as the electrolyte of flexible energy devices. (a) Flexible bacterial cellulose/PVA hydrogel electrolytes; (b) Schematic illustration of a flexible zinc-air battery based on cellulose/PVA membranes; (c) Galvanostatic charge and discharge cycle of a flexible zinc-air battery showing the good stability (Reprinted with permission from Ref. [23]; Copyright (2019) American Chemical Society). (d) Transparent, flexible, and tailorable mesoporous cellulose membrane (mCel-membrane); (e) Specific capacitances of supercapacitor at different current densities; (f) Relation curves of energy density and power density (Reprinted with permission from Ref. [23]; Copyright (2017) Wiley).

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gradable ion-conducting membrane, which was used as the electrolyte for the biodegradable thin-film magnesium battery. The battery was encapsulated in silk films and offered a specific capacity of 0.06 mAh·cm\(^{-2}\). Moreover, the whole device could be controllably degraded by adjusting the silk protection layers. In addition, bacterial cellulose network could be prepared by a simple and fast freeze-drying method. The internal cross-linking contributed to the high strength and provided abundant ionic passageways. Also, the cellulose network enabled a good liquid electrolyte absorbent capacity and delivered an excellent ion conductivity of 4.04 × 10\(^{-3}\) S·cm\(^{-1}\). The lithium metal battery on the basis of the polymer electrolyte possessed admirable electrochemical and safety performance. Chitosan-based supramolecular hydrogels were prepared by a facile and fast cross-linking between chitosan and Li\(^{+}/Ag\(^{+}\). The hydrogels demonstrated high thermal stability and excellent mouldable properties, which served as the solid electrolyte for an asymmetric supercapacitor with highly cyclic stability and outstanding flexibility.

Biopolymers have gained much attention in utilizing as flexible polymer electrolytes for the energy devices in terms of their abundance, functionality, low cost and eco-friendliness. Biopolymers act as the hosts for ionic conduction, and endow the electrolyte with mechanical robustness, high conductivity and thermal stability, as well as biodegradability, which advance their use in batteries, solar cells and supercapacitors. Besides, the modification can bring novel properties and synergistic effects to biopolymers, which offers effective methods for enhancing the performance of polymer electrolytes.

**Flexible Active Materials**

As an indispensable component of energy devices, active materials, such as electrodes and triboelectric layers, have a great effect on the performance of flexible energy devices. In principle, flexible electrode materials in batteries, supercapacitors and solar cells should possess not only good mechanical strength and electrochemical performance, but also structural integrity under deformation, cost effectiveness, easy fabrication and light weight. To accommodate the development of flexible and wearable electronics, varieties of electrode materials have been broadly explored to produce flexible energy conversion and storage devices, including carbon nanomaterials and composites, conducting polymers, 2D materials beyond graphene and carbon black NPs for a conductive nanofiber network. In particular, lithium iron phosphate particles were introduced into the solution containing CNCs and carbon black, and then the mixed suspension was treated by a freeze-drying process to form electrodes with high active material loading (up to 60 mg·cm\(^{-2}\)). The composites could be further post-densified for the compact and thick electrodes, in which nanoporous network offered the good electrolyte retention for ion transport and interconnected conductive scaffolds provided abundant electron transfer pathways. Flexible batteries based on the thick electrodes had unrivaled areal capacity, volumetric energy density, and excellent cycling performance (Fig. 13b), offering a promising strategy for flexible and high-performance energy storage devices with low cost and mass production. Moreover, as a water-soluble biopolymer, chitosan also plays an important role as the binder in designing and optimizing the fabrication of electrodes and performance of energy devices. However, flexible electrodes and energy devices based on chitosan and its derivatives are scarce, which should be paid with more attention.

More intriguingly, natural biopolymers-derived carbon materials are produced through a facile and scalable pyrolysis strategy, which is able to preserve the intrinsically hierarchical structure of biomaterials and enable applicable electrical conductivity. This technique is limited by more defects and
lower graphitization degree of carbon materials, as well as the inferior mechanical properties.\cite{4} Even so, the plentiful structures and chemical compositions endow the biopolymer-derived carbon materials with desired morphologies and properties, providing the promising application in energy devices. Especially, silk fibroin and chitin intrinsically contain nitrogen, and can be converted into N-doped porous carbon materials, which are able to provide excellent electrochemical properties.\cite{246−248} These stiff and porous carbon particles or sheets can be easily obtained after a pyrolysis process, showing the great potentials for the mass production of energy generation and storage devices with low cost.\cite{249,250} The pristine silk cocoons or fibers, and regenerated silk fibroin films have been carbonized at high temperature under an inert atmosphere, leading to the preparation of carbon nanoplates.\cite{247} During the carbonization process, metal salts-activation could induce high specific surface area of 2494 m$^2$·g$^{-1}$ and high pore volume of 2.28 cm$^3$·g$^{-1}$.\cite{246} The porous nitrogen-doped carbon materials were used as the anode of LIBs and the electrodes of supercapacitor, which exhibited a high reversible...
lithium storage capacity of 1865 mA·h·g$^{-1}$ and an excellent capacitance of 242 F·g$^{-1}$. Similarly, cellulose, chitin or chitosan and their derivatives can be thermally treated to convert into conductive carbon materials.$^{[251−253]}$ Moreover, processing temperatures are found to apparently affect the structures and electrochemical performance of as-obtained carbon materials.$^{[252]}$ More specifically, higher temperature resulted in the smaller specific surface area, more ordered structures, and fewer heteroatoms. Thus, the appropriate treatment temperature is of great importance to obtain structurally and functionally optimized carbon materials, which is essential for developing high-performance energy devices. Actually, these carbon particles or nanosheets are usually powders and lack flexibility, and should be further processed into films or aerogels for flexible energy devices. Wang et al. reported a defect-rich and N-doped nanocarbon material derived from the silk fibroin and commercial porous Ketjenblack carbon.$^{[249]}$ The carbon composites showed excellent electrocatalytic activities and good stability for oxygen reduction reaction/oxygen evolution reaction (ORR/OER), revealing the application in high-performance Zn-air batteries (Fig. 13c). Besides, the all-solid-state Zn-air batteries presented mechanical flexibility and outstanding charge/discharge stability (Fig. 13d), showing the great prospects in wearable electronic systems. Particularly, wood has unique and well-connected channels along the growth direction, which are perfectly maintained after a pyrolysis process.$^{[253]}$ These open channels contribute to the ion transport and gas diffusion, enabling the improvement in device performances.

Alternatively, intrinsically flexible biopolymer-based membranes, such as fabrics/textiles, aerogels and thin wood, have been used as the precursors to prepare carbon materials, enabling good flexibility for the energy devices. First, the regenerated films or aerogels derived from nanofibers can be directly carbonized for electrode materials.$^{[254−256]}$ Chitin nanofibers isolated from crab shells can assemble into chitin nanofiber aerogels, which are further transformed into N-enriched carbon aerogels.$^{[257]}$ With high surface area and high content of nitrogen, supercapacitor based on the aerogels displayed high electrochemical capacitance, good cycling stability and excellent good retention capability. Second, the existing films, papers, fabrics or textiles succeed in being processed into conductive carbon materials using the simple carbonization process.$^{[258]}$ Bao et al. has realized the direct conversion from cotton textiles to flexible activated carbon textiles, and fabricated the flexible supercapacitors, which provided a facile and low-cost way to functionalize textiles as the building blocks of energy device.$^{[258]}$ Besides, the intrinsically stretchable textiles-derived carbon materials can be applied to fabricate stretchable supercapacitors. As shown in Fig. 13(e), a large-scalable pyrolysis strategy is proposed to produce stretchable and conductive weft-knitted textile.$^{[186]}$ The intrinsically stretchable feature enabled the carbon textiles to sustain strains up to 125% as the conductivity remained stable, ensuring the application in stretchable supercapacitors. The textile-based supercapacitors exhibited outstanding stretchability as the structure integrity maintained and electrochemical performance was stable under tensile strain of 50% (Figs. 13f and 13g). Additionally, other function-
al materials can be deposited or coated on the biopolymer-derived conductive carbon materials to improve the electrochemical properties.$^{[335,261]}$ Typically, a unique nanostructured Ni(OH)$_2$ layer was coated on the surface of conductive carbonized cotton fabric via a facile electrochemical deposition process.$^{[253]}$ The Ni(OH)$_2$ endowed the carbon textiles with good hydrophilicity to promote electrolyte penetration, and offered abundant electroactive sites, enabling the improvement of capacitance performance. The specific capacitance of supercapacitors based on Ni(OH)$_2$ modified carbon textiles was 12 times higher than that of carbon textile-based ones.

Recently, LIG technique is becoming a good candidate to convert a substrate into the graphitic carbon materials, including the cellulose materials. Generally, cellulose materials have been treated by this technique in an inert atmosphere or with the aid of fire retardants.$^{[181,183]}$ Lee et al. demonstrated the conversion of CNFs to carbon materials under ambient conditions.$^{[182]}$ CNF film and paper were processed into conductive graphitic carbon by single and multiple lasing, respectively, which opened up a new way for the application in flexible planar energy devices.

Triboelectric nanogenerators (TENG), based on the coupling effect of triboelectrification and electrostatic induction, can realize the conversion from mechanical energy to electrical energy. Normally, the device needs two triboelectric materials with different electron-attracting abilities, which can be oppositely charged upon contact and generate a potential in the interfacial region during their separation. Numerous polymers and metals have served as the triboelectric materials for TENG, and biopolymers become a wonderful alternative as the triboelectric materials, promoting the development of renewable, naturally biodegradable, biocompatible and flexible TENG. The regenerated silk fibroin film prepared by an electrospinning method could be used for eco-friendly TENG (Fig. 14a).$^{[262]}$ The film possessed high surface-to-volume ratio and much rough surfaces, which were beneficial to the improvement of power generation (Fig. 14b). The electrospun silk film-based TENG exhibited high triboelectric surface charge density (1.86 μC·m$^{-2}$) and the favorable instantaneous electric power (4.3 mW·m$^{-2}$) (Fig. 14c), respectively. He et al. fabricated a hierarchical nanostructure composed of cellulose microfibers and nanofibers and Ag nanofibers, in which cellulose microfibers and nanofibers served as the triboelectric material for TENG, and Ag was deposited on the surface of cellulose to act as the electrode and antibacterial sites (Figs. 14d and 14e).$^{[263]}$ Hence, the TENG based on cellulose materials and Ag featured PM2.5 removal, antibacterial property, and self-powered breathing monitoring (Fig. 14f). Recently, Zhang et al. innovatively prepared CNTs@silk fibroin core-sheath fiber-based smart textile and further fabricated flexible TENG.$^{[264]}$ A coaxial spinneret was used to print core-sheath fiber-based patterns on the textile, in which CNTs as the core provided good conductivity, and silk fibroin served as a dielectric sheath (Figs. 14g and 14h). The smart fiber patterns could be used as electronic textile for harvesting mechanical energy of human body motions. The TENG had good performance with an open-circuit voltage peak of 15 V, and a short-circuit current peak of 1.4 mA, as well as the
applicable power density (18 mW·m$^{-2}$) (Fig. 14i), which could power LEDs or an electrical watch, showing the great potentials for wearable energy-management systems.

It is observed that biopolymers can serve as the binder to glue the electrode materials together, endowing the electrodes with good mechanical integrity and flexibility. In addition, the porous structures enable the increase in electrolyte absorption. Notably, biopolymer-derived carbon materials have been emerging as the good alternative electrodes for flexible energy devices, which have advantages of renewability, easy availability, low cost, large-scale production capability and environmental friendliness. Additionally, biopolymers have found application in TENG, imparting the natural biodegradability, biocompatibility, and eco-friendliness.
In this section, we demonstrate the application of biopolymers in flexible energy devices, which can serve as the flexible substrates to support active components, as the separators to isolate the two electrodes and ensure the ion transport, as the electrolytes to offer high ionic conductivity, and as the active materials to provide high performance. Therefore, due to their unique structures and properties, biopolymers have played important parts in the fabrication of flexible energy devices, and can provide more possibilities to construct high-performance energy devices, and boost the integration of flexible electronics and energy systems, as well as their practical applications.

CONCLUSIONS AND PERSPECTIVES

Natural biopolymers have intrigued growing interest because of their earth-abundance, tailorable structures and compositions, excellent biological properties, ease to fabricate, diverse material formats and low cost. Biopolymers, such as silk, cellulose and chitin/chitosan, can be feasibly made into various configurations, including fibers, yarns, films/membranes, papers, fabrics/textiles, hydrogels, aerogels and foams, which can be utilized as the key components for flexible sensing and energy devices. First, biopolymers can serve as the flexible substrates to support functional materials for the fabrication of flexible devices, endowing them with good mechanical flexibility and robustness, biodegradability, and biocompatibility. Second, the regenerated biopolymer-based materials (nanofibers, nanofilms, nanopapers, hydrogels, aerogels, etc.) meet the requirements of active middle layers in transistors and resistive switching memory devices. Third, biopolymers are supposed to be the suitable alternatives as flexible separators or electrolytes for energy generation and storage devices. Last but not least, combination of biopolymers and functional materials devotes to imparting biomaterials with specific functionalities, which provides a promising way for developing renewable, low-cost, flexible sensing and energy devices on a massive scale. Additionally, biopolymers-derived carbon materials have been prepared via a simple and scalable pyrolysis treatment or a laser induced graphitization process, offering desired active materials for flexible devices. Table 1 summarizes the properties and applications of natural biopolymers for applications in flexible sensing and energy devices.

Due to their appealing structures and properties, natural biopolymers have been playing important roles in the fabrication and application of flexible sensing and energy devices. Although great advances have been achieved, there are some issues that need to be solved. More profound understanding of the structure-property relationship is desired, such as the material structures and physicochemical properties, and molecular-level organization, which will be reliable to broaden the application of biopolymers as important components for electronic and energy systems. Besides, low-cost, large-scale and well-controlled fabrication processes should be further developed, aiming to provide admirable building block materials on a large scale. It is noteworthy that surface modification at the molecular level is able to improve the intrinsic properties and induce novel synergistic effects for biopolymers, which may accelerate the fundamental research of biopolymers toward practical applications. Also, there is an urgent demand to explore cost-effective, large-scale, eco-friendly fabrication techniques, especially the integration strategy of electronics, energy devices and data components, for the development of electronic systems. Notably, more attention should be paid to the stability and durability of biopolymer-based devices, which may be influenced by temperature, humidity and deformation. Although challenges still exist, it is believed that natural biopolymers hold great

| Applications                  | Types                  | Biopolymers                                      | Features                                                      | References          |
|-------------------------------|------------------------|--------------------------------------------------|----------------------------------------------------------------|--------------------|
| Molds                         | Sensors, batteries     | Silk (textiles), cellulose (plant leaves and flowers, wood) | Structural complexity and hierarchy                           | [112–118]          |
| Substrates                    | Sensors, transistors, actuators, optical devices, intelligent textiles, batteries, supercapacitors, solar cells | Silk (fibers or yarns, films, fabrics or textiles, aerogels), cellulose (fibers or yarns, films, papers, fabrics or textiles, wood, aerogels), chitin/chitosan (fibers, films, aerogels) | Flexibility, mechanical robustness, light weight, biodegradability, thermal stability, biocompatibility, low thermal expansion, low cost, easy processability | [65,66,119–121, 126–129,133,134, 138–144,147–150, 196,197,202–209, 213–215] |
| Active middle layers          | Transistors, resistive switching devices | Silk (films), cellulose (nanopapers), chitin/chitosan (films or membranes) | Flexibility, light weight, biodegradability, dielectric materials, biocompatibility, low surface roughness, bipolar resistive switching behavior | [153,154,158–161] |
| Active materials              | Sensors, actuators, electronics, batteries, supercapacitors, biofuel cells, triboelectric nanogenerators | Silk (fibers or yarns, fabrics or textiles, aerogels, hydrogels, composites), cellulose (membranes, wood, aerogels, hydrogels, composites), chitin/chitosan (films, aerogels, hydrogels, composites) | Mechanical flexibility and robustness, biodegradability, biocompatibility, diverse active sites, solution processing, diverse structures and material formats, natural biomaterial-derived carbon materials, large-scale and low-cost production capability, high safety, triboelectric effect | [167,171,173,175, 176,184,185–192, 242–249,251–253, 255,258,262–264] |
| Separators                   | Batteries, supercapacitors | Silk (fibers or yarns, fabrics or textiles, composites), cellulose (films, papers), chitin/chitosan (films) | Flexibility, light-weight, biodegradation, thermal stability, good electrolyte wettability, natural abundance, low cost | [220,221,223–228] |
| Electrolytes                  | Batteries, supercapacitors, solar cells | Silk (films, composites), cellulose (films, composites), chitin/chitosan (films, composites) | Flexibility, light weight, good processability, high ionic conductivity, good electrochemical stability | [230–236] |

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potential for fabrication of flexible sensing and energy devices, benefiting the practical application of wearable electronic systems, smart textiles and medical devices.

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