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REVIEW

Recent Progress in Cellulose-Based Flexible Sensors

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ABSTRACT

Flexible sensors are attractive due to potential applications in body exercise and ambient gas monitoring systems. Cellulose and its derivatives have combined superiorities such as intrinsic and structural flexibility, ease of chemical functionalization, moisture sensitivity, and mechanical stability, enabling them to be promising candidates as flexible supporting substrates and flexible sensitive materials. Significant progress consequently has been achieved to improve mechanical, electrical, and chemical performance. The latest advance in materials synthesis, structure design, fabrication control, and working mechanism of novel cellulose-based flexible sensors are reviewed and discussed, including strain sensors, humidity sensors, and harmful gas sensors. Various strategies were summarized to enhance sensor performance by surface group modifications, inorganic and organic conducting fillers optimization, multilayer structure design. Newly emerged processing techniques of self-assembly, vacuum filtration, and 3D printing were introduced as well to construct multiscale microstructures. The integration of multiple sensors toward smart and healthy exercise monitoring system is briefly reviewed. The facing challenges and future opportunities of cellulose-based flexible sensors were discussed and proposed at the end. This review provides inspiration and guidelines on how to design and fabricate cellulose-based flexible sensors.

KEYWORDS

Cellulose; flexible sensors; gas sensors; humidity sensors; strain sensors

1 Introduction

Recently burgeoning development of flexible sensors has been changing conventional rigid features by endowing it with multifunction of comfortability, remote control, disposal usage, and ergonomic design, which promotes the prospects of human activities monitoring and living ambient air evaluation. Flexible human activity and ambient air monitoring systems can be utilized for continuous, in-time feedback, comfortable monitoring [1]. The measurement of various signs, such as muscle movement, pulse, respiration rate, humidity level, and harmful gas, urgently demanding on the development of flexible sensors [2].

Consequently, flexible sensing electronics are emerging to capture signals of strain, humidity, harmful gas, and other health-relevant signs. Compared to rigid sensors, flexible designs make it possible to be conformably attached to skin or integrated with textiles, which requires materials and devices that are all soft, reliable, and human-friendly. Deformable structures design is an effective approach to fabricate

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flexible electronics, while it is complicated to balance various performances [3]. Exploring intrinsically flexible materials with desired functionalities is a more attractive strategy.

Cellulose, as a flexible, green, and sustainable material, has the most abundant natural source. It was initially reported by French chemist Anselme Payen in 1838 when he isolated it from wood chips by nitric acid-ethanol pretreatment and mechanical dispersion [4,5]. Cellulose is a linear chain polymer with plentiful hydroxyl groups, containing crystal and amorphous parts [4]. The monomer unit in cellulose has three hydroxyl groups, enabling it to form intra- and intermolecular hydrogen bonds [5,6]. These hydrogen bonds help to form a highly ordered three-dimensional network crystal structure. Due to the strong affinity of these hydrogen bonds, basic cellulose fibers tend to bind to each other and induce microfibers to gather into bundles. Multiple microfibril tows are packaged into a larger unit [6,7]. Printing paper is a typical product made from cellulose [8,9]. Thus, rich hydrogen bonds and hierarchical structures indicate the excellent mechanical performance (i.e., ultimate strength, modulus, and flexibility) of cellulose, which provides an alternative flexible sensor substrate partially instead of current material usages of plastic, glass, and silicon [9,10].

Cellulose possesses many derivatives, ranging from microscale cellulose microfibrils to nanoscale cellulose nanofibers and nanocrystals, which are building bricks to create the 3D matrix and multiscale structure for conducting materials and hydrogels [8,10]. Various functional and conducting fillers, like carbon [11,12], metal-based nanoparticles, or metal oxide [13] could be embedded within cavities to compose conducting path. Cellulose-derived hydrogels and aerogels are also matrix choices for extremely lightweight applications [5,10]. Since the electrical performance of these conducting composites incorporated with different inorganic or organic fillers is very sensitive to applied strain changes, cellulose-based conducting composites are selective functional materials of strain sensors [14].

Cellulose brings hydroxyl and ether groups, and other modified functional groups, which enables cellulose itself could be a chemical sensor [11]. It attracted enormous research interest in novel burgeoning fields in biomedicine, medical service, food storage, and flexible electronics, especially flexible sensors [14–16]. Thanks to the rich hydroxyl group and chemical modifications, cellulose is not only used as a flexible substrate layer, but also as a sensitive functional layer of sensors [10,17]. Its chemical structure enables chemical absorbance in the aqueous medium through numerous hydrophilic -OH groups [8]. The high donor reactivity of the hydroxyl group can trigger a wide range of chemical variability. Chemical functional groups are introduced into the cellulose molecular chain through chemical modification, which can adjust and control surface hydrophilic, charge polarity, and specific reactivity [8,18]. The chemical sensitivity of cellulose and its modifications make them a candidate for harmful gas sensing.

Preparations and fabrications are critical processes to producing multiscale structures and sensitive materials. The self-assembly technique [19] and the vacuum filtration method [20] are rapidly assembled of functionalization sensitive materials layer, such as graphene [21], carbon nanotubes [22], and metal oxide semiconductor [23] into a large-scale interpenetrating cellulose network. This approach can be achieved by stacking porous cellulose paper, which has advantages of cost-effectiveness, fast and straightforward operation, good controllability, and mass-production. Note that cellulose itself is not porous, it only can form hierarchy porous structures through various processing techniques.

In addition, attempts have been made by printing technology [24], physical depositing technology [25], chemical process [26], and assembly technique [27]. Through spin coating [28], electrospinning [29], and 3D printing process [30], dopant materials (like semiconductors [31], conductive polymers [8] or carbon materials [12,21,22]) interpenetrate cellulose networks, forming conducting path. Such porous interconnected three-dimensional nanostructure of conductive cellulose-based composites provide effective migration channels for electrons and ions, which can improve chemical reactivity.

Three-dimensional printing techniques can precisely control the printing process to build desired microstructures, thereby enabling the sensitive materials layer with specific functionalities [27,29,30,32]. To control the complex architecture of cellulose and its composites, the strategies demand developments in local alignment, multi-material printing, and gradient printing.

Microstructure regulation and interfacial engineering are common strategies for tuning the sensitive materials layer with specific functionalities [33]. The solution process can rebuild the hydrogen bond among cellulose chains and fillers to construct an internal interface. The interfaces between nearby layers are realized through sequential adsorption of oppositely charged components and ion pairings to form laminated morphology. This fabrication approach could balance the thickness and microstructure to enhance stress transfer. Through surface group modification, a variety of material assembly, high elastic properties, and excellent response can be obtained. It has potential prospects in the assembly of flexible, transparent, and portable electronic devices, such as organic light-emitting diodes, emerging intelligent electronics, supercapacitors, lithium batteries, and sensors [34–37]. Among them, flexible sensors have been a research hotspot in recent years, and publications in this field have increased rapidly.

Here, we focus on the progress in the materials design and fabrications of various cellulose-based flexible sensors to monitor body strain and ambient moisture level and possible harmful gas, toward a smart and healthy exercise system (Fig. 1). The hierarchical structure and multifunctional surface groups of cellulose and its derivatives are reviewed in particularly considering their applications in flexible sensors. The design, fabrication, mechanism, and performance of the latest developed flexible sensors were reviewed and discussed in detail, including strain sensors, humidity sensors, and harmful gas sensors. The integration of multifunctional sensors and the smart system is a future research direction. The existing challenges and future perspectives to advance cellulose-based flexible sensors are discussed and proposed at the end.

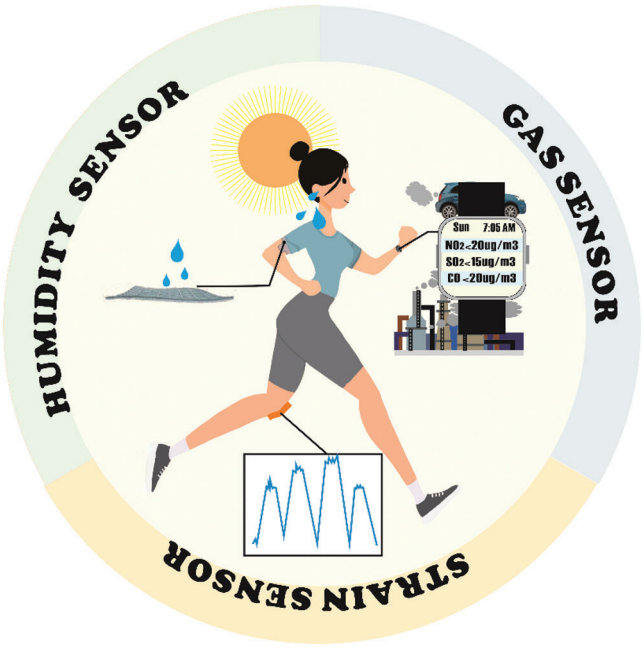

Figure 1: A smart healthy exercise system by integrating various cellulose-based flexible sensors

2 Cellulose-based Gas Sensor

The sense of smell is one of the basic perceptions of the human body. Gas sensors can sense the types and concentrations of different gases and have broad application prospects in the fields of biomedicine, environmental monitoring, food safety, aerospace and military. Gas sensors, characterized by high sensitivity, selectivity, stability, speed, and low power consumption and cost are the main field to be developed [10,38]. With the development of the Internet of Things and artificial intelligence technology, research on gas sensors will be promoted from functional performance research to an intelligent development route. Actively exploring the new principles, new materials, new mechanisms, and new devices of gas sensors has important scientific significance and use value for comprehensively improving the artificial sense of smell [14,39].

Gas sensors can be divided into electric sensors that detect the electrical signal, optical sensors for optical signal, and PH sensors for visual signal [40]. The electrical signal sensors include semiconductor type [41], electrochemical type [42], catalytic combustion type, quartz crystal microbalance type [43], and surface acoustic wave type [44]. In which the semiconductor and PH sensor have attracted significant attention due to their simple preparation, convenient operation and easy miniaturization [45]. Novel materials from biomass resources show outstanding potential in gas sensors [10,46].

Cellulose is a highly sustainable and environmental-friendly material as substrates of sensitive, selective and bio-friendly gas sensors [47]. The cellulose-based gas sensors improve the performance of inadequate sensitivity, response/recovery speed, reversibility, and selectivity. Cellulose has great potential in gas sensors applications owing to high sensitivity for various gases such as nitrogen dioxide (NO_2), ammonia (NH_3), carbon monoxide (CO), carbon dioxide (CO_2), and volatile organic compounds (VOC) [48].

Some previous works have proved the improvement of the gas sensing performance through doping strategy. Yang's group [49] chose bacterial cellulose (BC) as the supporting material of gas-sensitive layers. They employed *in-situ* chemical oxidative polymerization to prepare sulfosalicylic acid (SSA) and poly (2-acrylamido-2-methyl-1-propane sulfonic acid) (PAMPS) co-doped polyaniline (PANI) sensing composite on the surface of BC nanofiber. The process achieves high exposure of active sites, orderly accumulation of crystal islands for gas-sensitive sensing, and improved PANI surface reaction. It had high response values and sensitivity as shown in Fig. 2a.

BC is an excellent supporting material that can be used as functional nanomaterials for gas sensors. Abdali's group [26] combined PANI with functionalized graphene to improve the sensing performance. They combined polyaniline with functionalized graphene and then esterified with bacterial cellulose to form a bacterial cellulose-aminographene/polyaniline nanocomposite. The sensor has high sensitivity (50 ppm) and selectivity to carbon dioxide. And the sensor response has an approximately linear relationship with the CO_2 concentration.

Various functionalization methods were employed on the metal nanoparticles to improve the performance and sensitivity of their polymer nanocomposites. Sadasivuni et al. [50] reported the process of hydrothermal synthesis of iron oxide-containing cellulose nanochips. The sample has high mechanical strength, superparamagnetic property and high dielectric constant. As a nitrogen dioxide (NO_2) gas sensor, it can detect one part per million gas shortly.

Recent studies have incorporated metal-oxide nanoparticles in organic materials and tested their gas sensing properties. Hittini et al. [51] reported a novel, sensitive, selective and low-temperature hydrogen sulfide gas sensor based on copper oxide nanoparticles in carboxymethyl cellulose-based composite materials. Copper oxide is prepared by a colloidal microwave-assisted hydrothermal method, which can precisely control the size of the nanoparticles. Carboxymethyl cellulose (CMC) has been widely used as a support material or reducing agent for the synthesis of metal oxide nanoparticles.

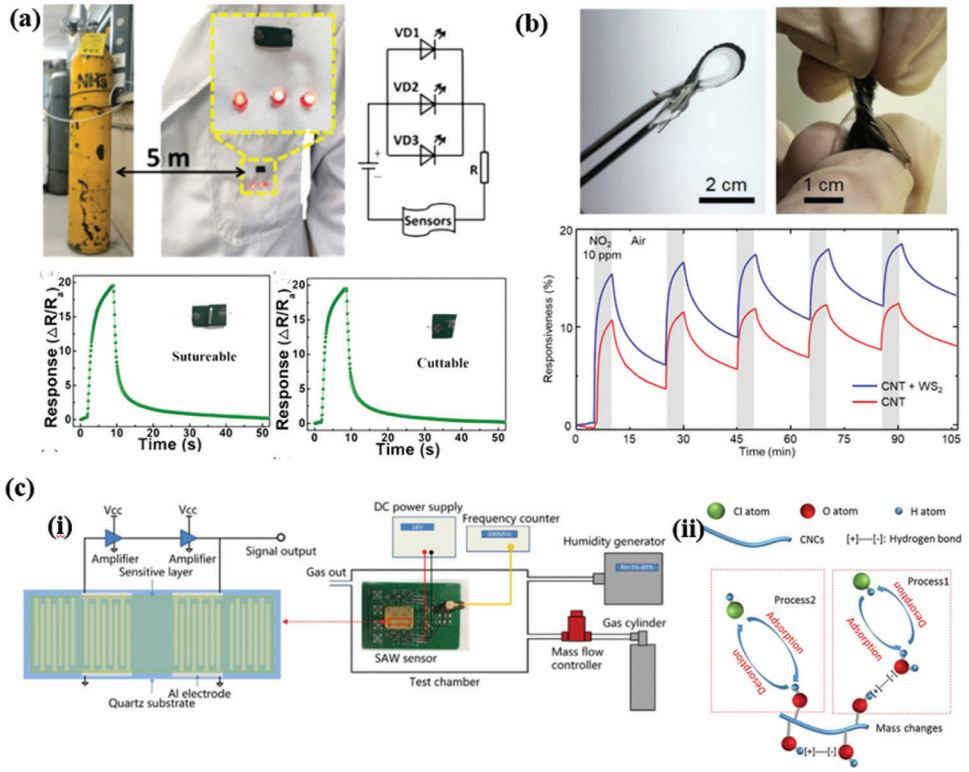

Figure 2: Different kinds of gas sensor based on cellulose: (a) Photographs of the BC/PANI-SSA/PAMPS aerogel sensor and dynamic response of the sensor after stitching and shearing [49]; (b) Photographs of the bent and twisted CNT-WS_2-cellulose paper mounted on a polydimethylsiloxane substrate, demonstrating its deformability and it sensitive to NO_2 [22]; (c) The schematic diagram of the SAW sensor (i) and HCl adsorption and desorption processes on cellulose nanocrystals layer (ii) [56]

Hybrid integration of carbon nanotubes (CNTs) and transition metal dihalides (TMDC) on cellulose paper may also be used to detect other harmful gases. Lee et al. [22] reported a highly deformable gas sensor with higher sensitivity, by integrating multi-walled carbon nanotubes (CNT) and nano-layered transition metal dihalides (WS_2 or MoS_2) on cellulose paper. Even in the case of severe deformation (such as severe folds and wrinkles), the sensor can detect gas stably and sensitively as shown in Fig. 2b. The hybrid integration of carbon nanotubes and TMDC on cellulose paper can be applied to low-cost portable devices that require reliable deformability.

It is generally regarded that a buffer layer can affect the absorption behaviors of the target gas. Kim et al. [52] proposed a mechanism by which the buffer layer affects the absorption behavior of the target gas. In their research, graphene was directly transferred to a cellulose membrane and used this membrane as a supporting substrate. The halloysite nanotubes as a buffer layer effectively increase the surface area of gas molecules, thereby improving the sensitivity of the graphene gas sensor built on the environmental-friendly cellulose film.

Designing the structure or morphology of conductive polymer can enhance the sensing performance of materials. Yang et al. [53] proposed a mechanism that the exposure of active sites on the surface of sensitive materials and the orderly accumulation of crystal islands can increase the resistance change of sensitive materials. They co-doped polyaniline with sodium dodecylbenzene sulfonate (DBSA) and poly (2-acrylamide o-2-methyl-1-propane sulfonic acid) (PAMPS). DBSA is a good dopant for polyaniline, and the uniform coating of polyaniline is very important to the conductivity and gas sensitivity of the composite material.

Since cellulose nanofiber (CNF) aerogel has a high degree of porous structure, it is very sensitive to vapor. Qin et al. [54] reported a new type of porous mixed aerogel as a fluorescent sensor for detecting nitroaromatic (NAC) vapor. It has good water solubility and can form electrostatic interactions in water. The highly porous structure of aerogel facilitates the rapid diffusion of NAC vapor into the mixed aerogel. The mixed aerogel has a high sensitivity to NAC vapor.

The gas sensor is prepared by the above process, and the sensing mechanism is that the sensitive network material with cellulose as the support reacts with the gas and the resistivity of the material changes. The disadvantage of this type of sensor is that it cannot modulate small signals. To amplify the output signal of the sensor, a field-effect device structure, a quartz balance type and a surface acoustic wave type are used to improve the sensitivity of the sensor.

Jia et al. [55] reported a new method, which is to prepare a sensor coating on a quartz crystal microbalance (QCM) to achieve fast and accurate ammonia detection. Using electrostatic layer-by-layer self-assembly technology, positively charged polyethyleneimine and negatively charged graphene oxide are sequentially assembled on the surface of negatively charged electrospun cellulose acetate (CA) nanofibers. The gas-sensitivity test based on the QCM sensor not only shows a low detection limit and fast response, but also shows good reversibility and selectivity in ammonia detection. Tang et al. [56] reported that cellulose nanocrystals can be used as a sensitive and selective coating on acoustic wave (SAW) sensors for in-situ HCl gas detection (Fig. 2c). It is still a challenge to distinguish gas molecules only by electrical signals. In order to improve the selectivity, a sensor array [57] composed of sensors with different surface chemical properties and a pattern recognition strategy to recognize gas molecules are proposed [58].

3 Cellulose-based Humidity Sensor

Humidity is one of the important factors that cause biological reactions of the human body, and physical and chemical changes in various products. The control of the environmental humidity range guarantees the normal life and production of human beings. Therefore, effective humidity detection is particularly important in the fields of industrial manufacturing, agriculture, food and drug storage, meteorology, medical health, and aviation [9,14]. The humidity sensor is the most common humidity detection and measurement equipment. An ideal humidity sensor should be able to determine humidity under different conditions, while having good performance such as high sensitivity and accuracy, wide detection range, good stability and cyclic responsiveness. Humidity responsive materials are an important part of smart materials. Conductive polymers, carbon-based materials, porous ceramics, metal oxides and other materials become ideal materials for humidity response. However, such materials still face challenges in terms of preparation cost, non-toxicity and degradability.

As the most abundant polysaccharide in nature, cellulose has good water absorption and swelling properties due to the abundant hydrophilic groups (-OH) in the chain [9], making cellulose a good choice for preparing humidity sensors. Combined with materials such as metal oxides, carbon materials, and polymers, cellulose and its derivatives can be used to design high-performance humidity sensors that meet the requirements of various applications.

The paper-based humidity sensor has good flexibility and biocompatibility, it has potential applications in the fields of respiration monitoring, non-contact switching and skin humidity monitoring. Guan et al. [59] used glycerol trimethylammonium chloride to modify the cellulose by a solution stirring method, and prepared a cellulose paper as the active material and substrate of the humidity sensor (Fig. 3a). This modification effectively regulates the content of hydrophilic groups, greatly improves the sensitivity of the sensor, and reduces the response time to 25 s. This work provides technical support for low-cost, large-scale manufacturing for developing multifunctional humidity sensors. Meng et al. [60] used cellulose nanocrystals and polyols (i.e., glycerol, xylitol and sorbitol) to prepare a flexible,

moisture-sensitive composite film. The addition of glycerol, xylitol and sorbitol improves the flexibility and color rendering of cellulose. The obtained composite film has a good response to humidity signals.

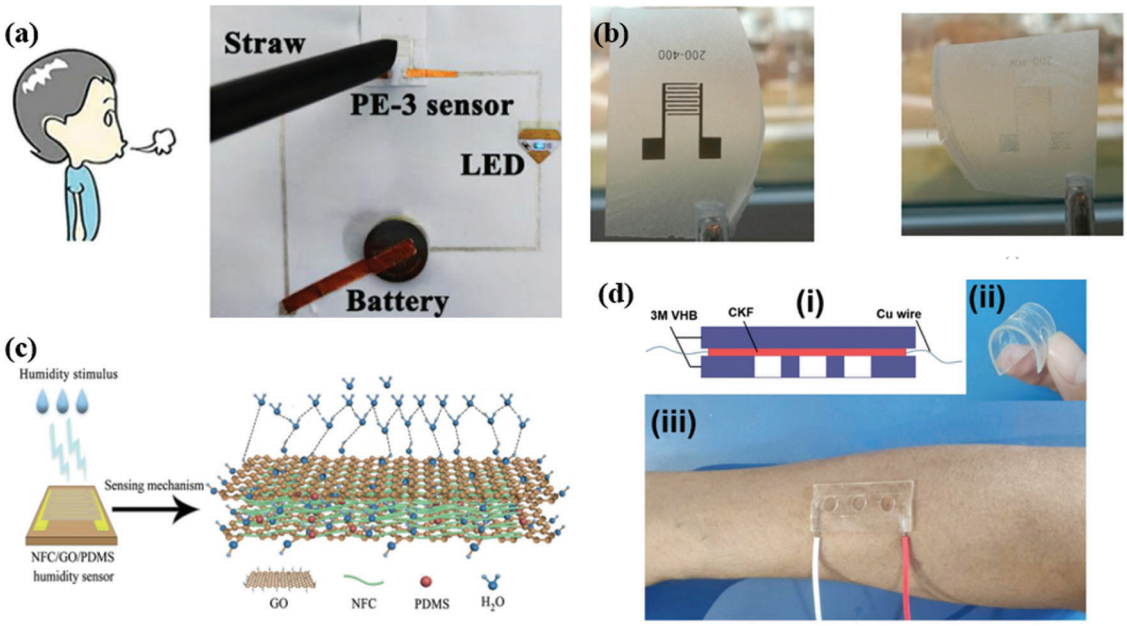

Figure 3: Cellulose-based humidity sensor: (a) A simple visual non-contact humidity device based on cellulose [59]; (b) Photos of the fabricated devices on cellulose film with electrodes [61]; (c) Schematic structure of cellulose/KOH composite ionic film-based skin moisture detector (i); the assembled skin moisture detector displays excellent flexibility and transparency (ii); the detector was fixed onto the human skin to assess the humidity changes (iii) [64]; (d) Humidity sensing mechanism for the nanofibrillated cellulose/graphene oxide/polydimethylsiloxane humidity sensor [62]

Developing a transparent and fully biodegradable humidity sensor can be used for air conditioning monitoring, smart food packaging, and respiratory and body temperature monitoring. It is a challenge to fabricate humidity sensory devices with flexibility and especially the transparency, to meet the requirement for integration into flexible/wearable devices, since the sensitive elements and substrates such as inorganic crystals and conductive materials are usually rigid and opaque. Rivadeneyr et al. [61] used CNF film as the active material layer, and prepared a PEDOT: PSS transparent electrode on the sensing layer by a screen printing process as shown in Fig. 3b. Wang et al. [62] prepared a humidity sensor based on cellulose/KOH composite membrane (Fig. 3c). The sensor has good transparency (87.14%), higher optical transmittance at 550 nanometers, mechanical stability, tensile strength (37.8 MPa) and elongation at break (43%), and a faster response/recovery time (6.0/10.8 s).

The impregnation and drying process has advantages in fabricating low-cost humidity sensors. Kan et al. [63] dipped the cellulose paper in a solution of cobalt chloride ($CoCl_2$). The modification of cellulose by cobalt chloride improved the hydrophilic performance of the active film. The sensor is in a range of RH 11%–98%. It shows a good response, and the color of the cellulose film changes from blue to red at the same time, and the color change is reversible. The sensor can still maintain excellent voltage response performance after 3000 times of folding. The device has been successfully applied to human breathing monitoring and movement frequency tracking. Biodegradable and renewable cellulose nanocrystal (CNC) was employed as the humidity sensing material due to its unique properties such as large surface area and abundance of hydroxyl groups. Wang et al. [37] prepared a humidity sensor with wood-derived cellulose

paper (WCNs). The humidity sensor based on WCNS enjoys the advantages of high sensitivity, fast response, low hysteresis, and a wide working range of relative humidity.

Reduced graphene oxide(RGO)/tin dioxide coated on cellulose paper could promisingly combine the advantage of high surface area, porosity, and exceptional electron transport. Khalifa et al. [25] prepared graphene-coated cellulose paper by dip coating. The active layer showed fast response and recovery as well as excellent repeatability characteristics. This work provides a low-cost, lightweight, and biocompatible material for smart wearable electronic devices. Yang et al. [64] prepared a humidity sensor based on cellulose/graphene/polydimethylsiloxane (PDMS) composite materials. The composite material is prepared through the process of blending-ultrasonic dispersion-freeze drying, and the addition of anhydrous ethanol in the preparation process can prevent the generation of cracks during the freeze-drying process. The combination of multiple materials improves the defects of a single material. Among them, nanofibrillated cellulose (NFC) and graphene oxide (GO) have strong adsorption of water molecules and are used as the flexible substrate of the device; the addition of PDMS can effectively improve the flexibility and stability of its porous structure (Fig. 3d). Kim et al. [65] prepared CNF-GO composite fiber by wet spinning. The composite fiber has a maximum Young's modulus of 23.9 GPa and maximum tensile strength of 439.4 MPa. A humidity sensor was prepared based on the mixed fiber. The humidity sensor with the GO concentration of 5 wt% responds to the moisture signal. Experimental results show response time delays of 40 s and 45 s, which is acceptable in humidity sensing.

The humidity-sensitive functional layer with a micro-nano hierarchical structure is designed for water molecules exchange between the coating and the external environment. Zhu et al. [66] used cationic cetyl trimethyl ammonium bromide (CTAB) to modify carbon tubes (CNTs). The CNTs were modified by CATB, in which way the positive charges were introduced on the surface of CNTs. The conductive fibers were achieved by electrostatic self-assembly process that positively charged CNTs are absorbed to the surface of negatively charged 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-oxidized cellulose fibers (TOCFs). A large number of hydrophilic hydroxyl groups on the surface of negatively charged cellulose provide adsorption sites for water molecules. The cellulose/carbon nanotube fiber network is formed under static electricity. Li et al. [67] used an imprinting process to prepare an asymmetric pattern on the surface of a cellulose nanofiber/graphene oxide composite film. The asymmetric pattern improves the moisture transfer rate and the flexibility of the composite film through local moisture constraints, thereby greatly improving the response range and sensitivity of the composite film to humidity.

Cellulose can play the role of the micro template for controlling the growth of nanostructures. Sahoo et al. [68] used hexamethylenetetramine as a surfactant and deposited nano-scale spherical particles and short rod-shaped ZnO crystals on the surface of the cellulose through a one-pot synthesis. Then, ZnO-Cellulose Nanocomposite materials are obtained. The ZnO-cellulose nanocomposite powder is placed in a hydraulic press for tableting processing. The humidity sensor can be used at room temperature, and detect humidity signals in the relative humidity (RH) range of 40%–90%.

The electronic humidity sensor is composed of a transducer and a layer of humidity-sensitive materials. Cellulose is an optimal layer of humidity-sensitive materials. Various kinds of transducers include quartz crystal microbalance (QCM), surface acoustic wave resonator (SAW), and capacitive micromachined ultrasonic transducer (CMUT). Yao et al. [69] firstly prepared a humidity sensor by depositing renewable cellulose nanocrystals as a sensitive material on the electrode. Then fabricated a quartz crystal microbalance humidity sensor, prepared polydopamine@cellulose nanocrystal nanocomposite (PDA@CNC) by self-polymerization on the CNC surface, and used it as a filler material to form a functional nanocomposite with graphene oxide [70]. The results show that adding PDA@CNC to the graphene oxide film can significantly improve the sensitivity of the sensor while maintaining high stability in the entire humidity range. Chen et al. [71] deposited a cellulose nanocrystal film on the

surface of the QCM to prepare a humidity sensor. The experimental results showed that the humidity sensor with CNC load of 2 μg has good logarithmic linearity, high sensitivity (32.35 Hz/% RH), good reversible performance, and long-term stability at RH of 11%–84%. Wang et al. [44] spin-coated bacterial cellulose on the top layer of a quartz surface acoustic wave (SAW) vibrator. The bacterial cellulose film is a highly porous network composed of ultrafine interwoven fibers, and its surface contains a large number of hydroxyl groups, which significantly improves the absorption capacity of the SAW sensing layer for water molecules. Zheng et al. [72] used a nitridation-oxidation wafer bonding process to prepare a capacitive mass humidity sensor. In this work, cellulose nanocrystalline material was spin-coated on the top layer of the vibrator as a moisture trapping layer. Experimental results show that the humidity sensor has the characteristics of high sensitivity response and recovery speed, low hysteresis, good repeatability, and long-term stability. This work provides a way to prepare a high-performance miniaturized humidity sensing platform.

It presents that cellulose is used as a humidity-sensitive material and/or substrate in the design of humidity sensors. Low cost, good hydrophilicity, good hygroscopicity and easy processing of cellulose are major reasons for the rapid development of cellulose-derived humidity sensors. In addition to cellulose itself, its derivatives, such as cellulose nanofibers, cellulose nanocrystals, and bacterial cellulose have also been extensively studied to make humidity sensors. These cellulose-derived humidity sensors have been proven to have good sensitivity and accuracy, a relatively wider detection range, better stability, fast and selective response capabilities.

4 Cellulose-Based Strain Sensors

With the development of emerging technologies such as artificial intelligence and wearable electronics, strain/pressure sensors that can transform external deformation and pressure loads into electrical signals, have been attracting more and more attention. Flexible strain/pressure sensors have many advantages, such as simple structure, low cost and high sensitivity. It is mainly composed of conductive active materials, flexible substrates and electrodes [73]. Among them, the performance structure of the active material plays an important role regarding performance indicators, like device sensitivity, flexibility, working range, stability, etc. In recent years, to develop low-cost, sustainable, and environmental-friendly wearable sensors, cellulose hydrogels and aerogels based on natural polymers are subject to strain/stress due to their biodegradability, biocompatibility, and non-toxicity. The preparation of such sensors has attracted much attention.

A chemical cross-linking agent was used to form a three-dimensional network structure with cellulose molecules, or the cellulose molecules were used to form free radicals to achieve intermolecular covalent cross-linking. A cross-linked network was formed by using non-covalent forces such as chain entanglement, hydrogen bonding, and hydrophilic-hydrophobic interactions. The dual-network hydrogel is composed of two interpenetrating networks. The first layer of network structure is a rigid and brittle polymer, and the second layer is a flexible and tough cross-linked network. Pei et al. [74] used a dual-network hydrogel formed by a combination of two interpenetrating networks. The first network structure used $FeCl_3$ as an oxidant to polymerize polypyrrole (PPy) in a dispersed nanocellulose solution to form a nanocellulose-polypyrrole network. The second cross-linking network is to combine cross-linking of nano-cellulose polypyrrole and polyvinyl alcohol (PVA)-borax gel to form a hybrid hydrogel with enhanced viscoelasticity, strength and toughness. Such dual-network hydrogel exhibits excellent mechanical properties, and its best mechanical strength can reach 5.7 MPa. The strain sensor prepared based on the hydrogel can self-heal, and the repeated cycle test shows excellent durability. This work has potential in biomedicine, biosensors, and flexible electronic devices. Jing et al. [17] prepared a polyvinyl alcohol/cellulose nanofibril (PVA/CNF) hydrogel with a double cross-linked network. Based on dynamic covalent reactions, they combined dynamic borate bonds, metal-carboxylate coordination bonds and

hydrogen bonds. The covalent bonds can be broken and re-form under certain stimulus conditions, thereby obtaining good self-healing properties, which can spontaneously self-heal within 15 s. Based on the hydrogel, a highly transparent capacitive strain sensor is prepared, with a light transmittance of over 90% and high sensitivity to micro-force testing (Fig. 4a). This work shows great potential in electronic skin, personal health care and wearable devices.

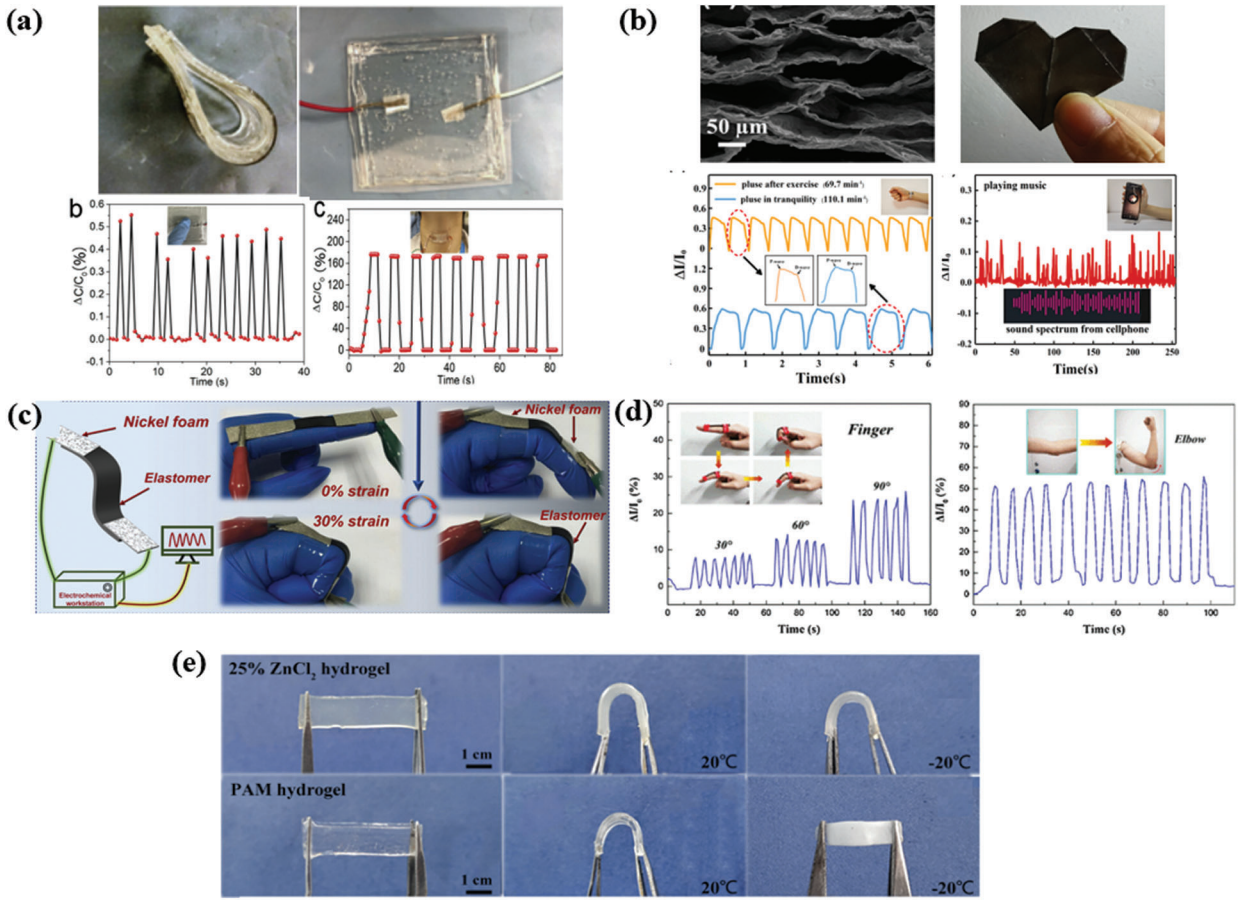

Figure 4: Cellulose-based strain sensors in a different form: (a) Photos of the PVA/CNF hydrogel-based ionic skin upon bending and water droplet falling onto the pressure sensor [17]; (b) MXene/CNF-foam shows great microstructure, foldable property and responsibility to tiny vibration [75]; (c) Photographs showing the hydrogel-based strain sensors attached on index fingers for recording the bending movements of fingers [42]; (d) The silver nanoparticles doped PDA@NCF hydrogel sensors for mechanotransduction signal applications [73]; (e) HPMC-ZnCl2–25% hydrogel shows excellent mechanical properties at different temperatures [76]

To improve toughness and mechanical strength, nanomaterials act as a toughening and reinforcing phase to achieve energy dissipation effectively. Su et al. [75] prepared a new type of piezoresistive sensor based on MXene/cellulose nanofiber foam as shown in Fig. 4b. Thanks to the special microporous structure of the hybrid foam, the sensor shows high sensitivity, low detection limit (4 Pa), short response/recovery time (123/139 ms) and excellent durability (10,000 cycles) in a broad linear range (419.7 kPa). The device can detect human activities, record the sound spectrum of the music in the smartphone software, and distinguish the subtle differences in the music score. It also has potential application value in the fields of

LED circuit protectors, wireless Bluetooth potential hazard detection equipment and paper-based environmental-friendly flexible electronic products. In addition, the MXene/CNF foam piezoresistive sensor is degradable in a very low concentration of H_2O_2 solution, meeting the demand for green and sustainable development.

Han et al. [42] used the *in-situ* oxidative polymerization of aniline monomer on the surface of the cellulose nanofiber template to form a CNF-polyaniline composite with ideal dispersibility and high aspect ratio, which was further uniformly dispersed into natural rubber latex. In the process, CNF-polyaniline/natural rubber elastomer with a three-dimensional network structure was synthesized through a latex co-aggregation process. The prepared composite materials have excellent mechanical properties: the tensile strength is as high as 9.7 MPa, Young's modulus is as high as 10.9 MPa, and the elongation at break is as high as 511%. The composite materials also have an electrical conductivity of $8.95 \times 10^{-1} Sm^{-1}$. The polyaniline elastomer is applied to a strain sensor, which has good repeatability and good electrochemical performance (Fig. 4c).

With the further medical application of flexible electronic skins and implantable equipment, it is necessary to obtain high-performance hydrogel-based sensors with highly effective and long-term antibacterial capability. Wang et al. [73] modified silver nanoparticles with dopamine and doped them in the cross-linked interpenetrating network of TEMPO nanocellulose and polyacrylamide. The nanocomposite hydrogel exhibits excellent mechanical properties and good self-healing ability. This research provides a feasible method for preparing bimodal nano-cellulose hydrogel sensors with high antibacterial efficiency and excellent mechanical properties. Such sensors can be widely used in the field of human motion detection and smart skin (Fig. 4d).

The profound challenge is that hydrogel does not possess high mechanical properties, which limits its potential applications in extreme environments. An effective strategy to reinforce hydrogel was based on the introduction of noncovalent interactions, such as dipole and hydrogen-bonding interactions. Chen et al. [76] fabricated a conductive cellulose hydrogel by grafting acrylonitrile and acrylamide copolymers onto the cellulose chains in the presence of zinc chloride using ceric ammonium nitrate as the initiator. The hydrogel has excellent anti-freezing performance, remarkable mechanical properties, and high electric conductivity (Fig. 3e). The hydrogel exhibited ultrastretchability (1730%), excellent tensile strength (160 kPa), high elasticity (90%), good toughness (1074.7 kJ/m^3), and fatigue resistance properties due to the existence of dipole-dipole and multiple hydrogen-bonding interactions on the hydrogel network. The introduction of the ionic compound zinc chloride makes the cellulose-based hydrogel still have good conductivity (1.54 S/m) at low temperatures (−33°C).

5 Conclusions

We summarized the recent advances in material synthesis, structure design, controlled fabrication of cellulose-based flexible sensors toward a smart exercise monitoring system. Owing to their unique properties of intrinsic and structural flexibility, ease of chemical functionalization, moisture sensitivity, and mechanical stability, cellulose-based functional materials demonstrated promises for applications in strain sensors, humidity sensors, and harmful gas sensors. Considering various requirements of variable flexible sensors, cellulose-based materials perform both as supporting substrates with designed microscopic morphologies and as structural matrices incorporated with functional fillers through controlled micro-and nanoscale cavities. The developments in materials synthesis, structure design, fabrication control, and working mechanism were discussed according to different sensors. The integration of multiple sensors and the smart system was demonstrated as well. Novel processing techniques, such as self-assembly, vacuum filtration, and 3D printing were utilized to construct multifunctional flexible sensors with multiscale structures.

Although cellulose-based materials and composites possess many merits for flexible sensors, some challenges and limitations still exist, such as material robustness, reliability, and stability of commercialized merchandise. Facing the difficulties, new materials development cooperated with structure design indicates opportunities to enhance performance and realize commercialization. Considering the future, strategies for mass production of cellulose-based materials with desired structures and morphologies at low cost, and novel functions and smart systems need to be developed.

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