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Functional biomaterials towards flexible electronics and sensors

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ABSTRACT

Biomaterials have gained increasing attention in the fabrication of a variety of flexible electronics due to their tunable solubility, robust mechanical property, multi-active binding sites, and excellent biocompatible and biodegradable characterization as well. Here, we review the recent progress of bio-based materials in flexible sensors, mainly describe nature biomaterials (silk fibroin, cellulose and chitin) and chemical-synthesized biomaterials as well as their applications in health monitors, biosensor, human-machine interactions (HMIs) and more, and highlight the current opportunities and challenges that lay ahead in mounting numbers of academia and industry. Furthermore, we expect this review could contribute to unveiling the potentials of developing outstanding and eco-friendly sensors with biomaterials by utilization of printing techniques.

1. Introduction

Flexible wearable electronic devices which can tolerate or withstand the stretching or bending forces, or other large deformation have been widely investigated in past decades (Wu et al., 2010). The flexible, extensible electronic device normally consists of traditional rigid board systems and stretchable materials: the former typically shows good mechanical properties and the lateral can be stretched like a rubber band (Zhang et al., 2014) and folded like paper (Yu et al., 2014). Particularly, the ever-growing demands for flexible electronic devices will dedicate to a rapid population growth. Meanwhile, the disposal of abandoned electronic devices has already received considerable concerns around the globe in recent years, which may cause adverse impact on the environment. That is because majority of previous developed electronic devices that are made up of non-biodegradable raw materials, like some plastics, cannot meet the trend of frequent updating of consumer electronics. Therefore, intensive studies are striving to challenge with this issue.

With the rapid development in electronic biomaterials and the relevant manufacturing techniques, researchers tend to combine bio-based materials with flexible electronic devices for sustainable development. The flexible sensor, one of the most essential parts of flexible electronics has its potential applications in monitoring human and robot motion (He et al., 2017; Jeong et al., 2013; Jung et al., 2014) and personal healthcare (Cheng et al., 2017; X. Wang et al., 2017), detecting overall hygiene in the food system (Dubal et al., 2018) as well as analyzing pesticide residues and toxic substances (Mishra et al., 2017). Furthermore, strategies to construct bio-based sensors with high mechanical durability, high sensitivity to deformations and responsive conductivity are also well addressed in numbers of published works (Kaushik et al., 2008; Zhu et al., 2013; Yuqing Liu et al., 2016; Yang et al., 2017).

Herein, we focus on the work of predecessors who committed to studying biomaterials and bio-based sensors. First, we summarize various biomaterials, including natural and conventional chemical-synthesized ones, and introduce fundamental processing properties of biomaterials and their great potential for bio-based sensors. Moreover, we highlight several applications with the example of respective biomaterials in individual healthcare, wellness pressure, sensing-based electronic skin (E-skin), biomedical diagnosis, food safety and environment governance. In addition, the future perspectives of bio-based sensors and the technological issues involved in applying biomaterials and practical devices are considered and prospected with the hope to improve the development and application of biomaterial-based flexible sensors in our daily life.

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2. Biomaterials

Biomaterials, also known as bio-based materials are produced from renewable resources. Specifically, those biomaterials are made from raw materials such as cereals (Diouf-Lewis et al., 2017), legumes (Voisin et al., 2014), straw (Paranthaman et al., 2009), bamboo powder (Hsieh et al., 2006) and other raw materials through biosynthesis, bioprocessing and biological refining process. Besides that, biomaterials also include bio-based plastics and fibers, sugar engineering products, and bio-based rubber made from biomass thermoplastic processing, which are degradable when exposed to microorganisms, carbon dioxide (aerobic) processes, methane (anaerobic processes), or water (aerobic and anaerobic processes) (Nair and Laurencin, 2007; Kumar et al., 2018; Stagner, 2016; Rivas et al., 2016). Polymer materials play irreplaceable roles in human daily life. However, except natural rubber and few other materials, most polymer materials are highly dependent on fossil resource (mainly oil and coal), which have induced lots of problems on environmental pollution, human health issues and destruction of the entire eco-environment (Brunner and Rechberger, 2016). To bring a significant reduction in greenhouse gas emissions and saving of fossil energy, sustainable and eco-friendly polymers have become increasingly important. Many efforts have been taken to fabricate various biodegradable materials from bio-based chemicals (Sheldon, 2014; Ummartyotin and Pechyen, 2016).

2.1. Chemical-synthesized biomaterials

The first generation of bio-based polymers focused on deriving polymers from agricultural feedstocks such as corn, potatoes, and other carbohydrate feedstocks. Natural biopolymers are the other class of biomaterials, such as proteins, nucleic acids, and polysaccharides (cellulose, chitin) (Badawy and Rabea, 2009). In addition, biodegradable polymers can be produced by chemical synthesis (da Silva et al., 2018), such as polylactic acid (PLA), polyurethanes (PUs), polydopamine (PDA) and polyhydroxyalkanoates (PHAs) with the chemical structures shown in Fig. 1.

2.1.1. Polylactic acid (PLA)

The original materials for synthesizing PLA mainly include corn, soybeans, beets, potatoes and other biological materials which are made of starch and sugar. One of the most important raw materials is corn, so that PLA resin is also known as "corn resin". Based on different optical rotation, PLA has three typical optical isomeric forms (Tsuji, 2013): optically active and crystalline form (poly (L-lactide) (poly (L-lactic acid) (PLLA)) and poly (D-lactide) (poly (D-lactic acid)) (PDLA)), optically inactive and amorphous poly (DL-lactide) (poly (DL-lactic acid)) (PDLLA). PLA is nowadays economically competitive and has been widely used in many day-to-day applications, mainly used in food packing (Carrasco et al., 2014) on the account of its outstanding advantages: ease of processing, superior transparency and environmentally benign characteristics. Furthermore, oriented PLLA materials exhibit unique piezoelectric properties (Ando et al., 2017), and the piezoelectric constant of PLLA increases with the draw ratio of the molecule and reaches the maximum at a draw ratio of around 4–5 (Ikada et al., 1996), which make PLLA a good candidate for piezoelectric sensors.

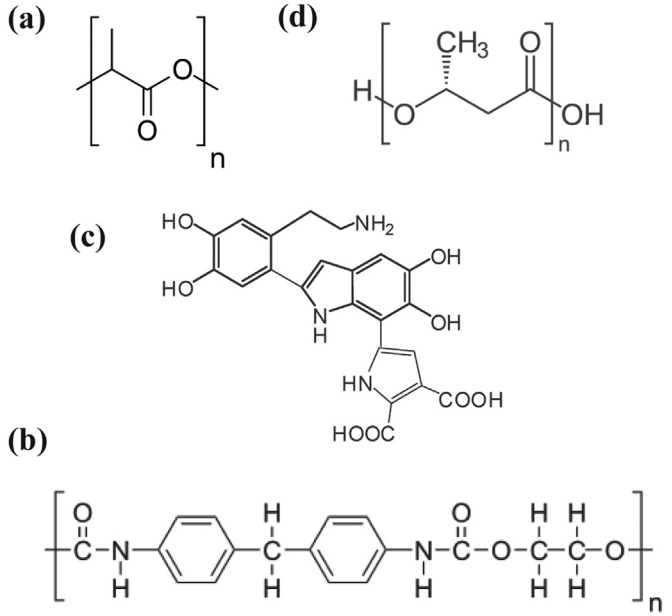

Fig. 1. The chemical structure of chemical-synthesized biomaterials: (a) PLA, (b) PU, (c) PDA, (d) PHAs.

2.1.2. Polyurethanes (PU)

PU refers to a type of polymer which contains a urethane feature unit in the main chain. PU is a block copolymer obtained by a stepwise addition reaction of isocyanate (NCO) and active hydrogen groups (Narayan et al., 2006), followed by chain extension and cross-linking. By changing the proportion of raw materials and the ratio of active hydrogen to NCO, properties of PU can be adjusted within a wide range: from soft sponges to elastomers, coatings to sealants, and shoe soles to elastic fibers. In particular, polyurethane (PU)-based materials have been used in different forms, such as in thermoplastic polyurethane (TPU), PU sponges, and PU yarn (Z. Wang et al., 2016). They are known for the favorable tensile properties and thus appropriate for preparing strain or pressure sensors (Huang et al., 2018; Xu et al., 2018). The sensors based on the above-mentioned materials can demonstrate high stretchability, little hysteresis, and long-term durability.

2.1.3. Polydopamine (PDA)

PDA is a principal pigment of natural melanin (eumelanin), which possesses many striking properties in optics, magnetics, electricity and biocompatibility (Liu et al., 2014). In addition, the multi-functional groups of PDA, such as amine, imine and catechol, act as the covalent/noncovalent binding of desired molecules and loading of transition metal ions, which further realize the emergence and extend the application of various PDA-based hybrid materials. Besides, PDA could be simply synthesized through various methods, such as simple polymerization of dopamine monomers in a mild condition (Hong et al., n.d.), enzymatic oxidation process (Tan et al., 2010), and electropolymerization (J. Wang et al., 2014). With these advantages, PDA has been widely used in energy, biomedical science, water treatment, and sensing applications (E. Lynge et al., 2011; Liu et al., 2014; G. Wang et al., 2017).

PDA is a promising functional material in the application of flexible electronics as the adhesive substrate and semiconductor, which has been inspired separately by the adhesive nature of catechols and amines and electron transition through π-system formed by aromatics and conjugated molecules (Chen et al., 2016; Ryu et al., 2018). Furthermore, incorporation with other materials via cross linking (Bie et al., 2016), in-situ deposition (Tan et al., 2010), and tethering (Xiaoling Wu et al., 2015) improves the mechanical and electrical properties of PDA complex, which further develops the connection between PDA-based materials and flexible electronics.

2.1.4. Polyhydroxyalkanoates (PHAs)

PHAs are a family of polyesters produced by bacterial fermentation with the potential to replace conventional hydrocarbon-based polymers, since they are thermoplastic, biodegradable, biocompatible, and nontoxic (Valentini et al., 2014). The most common PHAs includes poly-β-hydroxybutyrate (PHB), hydroxybutyrate copolyester (PHBV), poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate) (PHBH), and poly(3-

hydroxybutyrate-*co*-4-hydroxybutyrate) (P34HB) (Laycock et al., 2012). PHB, a typical representation of PHAs, has excellent performances in biodegradable, biocompatible and piezoelectric property, except the poor physical properties which make it hard to be applied due to the difficulties in the plastic processing. PHBV is the second generation of PHAs, which owns much weaker crystallinity and hardness, but stronger strength and toughness than PHB. PHBH is a copolymer composed of short and medium-long chains, which has much improved mechanical properties, compared with PHB and PHBV (Shimamuna and Shima, 1994). As the third generation of PHAs, P34HB is synthesized by alcaligenes eutropha in a sufficient nitrogen atmosphere and a culture medium containing 4-hydroxybutyric acid, 1,4-butanediol/butyrolactone (Xu and Guo, 2010). The presence of 4-hydroxybutyrate increases the flexibility of P34HB due to the reduced crystallinity, allowing it to be molded on conventional plastics processing equipment. Therefore, the advantages of PHAs in biodegradability, biocompatibility and flexibility make them candidates in the application of flexible sensors.

2.1.5. The composites of conventional biomaterials

Nowadays, massive efforts have been devoted to investigating the synthesis and properties of biodegradable copolymers. Through compounding with other dicarboxylic acids or diols, mechanical properties of these biomaterials can be improved in a large scale, which is promising for the application of flexible sensors. PLA mechanical performance could be substantially improved by melt blending with high crystalline isotactic PHB. Besides that, the processability and thermal stability of PLA/PHB blends can be improved by plasticization through adding micro-/nanoparticles. Furthermore, the fillers (such as catechin) (Arrieta et al., 2016), and nanofillers (such as nanocellulose and organically modified nanoclay (OMMT)) (Kelnar et al., 2016) could enhance the interfacial adhesion in the blend, leading to more homogeneous material in the final blend composites. Arrieta et al. (2014) pointed out that the mechanical performance of PLA/PHB blend matrix has been reinforced through combination with cellulose nanocrystals (CNC) and functionalized CNC by means of a surfactant (CNC-s). Jandas et al. (2013) further improved the flexibility of PLA-PHB by grafting of maleic anhydride (MA) in a reactive extrusion approach. The optimum flexibility of PLA/PHB/MA blends was reached more than 500% by grafting 7 wt% of MA. In addition, blending of PLA with PBS is an effective way to fine tune PLA brittleness. Supthanyakul et al. (2017) proposed a simple triblock copolymer for improving the mechanical PLA/PBS blend. The addition of plasticizers is another way to overcome the brittle nature of PLA and improve its flexibility (Y. Wang et al., 2014). Fortunati et al. (2017) added the isosorbide diester (ISE) plasticizer to PLA and PBS substrates, suggesting that ISE at 15 wt% represents the best choice to produce PLA/PBS plasticized blend films. Therefore, the mechanical properties of the conventional biomaterials could be improved through blending with other biomaterials, promising to be applied in the flexible sensors.

2.2. Natural biomaterials

Natural biomaterials possess outstanding advantages for high-performance and functional electronic devices on the account of their renewable, biocompatible, biodegradable and excellent mechanical properties, as well as multiple reactive sites for modulating novel functions. They have been bringing huge benefits to mankind in the aim of improving the hygiene, health and life conditions. The widespread applications of natural biomaterials have spread to the tissue regeneration (Francis Suh and Matthew, 2000), drug delivery system (Kanamala et al., 2016), implants, enzyme immobilization (Jia et al., 2014), wound dressings (Zhao et al., 2017), sensing (Cui et al., 2015) and electrical devices (Raeis-Hosseini and Lee, 2017). Recently, the applications of natural biomaterials in the flexible electric devices have been a research hotspot (Li and Cui, 2017). The ease processing of natural biomaterials with promising structures and forms (such as optical films and hydrogels), as well as adaptable performance make them potential in organic, electrical or ionic conductivities by incorporating with highly conductive materials or structure alteration via chemical modification. Here, we highlight three kinds of biomaterials which have gained lots of interests in the fields of flexible electronic devices: protein (silk fibroin), and polysaccharides (cellulose and chitin).

2.2.1. Silk fibroin (SF)

Silks are nature fibrous proteins existing in the glands of some arthropods, such as silkworms, spiders, scorpions, mites and bees. In recent years, silk from *Bombyx mori* (silkworm) has been widely studied due to its high yield (Kundu et al., 2013), excellent tensile strength (0.5–1.3 GPa) and toughness (6×10^4~16×10^4 J/kg) (Cebe et al., 2013), predominant biocompatibility, tunable biodegradability, and ease of processing (Altman et al., 2003). These predominant characterizations give silk proteins versatile applications in biological fields, including tissue engineering (Kundu et al., 2013; Liu et al., 2015; Melke et al., 2016), wound healing (Li et al., 2014; Yuangang Liu et al., 2016), and drug delivery (Li et al., 2015; Mottaghitalab et al., 2015). SF (≈75%, w/w) and sericin (≈25%, w/w) are the two major proteins of silk (Mandal and Kundu, 2009). SF protein is located at the corner of the silk fiber surrounded by the sericin proteins which could be removed by a thermo-chemical treatment (degumming) (Porter and Vollrath, 2009), as shown in Fig. 2a (Rockwood et al., 2011). SF is a natural fibrous protein composed of a heavy and a light chain that are linked together by a disulfide bond, as well as a 25 kDa glycoprotein (P25) non-covalently linked to these chains (W. Liu et al., 2017; Zafar et al., 2015). The hydrophobic domains of heavy chains containing repeated Gly-X (X being Ala, Ser, Thr, Val) form anti-parallel β-sheets, while the L-chain is hydrophilic in nature and relatively elastic (Kundu et al., 2013) (Fig. 2b). Under high thermal treatment, these crystal β-sheets could be reversed to random coils (Cebe et al., 2013) (Fig. 2c). Besides that, the crystal β-sheets structures of SF protein could be improved by water vapor annealing to increase its water insolubility which could be controlled under different annealing times and temperatures (Huang et al., 2014). The controllable structures of SF proteins by thermal treatment makes it possible to modify their degradation rates, enzyme/drug release ratios, and hydrophilic/hydrophobic properties.

Besides that, SF proteins properties could also be modulated by incorporating with other conductive materials. Graphene oxide (GO) with abundant oxygen functional groups (hydroxyl and carbonyl groups) could form intermolecular hydrogen bonds with SF by interacting with the hydrophilic blocks of amphiphilic SF, which increased the mechanical, biological and conductive properties (Zhang et al., 2016) (Fig. 2d). Similarly, carbon nanotube could also improve both the mechanical properties and conductivities of SF proteins by increasing the β-sheets structures of SF (Pan et al., 2015). Except the adaptable structure, mechanical and conductive properties, SF could be prepared into various formats, such as the porous scaffolds, hydrogels, optical transparent film, and fibers, which make it an excellent candidate in flexible electronic sensors. Furthermore, SF accesses to the third generation of biosensor because of good water solubility to avoid the usage of reagents and ease immobilization of enzymes in SF films (Musameh et al., 2018), which make it potential for solution-processed electronics (Minari et al., 2014; X. Liu et al., 2016; X. Liu et al., 2017). Therefore, SF is a very promising candidate for the flexible electronic devices due to its excellent biological and adaptable electrical properties.

2.2.2. Cellulose

Cellulose is a polysaccharide widely existed in the nature environment, such as the cotton, wood, cereal, fiber, and bacteria, composited by hundreds to thousands of ringed glucose molecules through β-1, 4 glucosidic bonds (J. Moon et al., 2011). As shown in Fig. 3a, the liner configuration of cellulose chains is formed due to the chemical

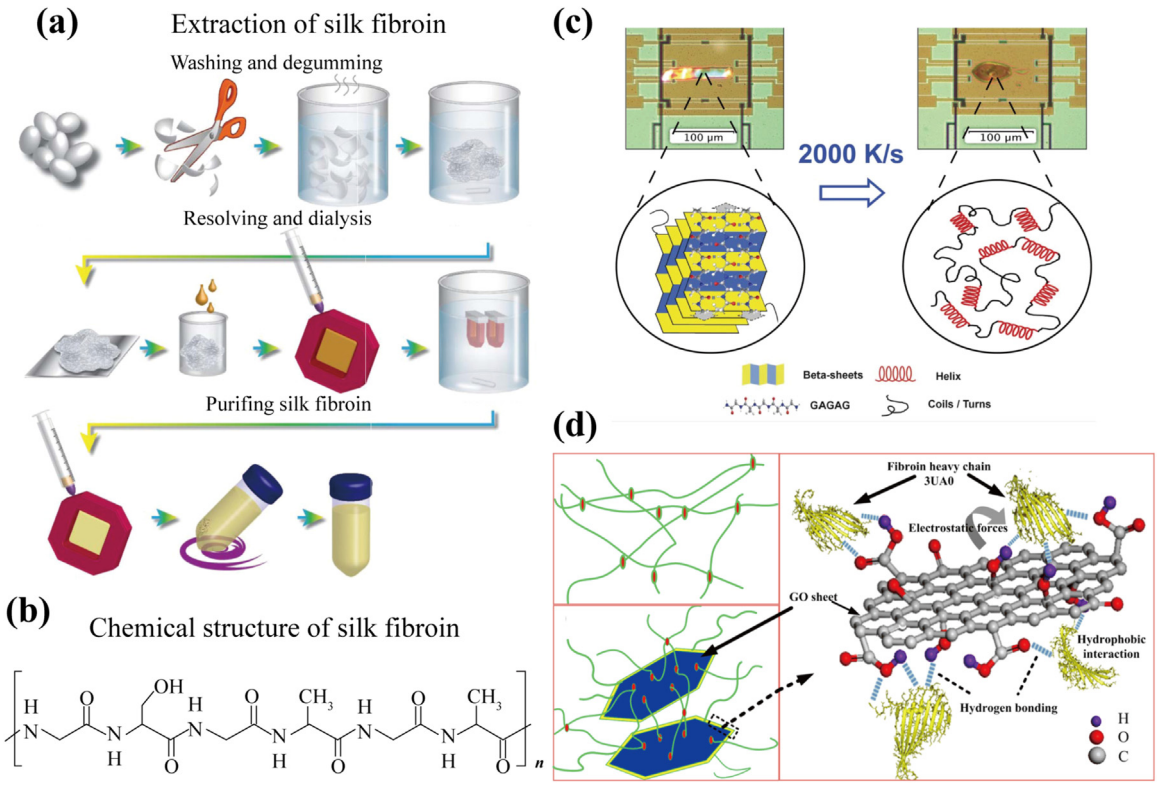

Fig. 2. The detailed information about the SF proteins: (a) The degumming process to extract pure SF protein from silk (Rockwood et al., 2011), Copyright 2011, Springer Nature; (b) The chemical structure of SF; (c) The revisable structure changes of β-sheets and random coils under high thermal treatment (Cebe et al., 2013), Copyright 2013, Springer Nature; (d) The chemical bonding between SF and GO (Zhang et al., 2016), Copyright 2016, American Chemical Society.

interactions between hydroxyl group and oxygens of adjacent ring molecules, which stabilize the linkages and form the parallel linear nanofibers. The cellulose chains are formed by amorphous-like (disordered) and crystalline (highly ordered) regions which are used to form the cellulose nanocrystals. The cellulose could be divided into three layer from the view of structure: 1) the formation of cellulose crystals with the diameter of few Å assembled by glucose macromolecular chains; 2) supramolecular layer further formed by above cellulose crystals with the sizes from 4 nm to 1 μm; 3) fiber bundles constructed by above nanofibers; and finally, the fiber bundles together with the amorphous molecules composite the fibrous cellulose in a self-assemble way.

Currently, nanocellulose could be obtained through mechanical, oxidation, and hydrolysis methods (Lin and Dufresne, 2014); and based on different preparation methods, two kinds of nanocellulose with different morphologies and chemical groups could be formed: cellulose nanofibrils (CNFs) and nanocrystals (CNNs), as shown in Fig. 3b. CNF is produced by mechanical methods with high shearing following homogenization at high pressure. CNF is a network structure formed by the fibrils with length in micrometer and width in nanometer scale (Zhang et al., 2013), containing both crystalline and amorphous regions. After removing the amorphous regions via acid hydrolysis, CNN could be formed with highly crystalline structures. In addition, the cellulose microfibrils could also be prepared by biosynthesis which is a multistep process depending on the organism producing the cellulose. Detailed preparation methods could be found in previous work of Brown (Jr, 1996), and Saxena and Brown (Saxena and Brown, 2005).

Cellulose fiber is a naturally renewable resource, which has been widely applied in the flexible and transparent bioelectronics due to its robust mechanical property, biocompatibility, and biodegradability, as well as high surface area, low thermal expansion, and good flexibility. In addition, as the carrier materials or skeleton supporting materials, the properties of cellulose fiber could be altered and expanded through combining with conductive composites via in-situ polymerization or filtering, such as combing with carbon nanotube (Kizling et al., 2015) and graphene (Weng et al., 2011) for the flexible electrodes, metal oxide for the photovoltaic materials and solar cells (Chetia et al., 2015), as well as conducting polymers (Esmaeili et al., 2015) for the electrochemical sensors, and so on. Therefore, with outstanding mechanical, biocompatible, flexible and adaptable conductive properties, cellulose could bridge the world between nature biomaterials and flexible bioelectronics.

2.2.3. Chitin

Chitin is a nature polysaccharide existing in ordered crystalline microfibrils and abundant in marine animals, such as crab, shrimp, and lobster shells, from which the global chitin output is around 6–8 million tons (Yan and Chen, 2015). In addition, it is an insoluble linear polymer of β-(1→4)-linked 2-acetamido-2-deoxy-β-d-glucose units, and could be extracted and purified by chemical and biological methods through deproteinisation, demineralization, discolouration and bleaching processes (Arbia et al., 2013). Based on the different polymer chain arrangement, chitin could be divided into α-, β- and γ-chitin. As shown in Fig. 4,the adjacent polysaccharide chains of α-chitin arrange in an alternating antiparallel form (Minke and Blackwell, 1978; Sikorski et al., 2009), the chains of β-chitin are arranged in parallel form (Dweltz, 1961; Cuong et al., 2016), while γ-chitin has an antiparallel and parallel structure (Jang et al., 2004). The diverse chain arrangements lead to the different mechanical properties of each chitin isomorph form (Casteleijn et al., 2018). Except that, due to intrinsic molecular polarization induced by the non-centrosymmetric crystal structure of α- and β-chitin polymorphs, chitin is endowed with piezoelectric properties, which shows the possible usage in flexible piezoelectric electronics (K. Kim et al., 2018; W. Kim et al., 2018). Nevertheless, the poor swellability and high hydrophobility of chitin confine it to be soluble in concentrated acids, inorganic salts, strong or highly polar solvents, and

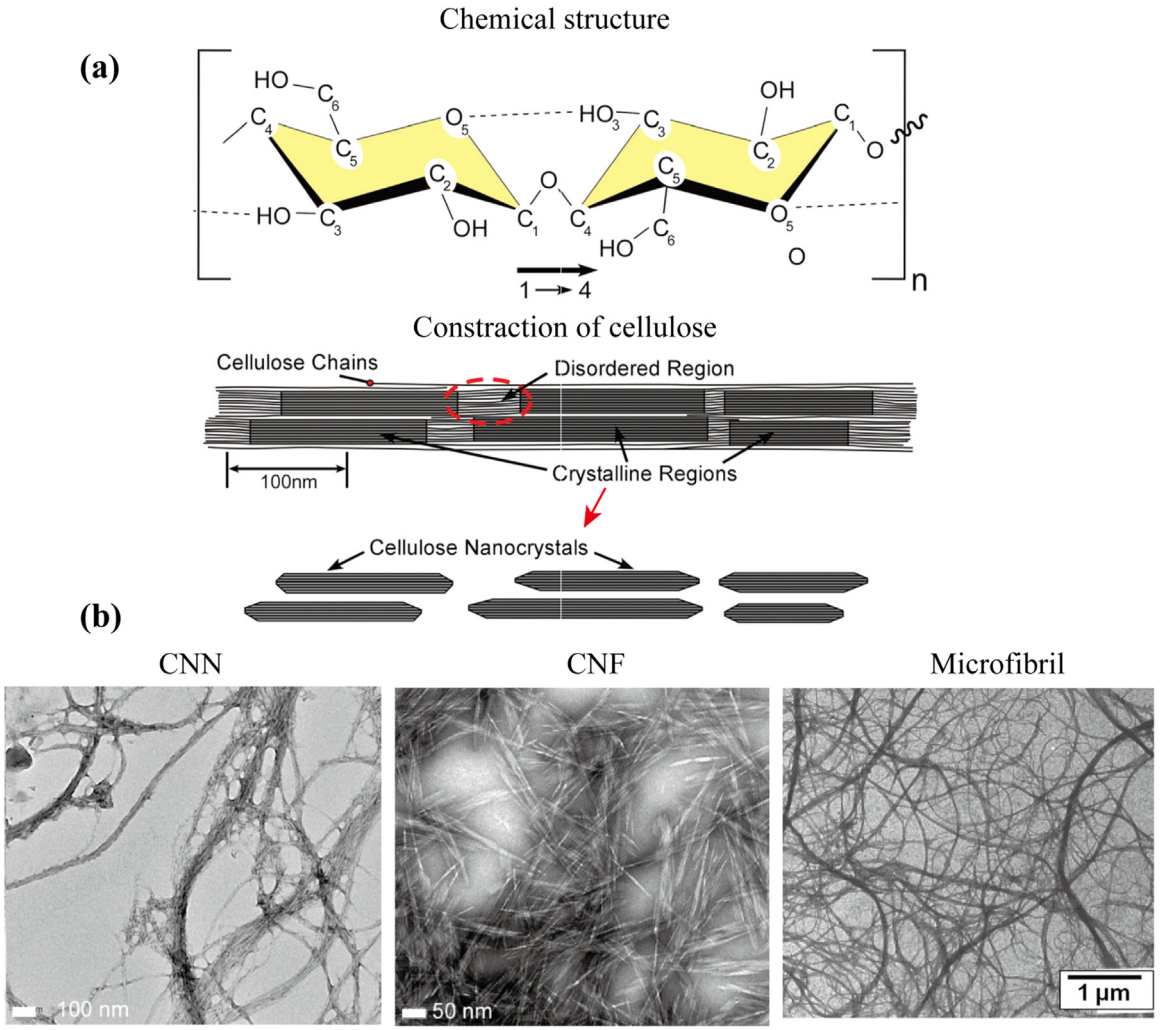

Fig. 3. The introduction of cellulose: (a) The chemical structure and construction of cellulose, (Moon et al., 2011), Copyright 2011, Royal Society of Chemistry; (b) The morphology of cellulose nanofibrils, nanocystals, (Xu et al., 2013) (Copyright 2013, American Chemical Society) and microfibrils (Moon et al., 2011).

others. Recently, a new method was developed by dissolving chitin in aqueous KOH/urea solution, which is a high-efficiency, energy-saving and green route to form transparent chitin film with extremely high strength, toughness and biocompatibility, expected to be substrate of flexible electronics (Junchao Huang et al., 2017). Therefore, chitin is a promising candidate natural material for the application in flexible and wearable electronics, considering its excellent biocompatibility, robust mechanical property and functional constitutes.

3. Biomaterials based flexible electronics and sensors

A sensor is a transducer which senses or detects some characteristics of environment, human activity and food safety and so on (Pothukuchi et al., 2010). Electronics with flexible, stretchable, and wearable features have risen exponentially to be next-generation electronics (Trung et al., 2015). Conventional strain-sensing platforms based on semiconductors and metal foils could not fulfill the requirements of wearable strain sensors because of their rigidity, low resolution, and low sensing range (usually < 5%) (Barlian et al., 2009). Various efforts have been made to develop flexible and wearable strain sensors by using nanomaterials as sensing elements coupled with elastic polymers as flexible, stretchable, and durable support materials, such as silicon nanoribbons (Kim et al., 2014), metal nanoparticles (Mayorga et al., 2018) or nanowires, and low-dimensional carbons (carbon nanotubes (CNTs), graphene, and carbon blacks) (F. Wang et al., 2017). In addition, to avoid the decomposition problem by using the traditional

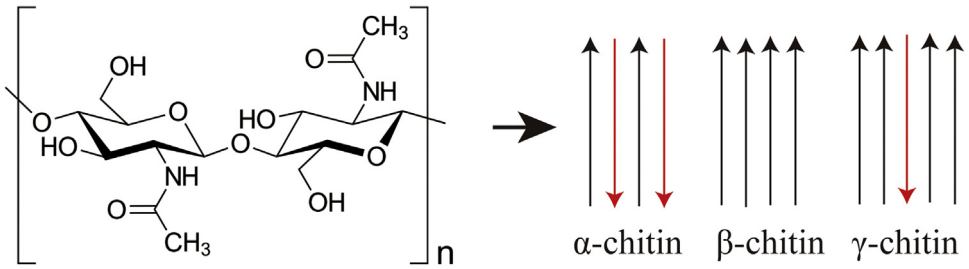

Fig. 4. The molecular and different polysaccharide chains arrangement of chitin.

plastics, biomaterials are chosen according to their robust mechanical property, biodegradability, biocompatibility and eco-friendly (Mühl and Beyer, 2014). For example, lecithin, the main component for the construction of lipid bilayer membrane in vitro has been applied in biosensors, in which the membrane proteins could be incorporated into the biosensor platform for measuring the function of membrane proteins (Reimhult and Kumar, 2008). In this part, PLA, PU and PDA, as well as SF, cellulose and chitin are respectively chosen as the representatives to explain application of the chemical-synthesized biomaterials and nature biomaterials based flexible electronics in improving the quality of human life and progressing of eco-friendly development.

3.1. Chemical-synthetic biomaterials-based flexible electronics and sensors

Recent advances in bio-nanotechnology have increased the demand for conductive, dielectric as well as other functional biopolymer nanocomposites. To become electrically conductive, polymers should possess conjugated π-bonds along their backbone, which loosely hold electrons and allow relatively easier delocalization of electrons (Balint et al., 2014). Flexible polymer-based dielectric materials that are used to store dielectric energy have widely been used in modern electronics and electric power systems, due to their relatively high energy density, light weight and low cost. Here, the PLA, PU and PDA based flexible electrics are highlighted to illustrate the novel applications of conventional biomaterials.

3.1.1. PLA-based flexible electronics and sensors

PLA has been widely used in the flexible sensors due to the polar groups in PLA molecules which induce the charge trapping effect and thus enhance photo- and thermal-sensitivity. The organic phototransistor (OPT) was fabricated using PLA as the gate dielectric material (Chu et al., 2016) (Fig. 5a), in which the charge trapping effect at the organic semiconductor/dielectric interface induced by the polar groups of PLA leads to reduced drain current of the device in the dark. To verify the photosensitivity, the PLA-based OPT was incorporated into a 10 × 10 array to sense a star object. The result displayed a similar pattern as the star object, indicating PLA-based OPT suitable for the optoelectronic applications. Similarly, one printable and flexible OPT was prepared through blending PLA with a common soluble organic semiconductor 2,7-dioctyl[1]-benzothieno[3,2-b][1]benzothiophene (C8-BTBT) (Jia Huang et al., 2017) (Fig. 5b). The sensitivity of the blended-OPT was improved due to the occurrence of the interfacial trapping effects at the molecular interfaces of C8-BTBT and PLA. Besides that, even under bending conditions, the photosensitivity was not affected, indicating the excellent flexibility of the device. Except on the application in the photosensitive devices, temperature sensing of PLA has also been studied (Xiaohan Wu et al., 2015). In this case, a three-arm stereocomplex PLA (tascPLA) was employed as dielectric and substrate materials, which increased the thermal stability of the flexible electronics. Moreover, the PLA-based flexible electronics was successfully applied to the skin-like temperature sensor (Fig. 5c). Therefore, combining with its transparency, degradability, and biocompatibility, the PLA-based flexible thermal electronics could be used as environment friendly electronics, implantable medical devices, and artificial skin.

To further understand the mechanism of the photosensing property induced by the interfacial effect between the organic semiconductors and dielectric polymers, several organic transistors were prepared including PLA-based transistor (Wu et al., 2017), in which PLA was one of the dielectric polymers to construct an organic semiconductor/dielectric interface. As shown in Fig. 5d, the charge carrier transportation rate was reduced because the charge carriers in the conducting channels was shallowly trapped by the functional groups of polymer dielectrics. Besides that, long OSC side chains and low polarity of polymer functional group induced weak shallow traps on the devices interfaces. However, only the traps with appropriate energy levels could lead to an obvious photosensitive μ change for the OFET, as indicated by the red rectangle (Fig. 5d). Therefore, PLA-based photo- and thermal-sensitive sensor was successfully fabricated due to the proper shallow traps between the interface of PLA and OSCs.

3.1.2. PU-based flexible electronics and sensors

For the fabrication of flexible sensors, the traditional printed circuits and electrical interconnects are made from copper foils and Sn/Pb solders (Liu et al., 1999), which have lots of feedbacks, such as high processing temperature, high cost and low fabrication speed. However, isotropically conductive adhesives (ICAs) show a huge promise in replacing the above materials. ICAs, composed by polymer and electrically conductive fillers could be processed under a low temperature, which is compatible with traditional printing methods. PUs have been widely applied in the composite of ICAs due to excellent biocompatibility, robust mechanical property, energy-economic, and eco-friendly. The water-based ICAs (WBICAs) were fabricated by using water-based aliphatic PU resin dispersant and micro-silver flasks, which showed a high conductivity (8×10^{-5} Ω cm) and long stability (at least 1440 h during 85 °C/85% RH aging)) (Yang et al., 2011). Besides that, the WBICA printed circuit with light emitting diode (LED) and radio frequency identification (RFID) antennas showed its excellent conductivity and easy processing on different flexible substrates (Fig. 6a), making it possible to construct green and low-cost flexible electronics. Based on this, poly (ethylene glycol) (PEG) was added as a curing agent of PU and reducing agent to reduce silver carboxylate for generating silver nanoparticles that could reinforce the conductivity (Li et al., 2013). The PU-based electrically conductive adhesive (ECA) performed a higher conductivity ($\approx 1.0 \times 10^{-5}$ Ω cm) which could be stably maintained even under bending, rolling, and compressing. In addition, it showed good adhesions to various flexible substrates and facile processing. Therefore, the PU-ECA could be applied in the flip-chip, three-dimensional integration, and wearable radio-frequency devices (Fig. 6b). Moreover, PU sponge could also act as a piezoresistive sensor due to its outstanding mechanical property. A flexible and sensitive PU microporous sponge was introduced with the coating of reduced graphene oxide (RGO) nanosheets as conductive layer (Yao et al., 2013) (Fig. 6c). The PU-RGO sponge performed high pressure sensitivity, long cycling stability (over 10,000 cycles) together with large-scale fabrication of the pressure sensors, which make PU-RGO sponge a promising low-cost E-skin. In addition, multiwall carbon nanotubes (MWNTs) (Shang et al., 2011) and RGO (Hsiao et al., 2014) were also added to improve the conductivity and mechanical property of PU-based electronics, expanding its application in flexible electronics.

3.1.3. PDA-based flexible electronics and sensors

PDA is a mechanically robust, thermochemically stable and environmentally friendly material; as such, it has been widely applied in tissue engineering, drug delivery system, photothermal therapy, and others (Liu et al., 2014; Ruan et al., 2013). Moreover, as self-polymerization of dopamine monomers with the inspiration of natural adhesive proteins in mussels, PDA could be coated on a wide range of material surfaces in dry or wet conditions (Lee et al., 2007). The excellent binding ability of catechols and amines in PDA expands the application of PDA in flexible electronics to functionalize the substrate surfaces via covalent or noncovalent modification (Ding et al., 2016). Wang et al. (2018) fabricated the strain sensor by coating the elastic band with carbon nanotube and PDA (pH 8.5) to increase the conductivity and mechanical property, which showed high performance on the sensitivity, durability and stability. Besides that, it was a good stain sensor candidate to monitor diverse deformation of the human body, potential to be expanded to HMI application. Different from traditional alkaline dopamine polymerization, PDA was polymerized in neutral condition to uniformly deposit on the bacteria cellulose (BC) film through hydrogen bonds (Xie et al., 2018). After deposition of PDA,

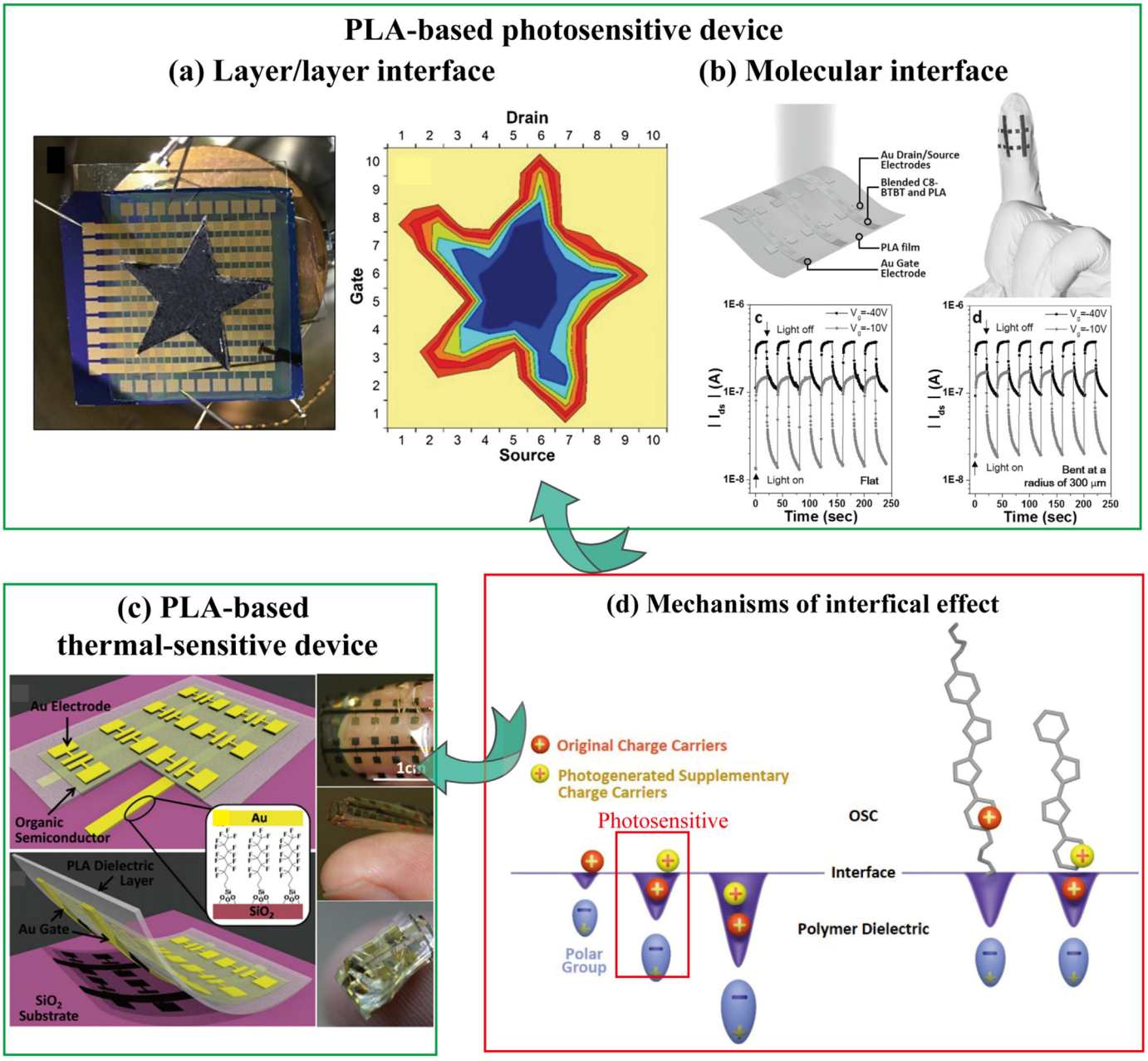

Fig. 5. The application of PLA in flexible (a, b) photo- (Chu et al., 2016; Junchao Huang et al., 2017; Jia Huang et al., 2017) and (c) thermal-sensitive (Wu et al., 2015) electronics and (d) the relative mechanisms (Wu et al., 2017) of interfacial effect between PLA and OSCs. Copyright, John Wiley and Sons.

except the improved mechanical property and biocompatibility, the conductivity and antibacterial property of BC/PDA film were both enhanced compared with those of bare BC film, which showed the advantages as the disposable electrocardiogram (ECG) electrode with outstanding signal stability and antibacterial properties. Therefore, PDA-based hybrid materials have enriched the application of PDA in various flexible electronics.

3.2. Silk fibroin-based flexible electronics and sensors

SF films provide an effective and attracting platform for the development of the bio-electronics with high biocompatibility and biodegradability, due to their compact and safe contact with the curved surfaces of tissues and organs. In addition, the robust mechanical properties, adaptable protein structures and excellent optical properties make SF a competitive candidate for the construction and application of flexible sensors, as it enables the elastic deformation/folding, programmable dissolution/biodegradation, and versatile processing at ambient conditions. Therefore, SF as an efficient medium has a widespread promotion in implantable devices, biosensor, and E-skin for electronic components transmission to the surfaces of various organs to get desirable functionality and conformal deformations with the organs. In this review, we mainly focus on new progress of SF in recent few years. To get further detailed information about the application of SF on flexible food sensor or various kinds of electronics, please refer to the published reviews (Koh et al., 2018; Tao et al., 2012; Zhu et al., 2016).

Optical diffraction-based biosensors are especially attractive in labeled and label-free bio-sensing on the account of the various diffraction efficiencies which depend on the bonding of chemical or biological molecular on a diffraction grating under a certain wavelength and detection angle, no matter with the fluctuations or damping of the probe lasers (Nolte, 2012). It has been reported that a set of bioactive

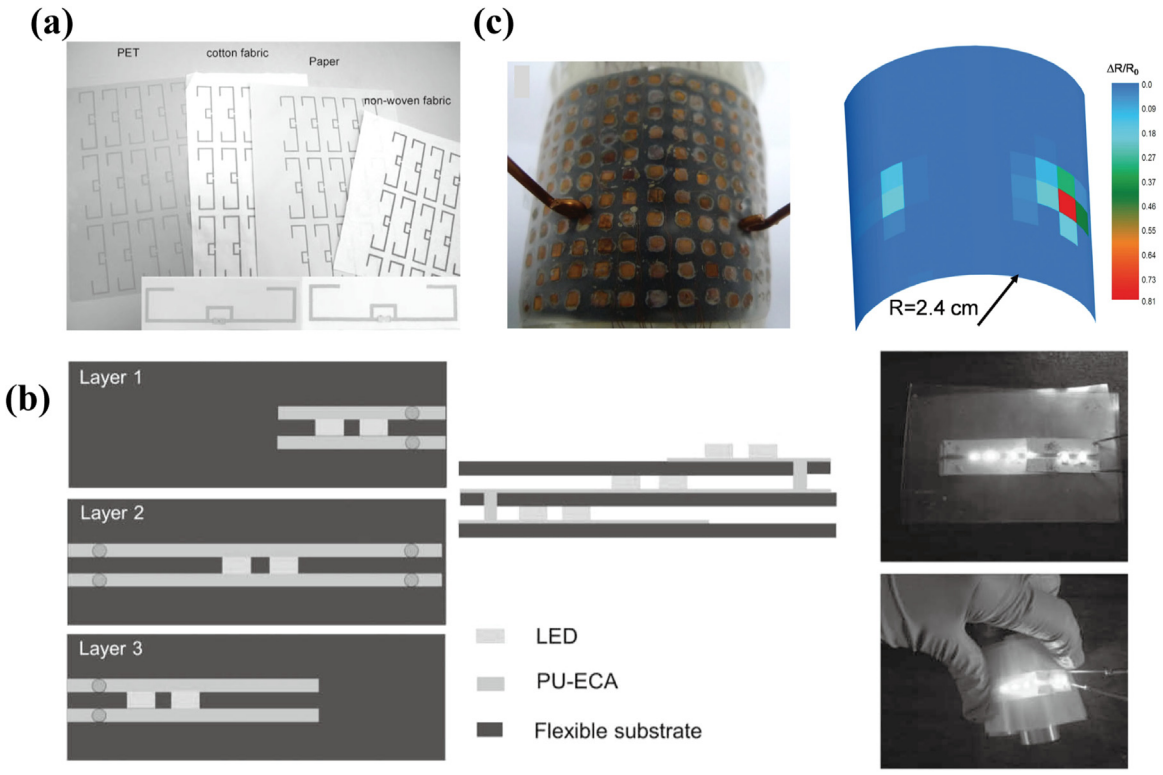

Fig. 6. The application of PU in the flexible electronics: (a) The PU-based WBICAs was used for printed circuit with LED and RFID on different substrates (Yang et al., 2011); (b) PEG blended PU-ECA for printed flexible circuits with LED and E-skin (Li et al., 2013); (c) Microporous RGO-PU sponge as piezoresistive sensor for the application as E-skin (Yao et al., 2013). Copyright, John Wiley and Sons.

diffractive optical elements (DOEs) were fabricated by functionalized SF film for optical diffraction-based sensing applications through modulating critical design sizes and facile water vapor annealing times (Zhou et al., 2017) (Fig. 7a). The results showed that 2 μm of the critical size of SF-DOEs owned a highest signal-to-noise ratio (SNR), meaning a much stronger optical signal. Through controlling the annealing time, the surface structure of SF-DOEs could be altered: the longer annealing time treatment, the longer degradation time due to the increased crystalline levels within the protein matrix. In addition, SF-DOEs showed excellent sensing activities: excellent optical qualities as sensitizing agents, precisely adjusted biological concealment via regulating the secondary conformation, hydration sensing, drug release monitoring upon degradation, and therapeutic treatment as well. In this work, a new class of transient optical devices were reported, which was safe to human and eco-friendly. In addition, the three-dimensional photonic crystals (3D PhCs) (also known as opals) of silk hydrogen film was introduced with the deformable, durable and biodegradable properties (Min et al., 2017) (Fig. 7b). The opals are prepared by self-assembly of colloidal crystals and their derivatives with a wide application in colorimetric sensors, photonic pigments, and full-color displays (Aguirre et al., 2010; Han et al., 2012; Ye et al., 2013). SF molecules were photo-cross linked with stilbene chromophore under short-wavelength UV exposure into the silk inverse hydrogel opals (SHIO) with porous structures. When weights were loaded to expose uniform pressure onto the SHIO, the reflection peak showed blue shifts due to the reduction of the interplanar space, which could be used to sense the intraocular pressure (IOP). In addition, when conformably loading the SHIO on an agarose gel hemisphere to mimic the human eye, the SHIO functioned like a concave mirror to reflect the red laser beam, which was expected to be an artificial *tapetum* to help improve human night vision. Furthermore, the UV-light cross linking decreased the degradation of SHIO, leading to long-term degradation of implantable devices.

To improve the mechanical and conductive properties of SF to widen its applications in flexible electronics, the synthetic or natural polymers were added, such as GO, nanotube, and PEDOT: PSS (Pan et al., 2012; Ryan et al., 2017; Teshima et al., 2016; Tseng et al., 2016; Y. Wang et al., 2016). Lv et al. (2017) prepared one kind of SF fibrous film hybridized with Kevlar nanofibrils through a biomimetic nanofibrous strategy (Fig. 7c). The adding of Kevlar nanofibrils improved the mechanical properties of SF film, two times higher than those of the pure SF films, due to the reinforcing effect of Kevlar nanofibrils and the increasing content of silk β-sheets. Furthermore, the Au single-crystal microflakes synthesized with the support of SF nanofibrils were patterned on the SF/Kevlar-nanofibrils membrane, showing excellent mechanical flexibilities, even being twisted, bended or wrapped without any clear conductivity decay. Ma et al. introduced a novel and highly conductive reduced GO/SF film (biopaper) with a large area (hundreds of cm^2) produced by printable GO/SF (98/2, w/w) solution via seriography (Ma and Tsukruk, 2017). This kind of biopaper generated a 10^6 increase in conductivity (up to 10^4S/m). Besides that, it showed excellent mechanical and flexible properties: no mechanical weak interfaces between dissimilar materials and unimpaired functionality of GO/SF microcircuits even after thousands of punitive folding cycles and chemical attack by harsh solvents. This novel approach upon low-cost and portable solution for printable and uniform micrometer-scale conductive circuits is potential to be used as wearable health monitors, E-skin, conformable displays and flexible biosensors.

Besides that, wearable devices are essentially tiny computers with the capabilities of sensing, processing, storage and communications, which have emerged as powerful tools for individual healthcare and wellness. Tseng *et al.* developed a novel trilayer wearable sensor (Fig. 7d) which could be mounted on the tooth enamel for the detection of foods during human ingestion (Tseng et al., 2018). This wearable sensor was constructed based on a conformal radiofrequency (RF) construct (an active layer encapsulated between two reverse-facing split

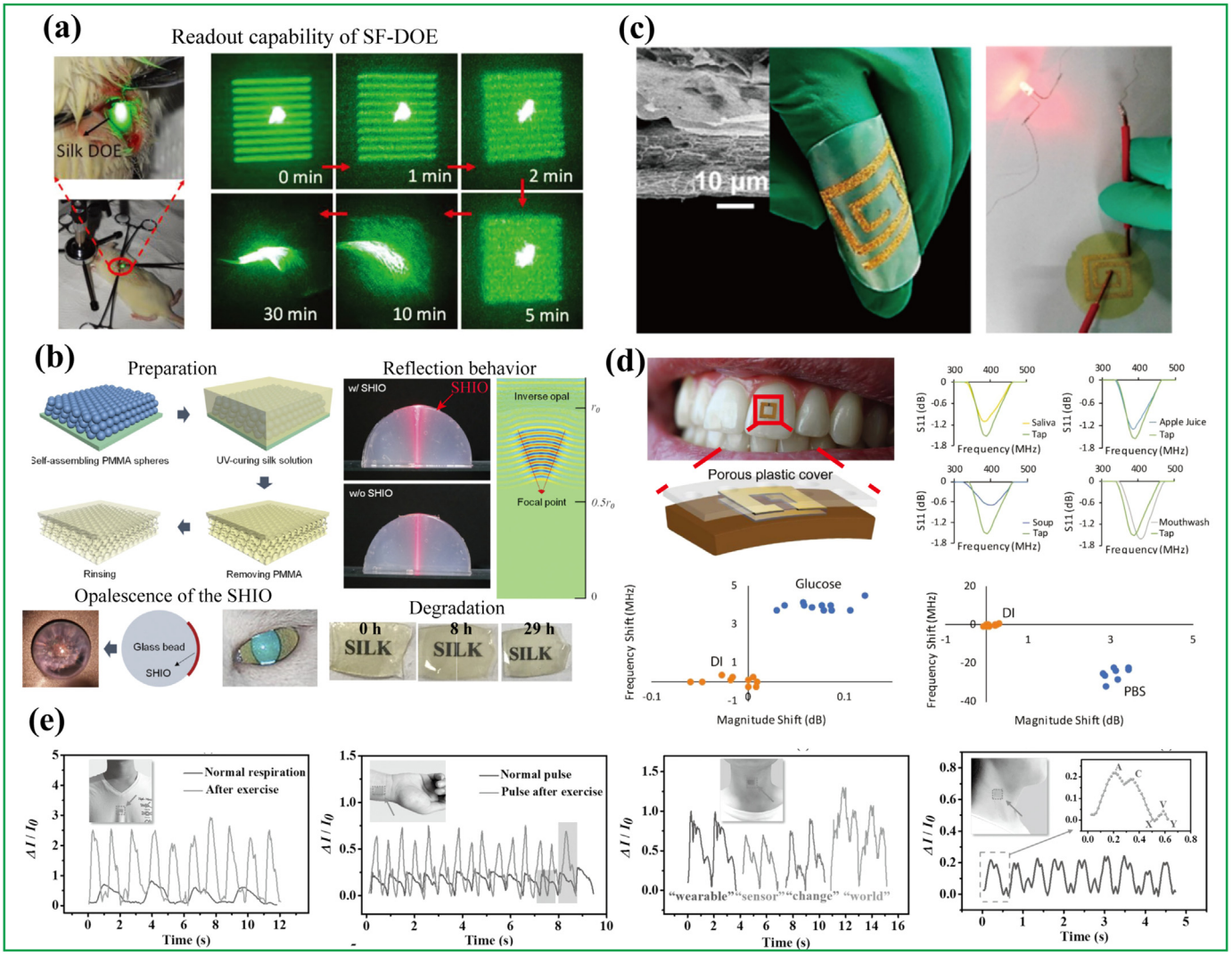

Fig. 7. The application of SF in the flexible bioelectronics: (a) Functional SF films for the application of optical diffraction based biosensors with read-out capability (Zhou et al., 2017), Copyright 2017, John Wiley and Sons; (b) Deformable and conformal SF hydrogel film as the inverse opals with the potential to improve the night vision of human with longer degradation time without affecting the visibility (even after 29 h) (Min et al., 2017), Copyright (2017) National Academy of Sciences; (c) Functional SF nanofibrous membrane as the substrate and electrode of the flexible electronics (Lv et al., 2017), Copyright 2017, American Chemical Society; (d) SF-based functional trilayer SRR sensor for tooth-mounted and wireless monitoring of the oral cavity and food consumption with high sensitivities and performances (Tseng et al., 2018), Copyright 2018, John Wiley and Sons; (e) Carbonized SF nanofiber member for the application as flexible, transparent and sensitive E-skin which could sense the tiny vibration of human organs (Wang et al., 2017), Copyright 2017, John Wiley and Sons.

ring resonators). On one hand, silk film was located as the outer layer due to its biocompatibility, controllable ability of absorption and swelling to different thickness, and penetrable ability by biomolecules, as well as adaptable transport properties by altering the conformation of SF proteins. On the other hand, silk film was also acted as the active layer for *in vitro/vivo* responses to solvents with varying degrees of ionic strength, glucose concentration, and solvent concentrations. Both *in vitro* and *in vivo* results showed good responses, high sensitivities, and outstanding repeatability and stability. The RF wearable sensor provides a new insight to the application of SF-based biosensors in various environments and allows distributed and multiplexed sensing via the additional responsive interlayer.

Furthermore, flexible and stretchable artificial E-skin has been eye-catching due to its great prospects in the application of wearable electronics and smart human-machine interaction (HMI). The pressure sensing-based E-skin has been wildly used in the health monitoring, smart robots and disease diagnostics (Chou et al., 2015; Y. Liu et al., 2017; Wang et al., 2015; Yang et al., 2018). Q. Wang et al. (2017) reported one flexible piezoresistive pressure sensors with the carbonized SF nanofiber membrane (CSilkNM) as the active materials to construct the skin-like pressure sensor (Fig. 7e) with high sensitivity (34.47 k/Pa), low detection limit (0.8 Pa), short response time (< 16.7 ms) and very high durability (> 10 000 cycles). When adhered on human skin to detect the human physiological signals and delicately collect physical signals, it showed highly sensitive and effective responses based on the different organs of humans.

Expect above applications, SF also has been used in the implantable sensor as a stiff support that enables insertion in mouse brain tissues (Lecomte et al., 2017), memristive device with bipolar resistive switching ratio of 10^4 and programmable device lifetime characteristics (Yong et al., 2017), and biosensor for the detection of nitric oxide (NO) at nanomolar levels (Musameh et al., 2018), as well as bio-triboelectric generator generating a high voltage with large surface area (Kim et al., 2016). Therefore, advances in SF-based flexible electronics would open new avenues for employing biomaterials (nature or synthesized biopolymers) in the design and integration of high-performance and high-biocompatibility electronics for future applications in biosensors, wearable sensor, E-skins, and biomedical diagnosis.

3.3. Cellulose-based flexible electronics and sensors

Cellulose as a natural biomaterial has been widely applied to flexible sensors due to its eco-friendly, easy woven to films, large surface areas, excellent mechanical and alterable conductive properties. To alter the conductivity and mechanical properties of flexible biosensor, some conductive materials, such as nanotube, graphene oxide, metals and semi-conductive polymers, are combined based on the various applications.

Flexible strain sensors could be divided into resistive-type, capacitive-type and piezoelectricity based sensors, which transduce mechanical deformations into electrical signals (Amjadi et al., 2016). Importantly, materials for flexible stain sensors should offer outstanding and stable mechanical and electrical properties due to repeated tensile and compressive strains (Amjadi et al., 2016; Si et al., 2017). Flexible stain sensors have gained growing applications in various aspects, such as HMI for signal collection of bio-mechanical movements (Argall and Billard, 2010; Kumar et al., 2012; Lim et al., 2015; Roh et al., 2015), virtual reality devices (Alshaal et al., 2016; Repetto and Riva, 2011), and smart living (Adapa et al., 2018). To overcome the disadvantages of some flexible sensors with weak response reliability and mechanical stability, one self-healing hydrogen stain sensor was firstly reported for HMIs with especially sensitive, stable and spontaneous self-healing capability at ambient temperature without any other stimulus (Cao et al., 2017) (Fig. 8a). With the inspiration by the multiple hydrogen bonding connection of deoxyribonucleic acid (DNA), the hydrogen stain sensor was constructed by layer-by-layer method, in which carboxyl cellulose nanocrystals (C-CNC) was employed not only to construct supramolecular multiple hydrogen bonding network with chitosan-decorated epoxy natural rubber (ENR) latex, but also a three-dimensional nanostructured conductive network with carbon nanotube (CNT). The results showed that the strain sensor could detect the signals with a low stain detection limit of 0.2%, fast (only 15 s) and repeatable self-healing ability. Furthermore, when detecting tiny human motions and HMI, it showed highly distinguishable and reliable signals of human motions, and bright prospect in controlling robot to improve the real-time speaking of the mute. However, when the stain increased from 0% to 10%, cracks appeared in the interconnected conductive network, leading to the significant decrease in current signals and enhanced signal intensities. Therefore, to realize the application of the stain sensor on recording both tiny and strenuous human motion, more work on improving stability of the conductive network should be carried on. In addition, silver nanofiber was added to construct a cellulose-silver nanofiber hybrid film with high conductivity, robust mechanical, thermally stable and transparent property (Ji et al., 2017). The hybrid film could response upon the multi-touch of human fingers (Fig. 8b), showing the potential to be the cover layer of flexible touchscreen panels (TSPs) in smart watches, wrist bands, smart glasses, and fitness or medical monitors without affecting touch performance. Furthermore, one flexible cellulose-based sponge (Cheng et al., 2018) was introduced with multifunction, which could be a flexible stain sensor via responding press and resistance, as well as a thermoelectric (TE) material for the self-powering by utilizing the temperature differences between the body and environment, showing the potential application in artificial intelligence products or remote medical monitoring devices. Meanwhile, Rajala et al. (2016) also displayed the excellent property of cellulose as a piezoelectric sensor material.

Moreover, cellulose has also got lots of attention in the application of flexible biosensors. A new fluorogenic esterase biosensor was prepared (Fig. 8c) in a chemo-enzymatic approach to activate the cellulose

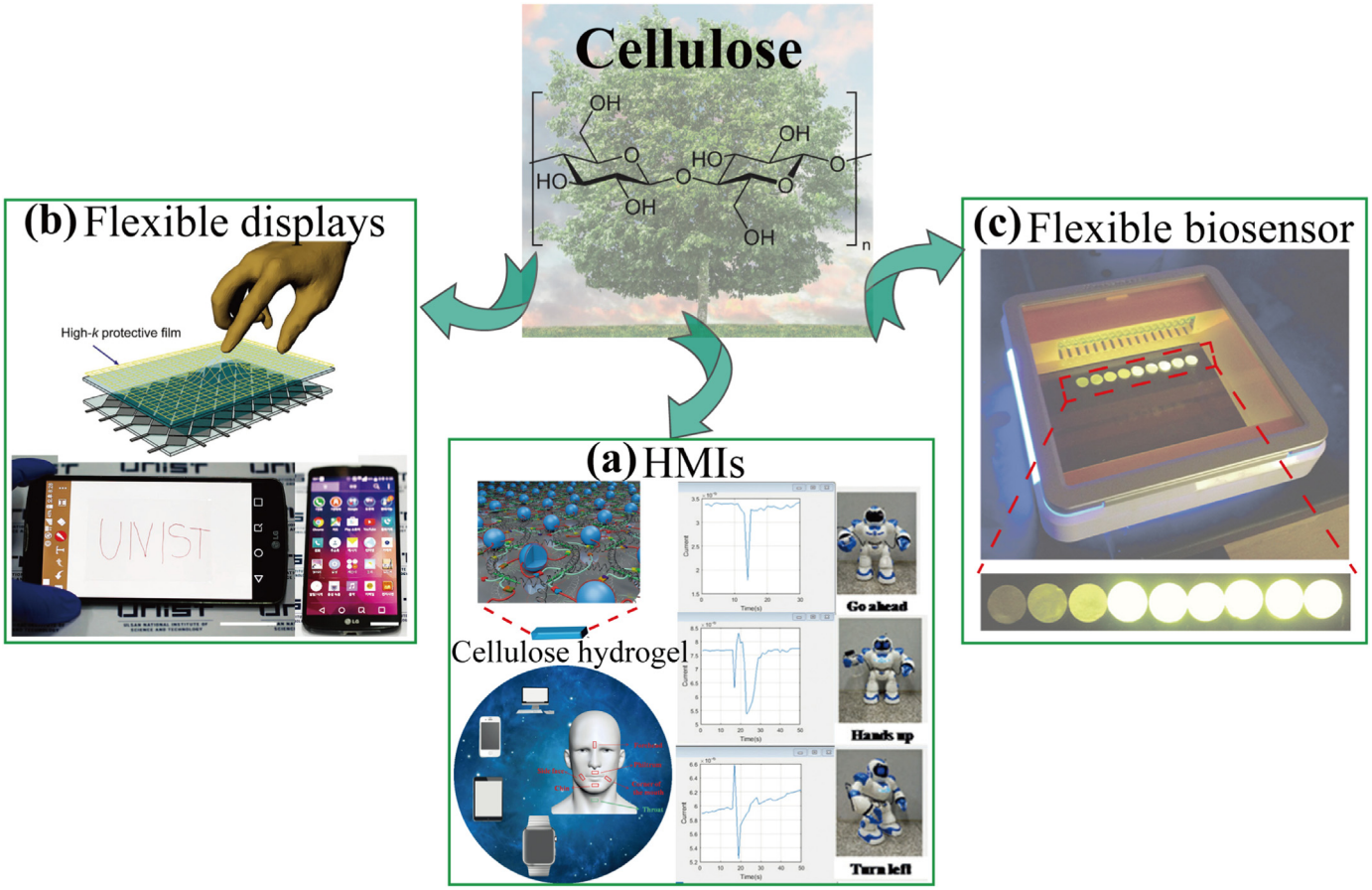

Fig. 8. The main applications of cellulose in (a) HMIs (Cao et al., 2017), Copyright 2017, John Wiley and Sons; (b) flexible displays (Ji et al., 2017), Copyright 2017, John Wiley and Sons, and (c) biosensors for fluorogenic esterase detection (Derikvand et al., 2016), Copyright 2016, American Chemical Society.

substrate, which broadens the application to cellulose papers, gauzes, and hydrogels (Derikvand et al., 2016). In addition, to predict some complications after subarachnoid hemorrhage (SAH), a novel label-free cellulose surface-enhanced Raman spectroscopy (SERS) biosensor was explored with the gold nanoparticle (AuNP), which enhanced localized surface plasmon resonance (LSPR) (K. Kim et al., 2018; W. Kim et al., 2018). The cellulose biosensor performed low detection limitation and high reproducibility, potential to be expanded to various neurosurgical diagnoses. In addition, a recyclable pH biosensor formed by cellulose could be used for human health monitoring based on the visual color changes against each pH (Devarayan and Kim, 2015). Except on the health monitoring and protection of human, cellulose biosensor has also been used in food and environment detection (Agarwal et al., 2012; Campanella et al., 2003; Kumari and Chauhan, 2014; Liu and Mattiasson, 2002; Nakatani et al., 2005). Interestingly, cellulose paper was also reported not only for oxygen sensor construction, but also as the self-powered bioelectrochemical devices (Conzuelo et al., 2018; Kizling et al., 2015).

In a conclusion, cellulose-based flexible electronics display lots of benefits to not only human health monitoring, but foods and environmental detection and governance, which promotes the progress of medical hygiene, health monitoring, food safety and environment governance.

3.4. Chitin-based flexible electronics and sensors

Chitin is an increasingly popular biomaterial with excellent properties, such as biocompatibility, biodegradability, bioactivity, antimicrobial properties, and low immunogenicity (Casteleijn et al., 2018), which has been extensively applied in the field of tissue engineering (Torres-Rendon et al., 2015), drug delivery system (Dev et al., 2010), energy storage (Ding et al., 2018), sensing (Chen et al., 2017; Naghdi et al., 2017; Solairaj et al., 2017), and flexible electronics (Jin et al., 2016). Recently, chitin film as the structural and functional platform has been widely used in flexible and wearable electronics and devices. In contrast to traditional paper, chitin transparent paper with good foldability, printability and transparency was fabricated in a bottom-up self-assembly regeneration of chitin nanofiber (ChNF) by centrifugal casting of a homogeneous chitin solution (Fig. 9a) (Jin et al., 2016). It displayed high performance in the fabrication of organic light-emitting diodes (OLED) devices, making it possible as the substrate of flexible green electronics. In addition, one novel chitin 2D nanosheet was synthesized by the same bottom-up assembly process of two-layer molecular chitin aggregations with super stability and amphiphilicity (Fig. 9b) (You et al., 2017). Though a combinational process of emulsifying and carbonization, it could be converted to the conductive carbon nanosheet that could be the conductive layer of strain/stress sensor with a high sensitivity. Hence, the hybrid films of chitin and carbon nanosheet offer the fully bio-based flexible devices with sustainability and biodegradability. To mimic the cuticles of insects and marine crustaceans, chitin nanofibers and silk-like proteins were chosen for fabrication of transparent CS film with excellent mechanical property (Fig. 9c) (Hong et al., 2018). The CS film showed excellent performances in the application of flexible electronics: combination with graphene field-effect transistor as the structural platform to fabricate contact-lens-based wireless sensor for glucose concentration in rabbit tear fluids; association with silver nanofiber as conductor for a wireless and wearable heater, and the possible usage as a scratch-resistant transparent display. Besides that, ChNF was reported to guide the growth direction of gold (Au) nanocrystals with diverse forms (nanoribbon, nanokite, and nanosheet) through binding and reducing Au ions on its deacetylated surface (Chen et al., 2017). Meanwhile, the Au nanosheets capped with ChNFs could be the conductive layer of flexible sensors for humidity and pressure sensing. Moreover, chitin film, a flexible piezoelectric material, could be the functional platform of the flexible piezoelectric sensors to realize a high-fidelity paper-type speaker and microphone with a wide operation frequency range (K. Kim et al., 2018). Furthermore, the active sites of chitin film (hydroxyl and acetylamido group) could be modified to functionalize the surface for the feasibility of flexible biosensors, such as the cross-linking with enzymes (Krajewska, 2004), chelation with heavy metal ions (Wan Ngah et al., 2011), covalent bonding and electrostatic interactions for fixation of biomolecules (Suginta et al., 2013), and so on. Therefore, chitin is a promising biomaterial for the application of flexible and wearable electronics, such as wireless glucose, pressure and piezoelectric sensor and wireless heater.

3.5. Room-temperature printing of DNA-based flexible electronics

Recently, a tremendous progress has been made on the development of printable electronics with mechanically flexible substrates, which performance well with high conductivity and reproducibility. Compared with the traditional fabrication of electronics, printable electronics have become urgent social needs due to the advantages of low-cost, large-area fabrication, time-saving, and eco-friendly. Printing electronics on flexible substrates are potential to develop flexible displays, sensors, E-skin, and others (Fan et al., 2009). However, high-temperature processes (> 150 °C) are typically used for printed electronics, which limits the use of common flexible substrates due to the distortion caused by heat (Minari et al., 2014). Minari, Kanehara and Liu et al. have accumulated lots of experience on the printable electronics fabrication at room temperature (RT) with high conductivity, resolution, and reproducibility. Organic thin-film transistors (OTFTs) were printed with π-junction gold nanoparticle (NP) ink on flexible substrates and exhibited average field-effect mobilities of 7.9 and 2.5 $cm^2V^{-1}\ s^{-1}$ on plastic and paper substrates, respectively (Fig. 10a) (Minari et al., 2014). It suggests that RT printing is potential to be applied in a large scale of thin-film electronic devices, such as light-emitting devices and photovoltaic cells. Based on this, much advanced OTFTs were fabricated with 1-micron resolution by printing methods at RT (Fig. 10b) (X. Liu et al., 2016). In the fabrication of the OTFTs, spontaneous patterning of narrow lines and gaps (down to 1 μm) of Au nanopartilces, as well as discrete organic semiconducting thin films, were achieved via forming sharply defined wettability contrast by the parallel vacuum ultraviolet (PVUV) system, which is promising for fully solution-processed, large-area, and high-resolution flexible devices. Recently, flexible electronics were combined with DNA as the dielectric layer to fabricate non-volatile transistor memory that displayed high performance in the hole mobility and memory window (Fig. 10c) (Liang et al., 2018), indicating that OTFTs are competitive candidates to combine with biomaterials for various applications. Therefore, the RT-printing process opens a new way to fabricate electronics on a large scale of flexible substrates, expending the application of flexible electronics in various fields, such as artificial skin, flexible display and biosensors via combining with biomaterials.

In a conclusion, we introduced the novel application of traditional chemical-synthesized and natural biomaterials which have been widely applied in industrial products and daily life. Due to the excellent mechanical property and biocompatibility, their new application in flexible electronics have been explored, which give us inspiration that exploring and studying the traditional biomaterials would bring lots of research interests and novel applications in flexible electronics to make our life much convenient and smarter.

4. Conclusions and future perspectives

Compared with petroleum-based materials, the biggest advantage of biomaterials is their capability of degradation in the environment, which allows for the sustainable development of flexible electronics. In this review, several representative biomaterials are introduced from the view of novel applications in biosensor, flexible displays, wearable devices, and others. Following that, the RT-printing processes for large-

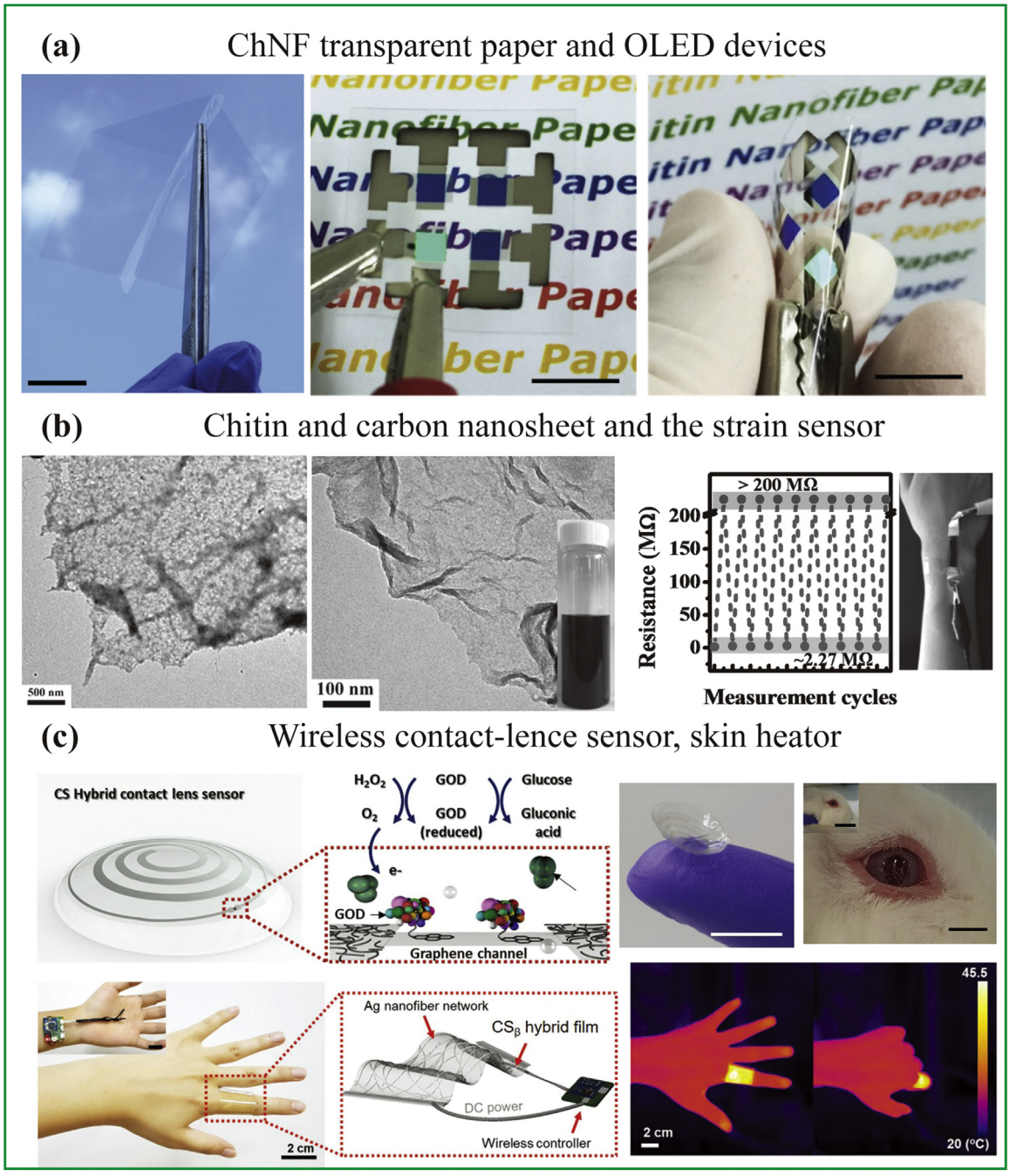

Fig. 9. The application of chitin films in flexible electronics: (a) ChNF transparent paper as the substrate of OLED devices (Jin et al., 2016); (b) the morphology of chitin and carbon 2D nanosheet and the application of carbon nanosheet as thhe conductive layer of strain sensor (You et al., 2017); (c) the CS hybrid transparent film as the wireless contact-lence glucose sensor and skin-attachable heater (Hong et al., 2018). Copyrights, John Wiley and Sons.

scale flexible OTFTs are discussed with high performance and new application in memory transistors by combining with DNA. Therefore, biomaterials exhibit specific advantages on the development and application of eco-friendly flexible bioelectronics.

In addition to satisfying the basic monitoring function, it is now possible to give the sensor with intelligent functions, such as the ability of self-healing when damaged, thereby enabling to realize long lifetime devices. Stimuli-responsive materials with sophisticated controllable shape-changing behaviors are also highly desirable in fabrication of smart sensors, which will devote to the development of electronic medical and health-care devices. However, some additives, such as GO, gold and silver nanomaterials are used to improve the mechanical properties of flexible electronics, which will cause the environmental stresses due to the weak degradation. Based on this issue, some measurements should be taken, such as the recycle of these materials and improvement of the usage lifetime of flexible electronics, and so on. Furthermore, even though completely degradable materials have made great strides as well, they are still not fully converted in industrial composting plants, which have seriously affected the sensitive waste management system. Therefore, E-waste must be carefully managed before it falls into an irreversible pollution matter. Besides raising the awareness of consumers to take the initiative to recycle, purchasing alternatives to traditional devices is also crucial. The usage of biomaterials would still bring different social values by promoting the development of plastics. Except that, it is also necessary to explore the adaptability of the degradation time of the various component

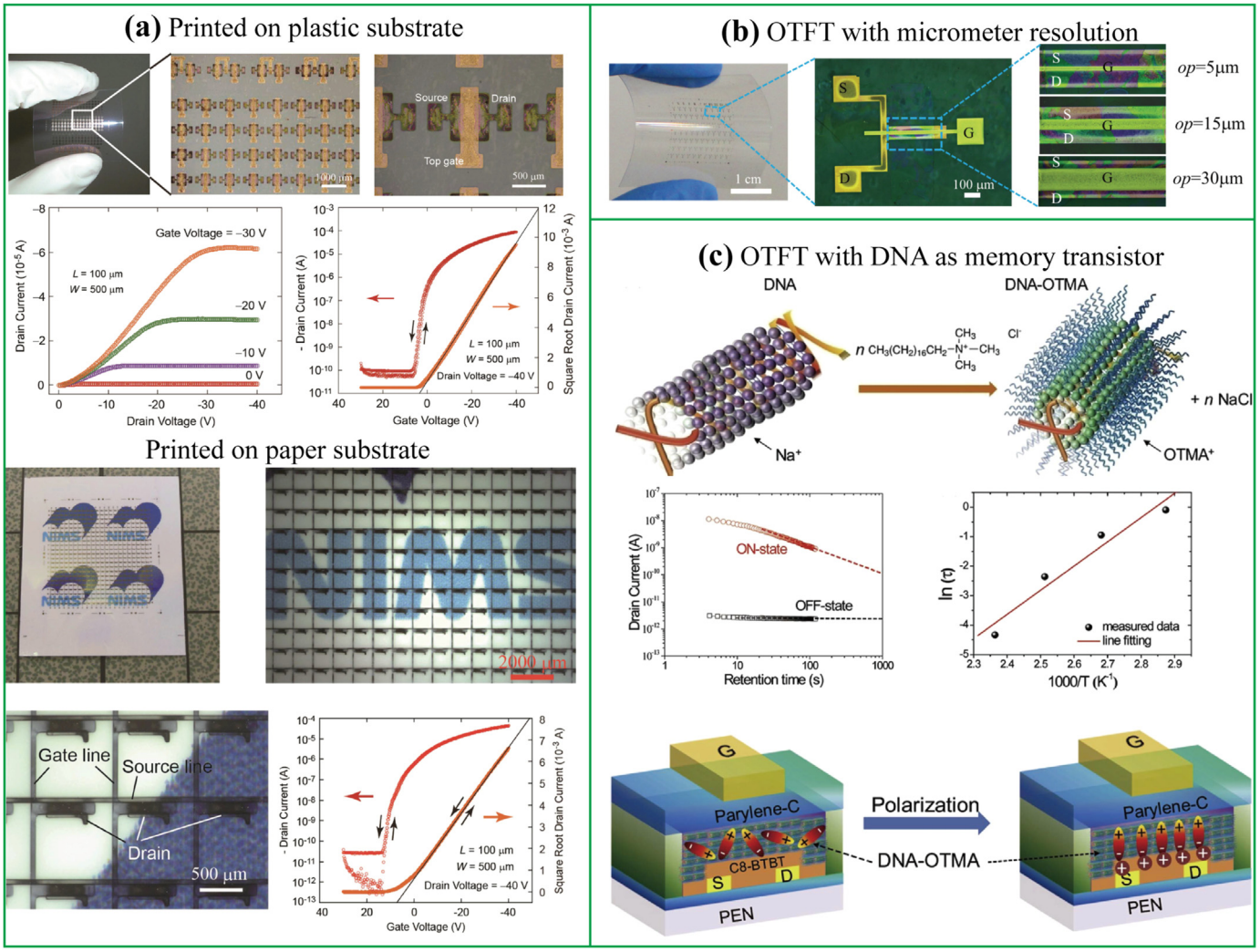

Fig. 10. The application of printable electronics on flexible substrates as OTFTs: (a) RT-printing of OTFTs on the plastic and paper substrate (Minari et al., 2014), Copyrights 2014, John Wiley and Sons; (b) Advanced OTFT fabricated at RT with 1-micrometer resolution (Liu et al., 2016), Copyrights 2016, John Wiley and Sons; (c) RT-printing OTFT combined with DNA as the memory transistor (Liang et al., 2018), Copyright 2018, Elsevier B.V.

materials in the device.

Another important consideration to note is the reliability of these bio-degradable materials under operational stress such as heating for prolonged use, UV exposure to the Sun, environmental temperature and humidity for detection stability, as well as cyclical mechanical deformation. Except above mentioned, the preparation technology of flexible electronics should be improved and widen as well. RT-printing methods are promising to be applied for construction of flexible electronics with sophisticated and multi-functional patterns. Meanwhile, device areas ranging from small (centimeter squares) up to large (meter squares) could be also achieved. Therefore, for the sustainable development of eco-friendly flexible electronics, more and more novel and functional biomaterials should be discovered and studied. Besides that, the functions, properties and fabrication methods of biomaterials-based flexible electronics should be explored and improved, such as by combining with internet of things or mimicking the human nerve systems for the development of precision medicine, neurorobotics, neuroprosthetics and Artificial Intelligence (AI), and so on.

Acknowledgments

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