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TOPICAL REVIEW

Wearable and printable devices for electrolytes sensing

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Abstract

With the development of biotechnology and the miniaturization of sensors, wearable devices have attracted extensive attention for real-time and non-invasive health monitoring at the molecular level. Among these, sensors for electrolytes analysis play an essential role in monitoring body physiological functions and metabolic activities. Herein, this review firstly summarizes the recent advances in electrolytes sensing via wearable devices, focusing on the most commonly adopted ion-selective electrodes, optical sensors and sensing platforms for effective body fluid collection and analysis. Innovative strategies based on nanomaterials engineering to achieve biosensing reliability, mechanical robustness as well as biocompatibility are also presented. Moreover, novel printable fabrication approaches to realize integrated wearable sensing systems with desirable compatibility and versatility are introduced. Finally, the challenges for practical applications and the perspectives on accurate and multi-functional sensing based on integrated wearable devices are discussed.

1. Introduction

With the continuous improvement of modern life quality, monitoring dynamic physiological indicators became one of the demands to realize personalized healthcare in a convenient fashion. Wearable biosensors have received extensive attention due to their attractive characteristics, such as flexibility, miniaturization and real-time data acquisition [1, 2]. Many strategies, such as potentiometric ion-selective electrodes (ISEs) [3, 4] and colorimetric sensing [5–8], have been adopted for electrolytes monitoring and show promising prospects. These could be used to quantitatively monitor biomarkers obtained from sweat [9–11], saliva [12, 13], urine, or tears [14] to understand the physiological states of the body under a state of health as well as sickness.

The major electrolytes in human body include K^+, Ca^{2+}, Na^+, Mg^+, NH_4^+, Cl^-, and H^+, which are widely distributed inside and outside of cells and are critical for important functions and metabolic activities. They play a vital role in regulating the balance of solvents in blood, helping with nerve conduction, regulating muscle contractions, and maintaining acid-base balance. For instance, Na^+ and Cl^- are critical to maintain osmotic pressure in the extracellular fluid, and K^+ is the main cation in intracellular fluid. Ca^{2+} is an important component of human metabolism and mineral homeostasis [15], and excessive changes of Ca^{2+} concentration in body fluid have adverse effects on the functions of multiple organs and systems, including myeloma, liver cirrhosis, renal failure, etc. According to the gradient of water space inside and outside the cell, electrolyte balance exerts an enormous function on the control of passive water movement [16]. Besides, the concentrations of electrolytes are closely relative to hormones and kidney functionalities. Disorders of electrolytes levels can also affect the activity of the heart and the nervous system [17]. Therefore, it is desirable to monitor changes in electrolytes concentrations to facilitate diseases management and pre-diagnostics.

Apart from analyzing electrolytes in blood and interstitial fluids (ISFs) invasively, body fluids that can be collected in non-invasive manners can also be utilized. For instance, sweat electrolytes imbalance could be relative to dehydration, hypo/hypernatremia, and hypo/hyperkalemia [18, 19]. Epidermal pH monitoring can not only indicate skin status (e.g. irritation, dermatitis, acne, and ichthyosis) but also serve as one of the indicators for wound healing [20, 21]. Normally wounds would show slightly acidic pH for healthy people, while it can be higher than 7.4 for patients with chronic diseases [22]. Besides, high concentrations of K^+ in tears (about 20–42 mM) could indicate ocular disease [23].

Research efforts have been devoted to developing wearable sensors with high performance and attractive form factors, including versatile device fabrication and integration of flexible nano-devices. The main structural materials of electronic devices can be divided into two parts: base materials and functional materials. The base material supports the flexible sensor and realizes the performance of the functional material during design. As a new material processing technology, printable technology has preliminarily demonstrated its unique advantages in the miniaturization of nano-devices, wearable devices and the integration of micro-electronic devices. It can be roughly divided into screen printing technology, gravure printing, inkjet printing and 3D printing technology. Nevertheless, it still requires efforts in materials engineering and system integration to further enhance user comfort and safety, as well as accurate and diverse biomarkers sensing via wearable devices.

This review aims to comprehensively summarize the state-of-the-art wearable electrolyte sensors and integrated systems, emphasizing the performance enhancement with micro/nano materials and fabrication versatility with printable techniques. The recent advances in wearable devices for electrolyte sensing via invasive and non-invasive approaches are firstly summarized. Afterwards, functionalized nanomaterials that play a critical role in sensing performance enhancement, including sensing and mechanical stability as well as biocompatibility, are discussed. Moreover, to achieve flexible sensors and systems for wearable applications, printable strategies that enable versatile design and compatible fabrication are presented. Furthermore, considerations on material toxicity and the accuracy of extracted signals towards next-generation wearable devices for biosensing are discussed.

2. Wearable sensing platforms for electrolytes sensing

The level of electrolytes in body fluids can assess the health of the body. There are mainly two monitoring methods for electrolytes, namely non-invasive and invasive monitoring. The invasiveness of traditional sensors brings unavoidable pain barriers to patients, and it is impossible to obtain the required sample information continuously. For newborns and the elderly, blood sampling is particularly challenging [24]. Microneedle-based sensors provide new options for minimally invasive techniques. In recent years, microneedles with micro-sizes have been successfully used in numerous devices for percutaneous sensing, sampling, and molecular delivery [25]. Most importantly, the microneedle structure is painless. Many works related to microneedle technology have been published. For instance, Narayan *et al* fabricated a microneedle-based biosensor array to monitor pH, glucose, and lactate simultaneously. At the same time, a cell adhesion experiment was performed to limit the adhesion of macrophages to acrylate-based polymers, which demonstrated good biocompatibility [26]. Polsky *et al* fabricated a percutaneous microneedle sensor for sensing K^+ based on porous carbon electrodes, and integrated nanomaterials into the microfluidic platform [27]. With the demand for wireless communication in wearable devices, Crespo *et al* have produced a wearable microneedle patch based on glasses, which is used to monitor intradermal K^+ and lactic acid, and can be transmitted wirelessly through the eyeglass frame [28].

Compared with traditional invasive electrolyte sensors, non-invasive electrolyte sensors have attracted increasing attention in health monitoring because they can avoid pain and infection and conduct continuous analysis. Considering the discomfort of intrusive sensors, non-invasive sensors are becoming increasingly popular. Wearable sensors have won widespread interest due to their great prospects in numerous applications. With the continuous development of wireless transmission technology and the intervention of high-performance chips in the electronic industry, the concept of the internet of things is rising. Wearable devices have gradually moved from conceptualization to industrialization, and many technology companies are gradually exploring this new field.

With the demand for non-invasive and miniaturized devices, the form and application of wearable sensors are constantly changing. As shown in figure 1, we summarize the latest developments in wearable non-invasive electrolyte sensors for different parts of the body, such as the arms and head. Researchers have recently made considerable efforts to develop wearable non-invasive electrolyte sensors that have been integrated into common objects, such as glasses [29], sweat-bands [30], gloves [31], patches [32, 33],

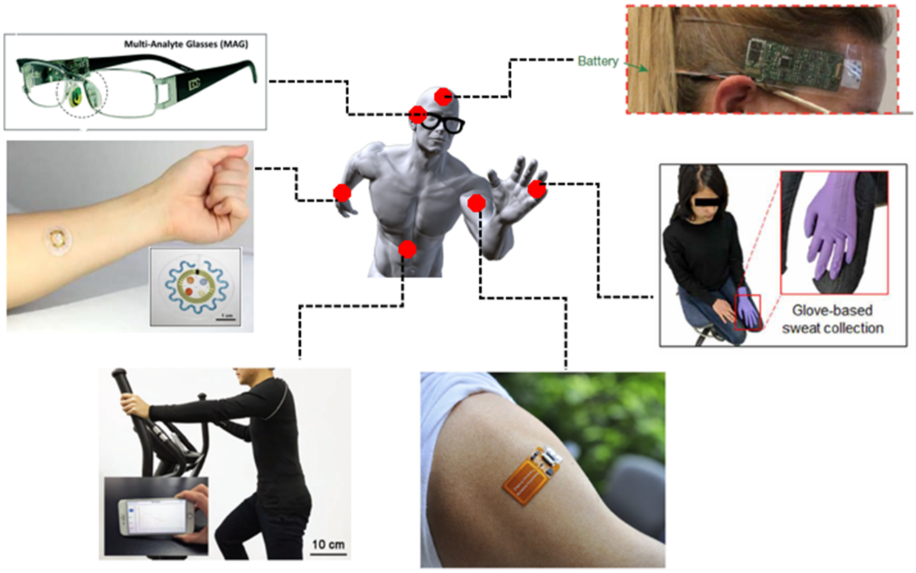

Figure 1. Wearable sensors for non-invasive monitoring. Clockwise from top: eyeglasses-based wearable electrolyte sensor. Reproduced from [29] with permission from the Royal Society of Chemistry. A subject wearing a smart headband to monitor health. Reproduced from [30], Copyright © 2016, Springer Nature Limited. Glove-based sensors for monitoring electrolyte in sweat. Reproduced with permission from [31]. CC BY-NC 4.0. Battery-free and flexible electrochemical patch for monitoring Ca^{2+} and Cl^{-}. Reprinted from [33], © 2019 Elsevier B.V. All rights reserved. The application of electrolyte sensor by wearing the garment device during exercise. [36] John Wiley & Sons. © 2018 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. Colorimetric Sensing electrolyte in sweat on arm. From [32]. Reprinted with permission from AAAS.

clothes [34], contact lenses [35], etc. These devices directly display the monitoring results of electrolytes and have made outstanding contributions on personalized medicine.

3. Types of extracted signals from wearable electrolytes sensing

With the development of various biosensors, electrolyte composition can be identified quantitatively. In general, the selective reaction between target electrolyte ions and active materials on the sensor electrodes can be monitored with the extracted electric and optical signals. Various biosensors used for electrolyte monitoring can be mainly divided into potential ISEs and optical sensors.

3.1. ISE sensors

ISE belongs to the potentiometric method. The critical component of ISE is an ion-selective membrane (ISM), which blocks interfering ions and allows the designed ions to pass through. It is usually placed between the sample and the internal solution containing the analyte ions. Glass, crystalline solid, or liquid has the opportunity to become ISMs.

It has been proved that the wearable ISE can be used to measure electrolytes, such as K^{+}, Ca^{2+}, and Na^{+}. For example, valinomycin, Ca^{2+} ionophore, and Na ionophore X are commonly used as part of the sensing layer, allowing the passage and accumulation [15, 37]. A stable potential was generated at the inner boundary of the membrane and the interface of the inner reference electrode. Wang *et al* fabricated a potential sensor based on a temporary transfer tattoo on the epidermis, and combined it with a small wearable wireless transceiver for the noninvasive monitoring of sodium ions in sweat [38]. The concentration of Na^{+} was monitored in real-time and wirelessly transmitted from the sodium tattoo sensor to the laptop through the transceiver carried by the tester to get good data analysis. In addition, tattoos could adapt to many external factors, such as bending and stretching.

From the above understanding, one side of the ISM can directly contact the solid phase, while the other side needs to face the aqueous sample. In this case, the solid can be selected as a conductor, semiconductor or insulator [39]. Ion-sensitive field-effect transistor (ISFET) is a kind of microelectronic ion-selective device, which constitutes a solid contact potentiometer and possesses the dual characteristics of electrochemistry and transistor.

ISFETs provide the advantages of fast response, high sensitivity, low output impedance, low sample consumption, easy mass production and low cost. Therefore, ISFET has been widely used in clinical medicine [40, 41], food [41, 42], environmental science [43–45], military science, and even robot technology [46, 47]. In recent years, it has displayed great potential in many fields, especially in biochemical sensors. For

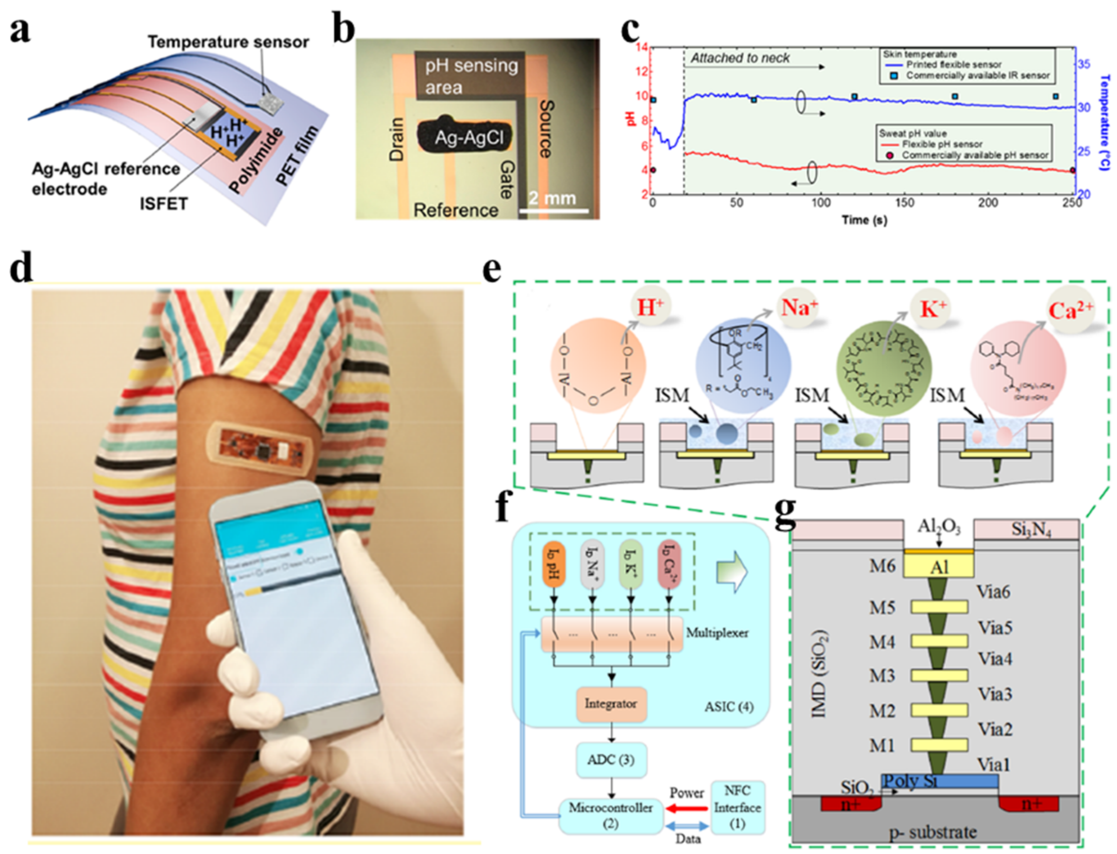

Figure 2. Ion sensitive field effect transistors for electrolyte sensors. (a) Schematic of a multifunctional healthcare device integrating pH and temperature sensors. (b) Optical photo of the ISFET component without covering polyimide. (c) Real-time monitoring of pH and skin temperature by the device compared to commercial pH and IR sensors. Reprinted with permission from [48]. Copyright (2017) American Chemical Society. (d)–(g) The photo and device schematics of the wearable 3D-EMG-ISFET sensor with Al_2O_3 as pH Na^+, K^+, and Ca^{2+} sensing. Reprinted with permission from [50]. Copyright (2019) American Chemical Society.

example, Takei et al prepared a multifunctional ISFET chemical sensor for measuring both sweat pH and skin temperature, as shown in figure 2(a) [48]. For ISFET, InGaZnO film was regarded as FET material and temperature sensor was printed on polyethylene terephthalate (PET) film. The Al_2O_3 layer was used for pH sensing film, which could be manufactured on the polyimide (PI). Figure 2(b) shows an ISFET component that covered the PI. By monitoring pH and skin temperature in real-time using flexible multifunctional devices, it is found that the sensor reading is almost constant at 31 °C and pH 4.0, which is in good agreement with the results of commercial pH and IR sensors, as shown in figure 2(c). The real-time measurement results from Adrian *et al* show that ISFET had high sensitivity and linear response to the detected ion concentration [49]. The research results provide a basis for ISFET to be used in the field of wearable sensors for simultaneous multi-ion sensing in the future.

By combining complementary metal oxide semiconductor technology with ISFET, multiple electrolyte ions can be monitored simultaneously. Ionescu et al fabricated three-dimensional-extended-metal-gate ISFETs (3D-EMG-ISFET sensor) incorporating picowatt to achieve the aim of monitoring multi-ions, such as H^+, K^+, Na^+, and Ca^{2+}, in body fluid as depicted in figures 2(d)–(g) [50]. When the mobile phone was close to the sensor worn on the subject's arm, the sensor would collect energy through the near field communication (NFC) device.

3.2. Optical sensors

Colorimetric sensing is one of the optical sensing technologies, which relies on the straightforward reading of the color change of the solution containing the analyte. Colorimetric methods based on metal nanoparticles have been proven to be a successful analytical strategy because of their simplicity, rapidity, and cost-effectiveness, enabling them to identify and quantify various molecules in complex samples. A large number of studies have been carried out on the selective and sensitive identification of various species (including electrolytes [51], drugs, proteins, and aptamers) in a small number of samples using metal nanoparticles as colorimetric sensors.

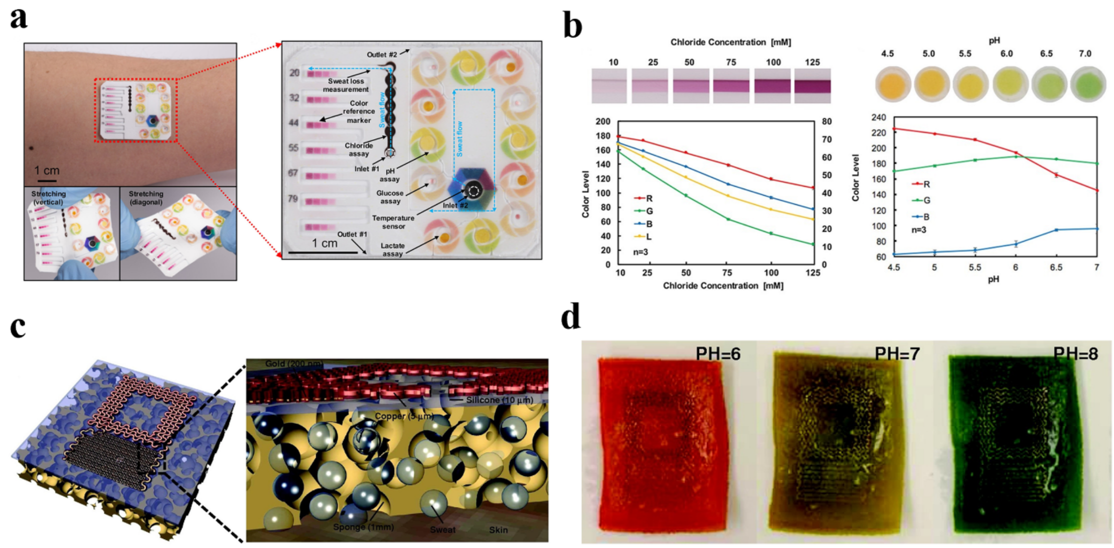

Figure 3. Colorimetric electrolyte sensors. (a) Optical images of soft, flexible microfluidic devices for colorimetric analysis of sweat and top view illustration of microfluidic channels filled with blue-dyed water. (b) Color level for each color of chloride and pH. Reprinted with permission from [52]. Copyright (2019) American Chemical Society. (c) Schematic diagram of the passive wireless capacitive sensor. (d) Pictures of a sensor doped with a pH indicator, each collected with absorbed water at a different pH value. [53] John Wiley & Sons. © 2014 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

John *et al* designed a colorimetric sensing system for real-time measurement of total sweating amount, sweating rate, sweating temperature and the concentration of electrolytes and metabolites in sweating, as shown in figures 3(a) and (b) [52]. Color reference markers integrated into different environments provided a colorimetric estimation of different analyte concentrations under various light conditions and integrated digital imaging technology to extract quantitative information. Moreover, they also developed ultra-thin stretchable wireless sensors, as shown in figures 3(c) and (d) [53], which were installed on a functional elastomer matrix to measure the characteristic epidermis of sweat by dielectric detection and colorimetry. The colorimetric change of the substrate could affect the microwave radio frequency characteristics of the integrated electric antenna, and the sweat could be absorbed spontaneously by capillary force to eliminate the direct contact between the skin and the electrode, to minimize the possible skin discomfort. Nadnudda *et al* manufactured a non-invasive textile sensor using a non-vacuum extraction colorimetric method to detect sweat pH and lactic acid simultaneously [37]. The color indicator of the sensor was composed of a mixture of methyl orange and lactic enzyme. As the concentration of lactic acid increased, the sensitivity of the pigment increased, and the indicator area of the sensor changed from red to blue. The pH of sweat was determined by comparing it with the standard calibration color card.

The design and manufacture of the sensor array for colorimetric detection need to combine the unique functional nanoparticles to achieve high stability and reproducibility. However, the lack of continuous monitoring conditions and low accuracy could pose certain limitations.

4. Wearable platforms for effective body fluid collection and analysis

The demand for the integration and assembly of wearable biosensors tends to choose a relatively stable body fluid absorption system, including proper design of the drainage and discharge of body fluids, and self-assembly through effective methods to establish a complete system.

The sampling method dramatically influences the accuracy and reliability of body fluid analysis results. Traditional body fluid sampling cannot meet the needs of dynamic, real-time monitoring, and may lead to sample evaporation or contamination problems. It is necessary to establish a proper fluid sampling system, such as the application of microfluidic technology, to realize the effective transmission of biological liquid on the sensor and ensure a reproducible and accurate signal.

Microfluidic technology involves the use of microtubules to process or manipulate microfluidic systems to manipulate fluids in micro/nano-scale space. It is a new interdisciplinary subject involving chemistry, physics, microelectronics, materials, and biomedical engineering. Microfluidic technology uses low dose samples and reagents for high precision and high sensitivity separation and detection. It has the advantages of low cost, short analysis time, and small size. Microfluidic chip materials include glass, silicon wafer, paper, polydimethylsiloxane (PDMS), polymer, etc. It also takes advantage of the less obvious characteristics of

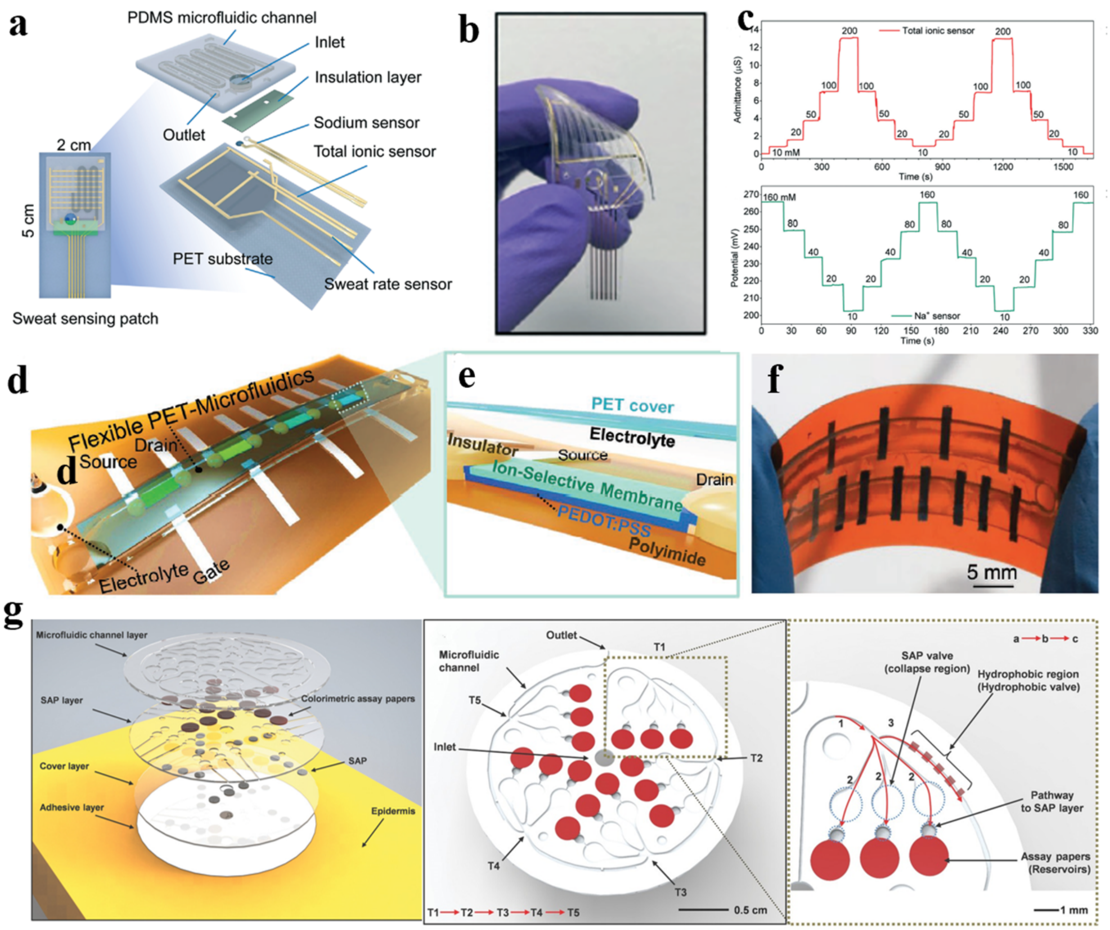

Figure 4. Microfluidic technology for electrolyte sensors. (a) Schematic of multi-modal sweat sensing patch with sensors for sweat rate, total ionic charge concentration, and Na^+ concentration. (b) The structure of the multi-modal sweat sensing patch on the PET. (c) Characterization of sensors for total ionic charge concentration and Na^+ concentration. Reproduced from [54] with permission from the Royal Society of Chemistry. (d) Schematic of the integrated organic transistors into the microfluidic system and zoom with the cross-section in (e). (f) Images of the transistors with microfluidics. [56] John Wiley & Sons. © 2020 Wiley-VCH GmbH. (g) Schematic diagram of the epidermal sampling microfluidic device used for sweat chloride monitoring. Reprinted from [58], © 2020 Elsevier B.V. All rights reserved.

microchannel fluid, such as laminar flow, and is favored by researchers. It essentially provides the ability to centrally control molecules in space and time. For instance, Javey *et al* prepared a multi-modal sweat sensing patch by microfluidics technology for monitoring Na^+, sweat rate and total ionic charge (figure 4(a)) [54]. The working electrodes were patterned on a flexible PET substrate, as shown in figure 4(b). The performance of the total ionic change and Na^+ sensor is shown in figure 4(c). Because of its miniaturization and integration, microfluidic technology has been considered to have great development potential and wide application prospects in biomedical research. Sempionatto *et al* proposed a skin-based microfluidic sensor to detect the concentration of Na^+ and K^+ in sweat during exercise [55]. The potential signal generated between the electrodes was transmitted to the mobile phone via Bluetooth communication. Through the microfluidic structure, multiple electrolytes were selectively combined with more ISEs to realize the measurement of multiple electrolytes. Adrian *et al* combined ISFET and microfluidic network for multi-channel sweat electrolyte analysis with ISFET only occupying one square centimeter on the substrate [49]. For electrolyte sensors, it is difficult to integrate into a microfluidic platform due to high output impedance. Organic electrochemical transistors (OETCs) can amplify signals and obtain flexible organic materials, so they have been widely used in the sensor field. Therefore, the combination of OETCs and microfluidic technology realizes the simultaneous monitoring of electrolytes (K^+, Na^+ and H^+) [56]. As can be seen from figure 4(d) that the OETCs are composed of three parts, namely drain, source, and gate. As shown in figure 4(e), the drain and source were connected by an ISM modified by polymer poly(3,4-ethylenedioxythiophene): poly(styrenesulfonic acid) (PEDOT: PSS). John *et al* designed a multiple-layers geometry to integrate the microfluidic channel and a set of superabsorbent polymer materials [57]. Active valves were utilized to ensure the sweat successively flowed through the reservoir and reached the superabsorbent material valve at both ends. The material would then be activated and expanded to shut down the outlet and inlet, so as to guide the sweat flow direction and prevent sweat from seeping due to internal hydration. The concentration of chloride was determined by colorimetry, and the quantitative analysis was aided by digital image processing, as shown in figure 4(g) [58]. The inspiration is to make full use of microfluidic technology, combined with other technologies, such as printable technology, to develop a new wearable health monitoring sensor.

Although microfluidics technology has made great progress in wearable devices, manufacturing highly integrated multi-channel sensors is still a huge challenge. When combined with the colorimetric method, analysis of samples with too low concentrations is difficult to detect. Part of the body fluid may remain in the channel, and evaporation during transportation will reduce the utilization rate. Furthermore, for some fluid samples with low surface tension, the hydrophobic area may not have enough hydrophobicity, which will cause sweat leakage.

Various modified absorbent materials, such as paper, fabric, and hydrogels, have also been widely used for sweat sampling in wearable sensors. At the same time, functional porous substrates can be introduced as sensing components. John *et al* reported a retractable wireless capacitive sensor with interdigital electrodes mounted on a hydrophilic porous substrate, which could detect the pH of sweat [53]. This functional substrate allowed sampling by capillary force without needing a complicated microfluidic processing system. Javey *et al* placed a thin rayon pad between the skin and the sweat sensor to absorb sweat and prevent direct contact between the sensor and the skin [30]. The newly generated sweat entered the silk pad in a volume of 10 microliters, and the old sweat is washed away, acting as a proxy to stabilize and reliable data.

5. Performance improvement with nanomaterials

Although common electrolyte electrodes can be fabricated according to different sensing methods, it is still necessary to improve the performance, such as simultaneous monitoring, stability, sensitivity, stretchability as well as assembly of the sensor system.

The selection of suitable material is crucial for the sensitivity and detection range of the sensor [1]. The flexible substrate is used to support other materials in wearable sensors. For wearable sensor devices, the sensor element needs to be perfectly combined with a flexible substrate to obtain more reliable data and a comfortable feeling.

There are many substrates available for wearable sensors, including PET [59], polyimide [60, 61], PDMS [62], polyethylene naphthalate, poly(methyl methacrylate) [63] and polyurethane (PU) [64, 65]. Using textile [66] and paper [67] as the substrate has also successfully proved the use of disposable wearable sensors. Besides, PET is widely used because of its low price and good flexibility, while textile has good water absorption, flexibility, stretchability and durability which can be extracted from a variety of natural or man-made materials. The elastic modulus of PDMS is close to that of human skin, which makes PDMS have high biocompatibility and fit skin better. Because of their environmental friendliness and biocompatibility, biomaterials such as silk fibroin, cellulose and bacterial cellulose are good choices for flexible materials.

Considering the good mechanical properties, gold [30], silver [66] and carbon (e.g. graphene, carbon nanotubes) [34, 68, 69] are often used as working electrodes. Silver nanowires have excellent electrical and optical properties and have been widely used in flexible electronic products. Recently, many studies have been devoted to improving strain performance, of which carbon nanotubes reveal a high strain of 280%, showing excellent stretchability [34].

In addition to the above-mentioned, many conductive materials are used in the field of flexible wearable sensors, which is corresponding to the ISM. For example, the Na^+ selective membrane consisted of Na ionophore X, sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (Na-TFPB), high-molecular-weight polyvinyl chloride (PVC), and bis(2-ethylehexyl) sebacate (DOS) [30]. The K^+ selective membrane was composed of valinomycin (K^+ ionophore), NaTPB, PVC, and DOS. Ca^{2+} selective cocktail was prepared by dissolving PVC, Na-TFPB, DOS, Calcium ionophore II (ETH 129) and tetrahydrofuran [15]. For the pH sensor, polyaniline (PANI) was used as the sensing material because it could recognize hydrogen ions on the electrode surface [70]. As shown in table 1, the sensitivity of different sensing technologies is summarized. At present, the detection methods for electrolytes are divided into ISM methods and optical methods (colorimetry).

5.1. Simultaneous monitoring

Body fluids, like sweat, urine, and tears, contain a variety of biomarkers, and there is a development trend that requires simultaneous non-invasive monitoring of multiple analytes at different sites or the same site. The use of non-invasive wearable sensors to monitor a single physical parameter has already been used in many products on the market, such as electrocardiogram (ECG), blood pressure (BP), and biochemical parameters including blood sugar.

Table 1. Summary of the representative sensitivity for different sensing techniques based on sensing analytes.

Analyte	Sensitivity (mV/decade)	Sensing techniques	Substrates	Electrode materials	Disease correlation	Sweat/tear/saliva	References
Na^+	188 ± 12	Potentiometry	PDMS	Na^+–ISM	Hyponatremia/ hypernatremia	Saliva	[25, 61]
K^+	55	ISFET-based	PET	K^+–ISM	Hypokalemia/ muscle cramps	Sweat	[62]
Ca^{2+}	32.7	Potentiometry	PET	Ca^{2+}–ISM	Cirrhosis/renal failure	Sweat	[63]
NH_4^+	60.1 ± 1.4	Potentiometry	Paper	NH_4^+–ISM	Anemia	Sweat	[64]
H^+	63.3	Potentiometry	PET	Polyaniline	Dermatitis/fungal infections	Sweat	[63]
Cl^-	$52.8 + 0.7$	Potentiometry	PET	Ag/AgCl salt bridge	Cystic fibrosis	Sweat	[65]

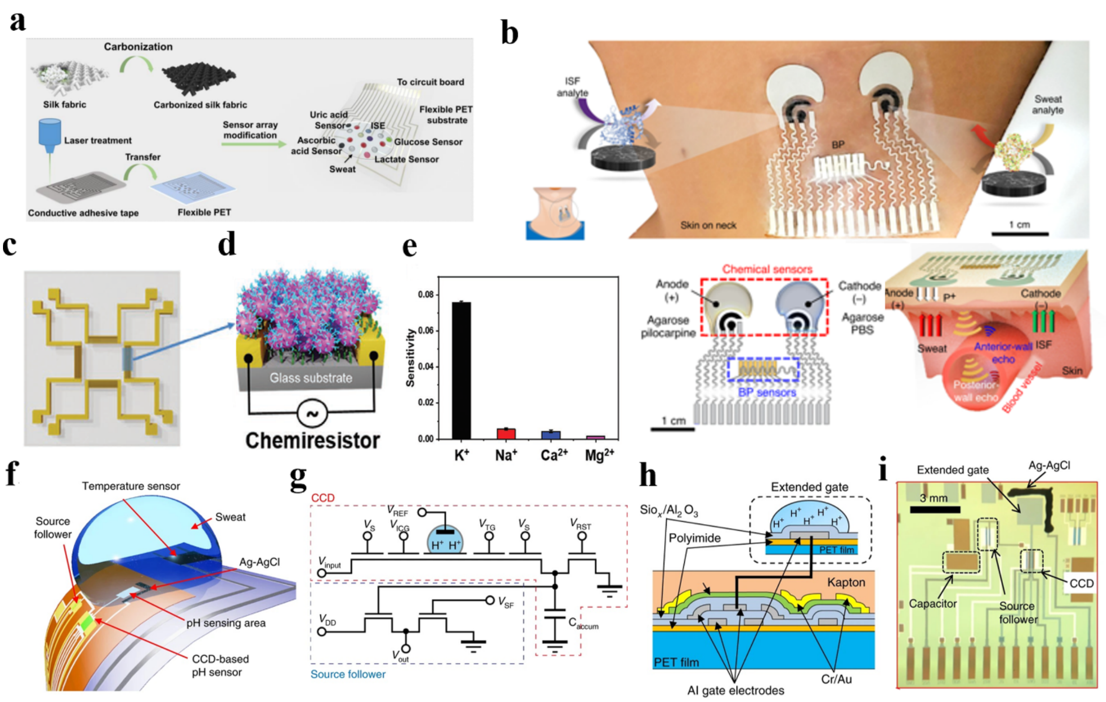

Figure 5. Performance improvement of electrolyte sensors. (a) The detailed process of wearable electrolyte sensor for simultaneous monitoring of sweat analytes. Reproduced with permission from [71]. CC BY-NC 4.0. (b) Design and mechanism of scalable Integrated BP chemical sensing patch. Reproduced from [73], Copyright © 2021, The Author(s), under exclusive licence to Springer Nature Limited part of Springer Nature. (c), (d) Schematic of chemiresistors based on covalently assembled by 3D networks of Au Nanoparticles- dibenzo-18-crown-6 (AuNPs-DTDB-18C6) for monitoring K^+. (e) The sensitivity improvement of chemiresistors toward different ions, such as K^+, Na^+, Ca^{2+} and Mg^{2+}, based on AuNPs-DTDB-18C6 networks. Reproduced from [75]. CC BY 4.0. (f)–(i) Schematic diagram of flexible pH sensor based on CCD integrated with temperature sensor. Reproduced from [76], Copyright © 2018, The Author(s), under exclusive licence to Springer Nature Limited.

Javey *et al* fabricated a wearable electrochemical sensor for noninvasive simultaneous monitoring of Ca^{2+}, pH and temperature [15]. Meanwhile, a wearable sensor array was constructed for the simultaneous monitoring of four analytes of sweat metabolites (glucose and lactate), electrolytes (K^+ and Na^+), and temperature [30]. This shows that in the field of wearable electrolyte sensors, it has achieved a leap from the simultaneous monitoring of two analytes to four analytes. It is gratifying that Zhang *et al* have fabricated a textile sensor patch for simultaneous monitoring of six bio-analytes (Na^+, K^+, glucose, lactate, ascorbic acid and uric acid) in sweat [71]. The material of the working electrode is a key factor because it has a great influence on electrochemical performance. Instead of using traditional electrode materials, they used an ancient natural fiber, silk, as working electrode material. The material has some unique advantages, such as a particular N-doped graphitic nanocarbon structure, good electrical conductivity, high mechanical strength, flexibility, and biocompatibility. They used a laser processing method to manufacture wearable sensor arrays based on silk, as shown in figure 5(a).

A large number of heavy metals, including Zn, Cd, Pb, Cu, and Hg, exist in body fluids (such as blood, sweat, and urine), which are closely related to human health. Monitoring multiple heavy metal ions in body fluids is essential for human health and has attracted extensive attention. Gao *et al* described a wearable microsensor array for simultaneous multiplexed monitoring Zn, Cd, Pb, Cu, and Hg via electrochemical square wave anodic stripping voltammetry on Au and Bi microelectrodes [72]. The wearable microsensor arrays also display good repeatability and stability for heavy metal analysis.

During this period, researchers are also exploring more multi-sensor combination schemes, such as the combination with ECG electrodes. Joseph *et al* developed the first wearable device that could simultaneously monitor cardiovascular signals and a variety of biochemical levels (glucose, alcohol, caffeine, lactic acid, etc) of the human body [73]. Through the integrated wearable device for continuous and synchronous acoustic and electrochemical sensing, it is of great help to the prevention, diagnosis, and treatment of many diseases. Figure 5(b) illustrates the location of the enzymatic chemical sensor of ISF and sweat, along with the acoustic and electrochemical sensing components of the sensor. The results support the possibility of developing hybrid wearable sensors on a single conformal wearable patch through the complex integration of chemical and physical sensors. Only by choosing materials wisely, optimizing the structure and manufacturing process, reliable and comprehensive skin sensor integration can be achieved. Although the integrated device shows attractive features, there are still many prospects for improvement in the measurement of BP and heart rate. For example, the integrated patch relies on the stimulation of pilocarpine to sweat; extensive verification of a large number of individuals with different health conditions; the equipment has not yet been fully miniaturized, etc. The advent of the sensor represents the continuous development of scientists towards multi-modal wearable sensors, committed to more comprehensive human physiological and remote monitoring. The skin conformal sensor patch opens a new path for developing next-generation wearable devices.

5.2. Sensitivity

Sensitivity is an essential character in the assessment of wearable electrolyte sensors. Moreover, it shows the accuracy and efficiency of the wearable sensor. The sensitivity measurement methods of different sensors are not the same. For example, the sensitivity of a pressure sensor is measured by a scaling coefficient, while the sensitivity of a glucose sensor is measured by an electric current. For the best sensitivity and detection range of biosensors, the characteristics of the selected material, such as morphology, conductivity, porosity, surface area, and mechanical properties, are indispensable to be considered [1]. Due to its excellent mechanical, chemical resistance as well as electronic properties, carbon-based nanostructured materials (such as carbon nanotube (CNT)) have been widely integrated into biosensors to improve their sensitivity. It has also been proven that doping carbon electrospun nanofibers with metal nanoparticles is an effective method to improve the sensitivity and stability of biosensors, such as the enzyme electrode filling of multi-walled carbon nanotubes [74]. Samorì *et al* prepared a 3D hybrid gold nanoparticle network chemical reactor linked by supramolecular receptors for selective sensing of K^+ in saliva (figures 5(c) and (d)) [75]. The 3D network structure was composed of gold nanoparticles (Au nanoparticles), and molecular organic crown ethers and dibenzo-18-crown-6 acted as a linker and supramolecular receptors for K^+. The sensitivity and selectivity toward K^+ were tested in the presence of other interference ions (Na^+, Ca^{2+} and Mg^{2+}). It can be seen from figure 5(e) that compared with other body fluids, the chemical sensitivity of K^+ was much higher. Kuniharu *et al* showed a pH sensor combined with a flexible charge-coupled device (CCD) and integrated it with a temperature sensor, as shown in figures 5(f)–(i) [76]. The CCD-based pH sensor achieved a sensitivity of about 240 mV/decade through the accumulation cycles of electron charge transfer. This remarkable pH sensitivity is a around four times higher than the normally reported one of 59 mV/decade determined by Nernst equation. Apart from ion sensing sensitivity, Tai *et al* described a non-invasive wearable band capable of monitoring sweat nicotine. The wearable sensor with the Au nanodendrites (AuND) functionalized working electrode exhibits a high sensitivity of 4.3 nA μM^{-1}, compared with the lowest detection limit in a few μM level with thin film electrodes. It is mainly attributed to the largely enhanced surface-to-area ratio on the as-designed nanostructured electrodes facilitate the ion/molecular interaction and electron transfer [77]. Besides, with the enhanced active surface area for ion/molecular absorption, the linear response range can also be broaden, which could contribute to compatible biomarkers analysis in multiple body fluids with different concentration levels.

5.3. Stability

The stability of nanomaterials is another critical factor in the measurement performance in the field of wearable sensors. Wearable devices must overcome the stability problems caused by long-time work under uncontrolled conditions as well as the inherent instability of biological contamination and biometric

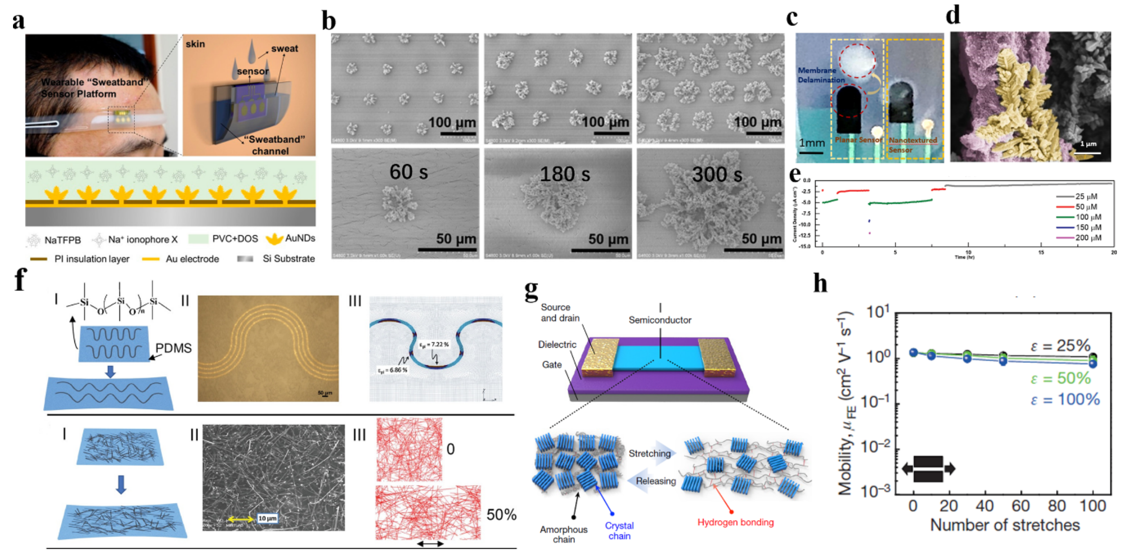

Figure 6. Performance improvement of electrolyte sensors. (a) Schematic diagram of all-solid-state ISE based on AuND. (b) SEM image of AuND prepared *in situ* on the chip by electrodeposition. The electrodeposition time is 60 s, 180 s and 300 s, respectively. Reprinted with permission from [78]. Copyright (2017) American Chemical Society. (c) Photos of porous enzymatic membrane from planar electrode (left) and nanotextured electrode (right). (d) SEM images of the nanotextured electrode anchored on porous membrane. (e) Stability test of nanostructured glucose sensors for 20 h. [79] John Wiley & Sons. © 2019 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (f) A schematic diagram of the stretching principle of the horseshoe-shaped nanowire embedding strategy. [81] John Wiley & Sons. © 2020 Wiley-VCH GmbH. (g) Performance improvement of stretchability. (h) Schematic diagram of stretchable semiconducting polymer and field-effect mobility versus a number of stretching cycles test along perpendicular to strain direction. Reproduced from [83], Copyright © 2016, Macmillan Publishers Limited, part of Springer Nature. All rights reserved.

components. It is affected by many factors, such as the structure, shape, preparation method, and process of the material.

Zhang *et al* combined micro-nano processing technology to design and fabricate electrode chips with micro-hole arrays as templates [78]. They used electrodeposition to fabricate a three-dimensional gold nanostructure ion/electron conduction array electrode with a large specific surface area and controllable (space-constrained electrochemical deposition method, *in-situ* preparation of gold nanodendrites on the chip), as shown in figure 6(a). It has the advantages of simple preparation and good repeatability. Compared with planar electrodes, electrodes with three-dimensional nanostructures have better stability. As figure 6(b) shows, the electrochemical properties of gold nanoelectrodes with different structures confirmed their differences in specific surface area. The specific surface area from the bare gold electrode to the AuND electrode increased significantly with the longer deposition time. The AuND ISE with a large surface area and high double-layer capacitance exhibited enhanced potential stability.

In addition, Lin *et al* fabricated a nano-textured glucose sensor modified by a porous enzyme membrane (figures 6(c) and (d)) [79]. The nanoporous structured enzyme membrane technology eliminated the escape of enzymes and provided sufficient surface area to ensure the sustainable catalytic activity of the sensor and generate reliable and measurable signals. The solid contacts of the sensor electrode were textured with dendritic nanostructures, while the sensor uses gold dendritic nanostructures to act as anchor points for the porous enzyme membrane, and achieves the enhanced mechanical robustness. As shown in figure 6(e), the assembled nanostructured glucose sensor showed reliable cycle sensitivity and long-term stable monitoring for up to 20 h. In short, it is an efficient method to change the material structure to improve the stability of nanomaterials.

Signal drift is an essential factor for sensing stability evaluation. Wang *et al* described a nanotextured biosensor for sensing Na^+ [80]. Compared with thin film sensors, the nanotextured sensor can significantly enhance long-term sensing stability, owing to the suppressed charge accumulation on the nanotextured electrodes with an increased electrode surface.

5.4. Stretchability

The latest interest in wearable or portable electronic devices has drawn attention to high-quality flexibility and stretchability. Next-generation flexible electronic device applications are interested in these characteristics, such as flexible displays, flexible and/or stretchable circuits, artificial electronic skin, and various forms of sensors. In short, stretchability refers to the ability of a material to return to its original state after a series of body bends and skin deformations. Therefore, this is also a very important problem that needs to be solved continuously in the field of flexible electronics.

Flexible conductive materials mainly include CNTs, graphene, metal nanowires, organic polymer films, and their composites. Polymer thin-film transistors have received extensive attention in wearable electronics because of their good stretchability. Currently, two main strategies have been proposed for the manufacture of stretchable electronic devices [81]. One strategy is to place the active material on the elastic substrate (PDMS). When the substrate is stretched, the strain on the active material will be eliminated by the designed structure, but the stretching range of this method is small. The horseshoe-shaped metal film on the PDMS substrate is widely used to make stretchable conductors, and its performance also highly depends on the characteristics of the PDMS substrate. A schematic diagram of the stretching principle of the horseshoe-shaped nanowire embedding strategy is shown in figure 6(f). The strain of PDMS may increase the local strain in the horseshoe-shaped metal conductor, which may eventually lead to permanent damage to the conductor. In this method, the PDMS substrate is required to provide high adhesion to the metal film to enhance the stability of stretchable electronic devices. Embedding conductive nanomaterials (e.g. silver nanowires, CNTs) into PDMS substrates is another way to make stretchable electronic devices. Specifically, nanomaterials with excellent electrical and mechanical properties are mixed with elastomeric prepolymers. After curing, the nanowires are buried in the PDMS substrate and peeled off the substrate. Here, the nodes between the nanowires form a network that can provide a path for electron transfer. Nanomaterials cross-connect with each other, and even under strain, most of the connection sites are maintained. This device can be used as a stretchable electrode or a stretchable resistance-sensitive strain sensor.

Lin *et al* proposed a highly stretchable and durable electrode based on a multilayer Au NS film embedded in a PDMS matrix [82]. As Au NS embedded in PDMS has excellent mechanical durability and stretchability, it can be used repeatedly. The design of the Au NS electrode greatly improves mechanical flexibility and stretchability, which proves that it has excellent output stability in repeated push–pull tests. Bao *et al* doped flexible molecules in flexible semiconductors to increase the stretchability of transistors, as shown in figure 6(g) [83]. After repeated stretching, it was found that the device still maintained good mechanical robustness after 100 cycles of 0%–100% strain along the perpendicular direction (figure 6(h)). With excellent electrical conductivity and flexibility, carbon aerogels have been widely adopted in electronic skin and wearable flexible electronics [84, 85].

5.5. Biocompatibility

Considering that the wearable electrolyte sensor fully covers human skin, the biomaterial must be non-toxic, non-irritating, and antibacterial. Biocompatibility has always been extremely important in the medical application of biomaterials. Biocompatibility assessment is an indicator to measure the degree of adverse changes in homeostasis mechanism in the host. This is dynamic because during this period the characteristics of the material and host reactions (e.g. corrosion, aging, and allergic reactions) change with time dimensions. Biocompatibility of materials generally means that no matter what the expected purpose of materials is, they will not cause harmful biological reactions not only refers to the absence of cytotoxicity but also includes their positive biological functions.

More and more researchers are now paying attention to the biocompatibility of nanomaterials in wearable electrolyte sensors. For instance, Zhu *et al* fabricated a multifunctional zwitterionic hydrogel dressing optical sensor, which could simultaneously monitor pH and glucose levels in the wound of diabetic patients [86]. Hydrogel dressing consisted of a pH acid-base indicator, glucose oxidase, and horseradish peroxidase (figure 7(a)). This novel optical sensor could accurately monitor pH ranges and glucose levels, which were 4–8 and 0.1–10 $\times$ 10^{-3} mol L^{-1}, respectively. *In vivo* experiments showed that the biomaterial had no obvious blood coagulation and high hemolysis rate (figures 7(b) and (c)), so it can be inferred that the biomaterial owned good biocompatibility. Antibacterial activity is also a property that needs to be considered for biocompatibility. Jiang *et al* constructed a self-bactericidal polymer membrane sensor doped with environmental friendliness and good antibacterial activity of 6-Cl indole to prevent sedimentation of marine organisms, as shown in figures 7(d) and (e) [87]. It can be seen from figure 9(f) that compared with the Ca^{2+} membrane without 6-Cl-indole, the ion membrane doped with 6-Cl-indole could effectively inhibit the growth of bacteria. Kazuhiko *et al* developed a wearable paper-based field-effect transistor biosensor for wireless potential measurement systems for pH and sodium ion detection [88]. The Ta_2O_5 film on the paper-based electrode and ion-sensitive membranes without plasticizer directly contacted the sample solution and formed a biocompatible sensing surface.

Biocompatible materials such as cellulose, fibrin, and chitin, with good biocompatibility and mechanical properties, have received extensive attention and in-depth studies. The composite film (polyvinyl alcohol and silk fibroin) has good tensile properties [89, 90] and unique self-healing properties [91, 92]. Chu *et al* created a printed composite silk stretchable wearable sensor with self-healing property for simultaneous monitoring

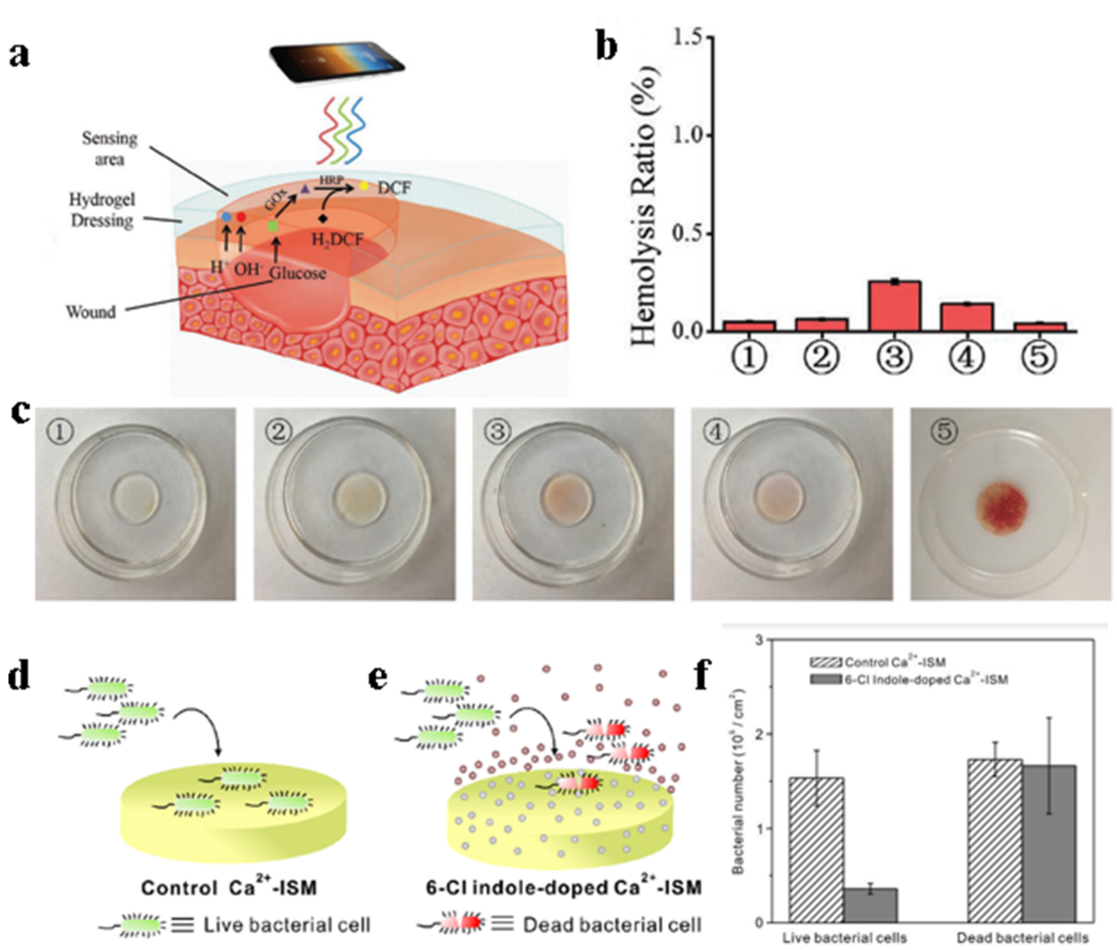

Figure 7. Nanofabrication strategies for biocompatibility. (a) Scheme of the zwitterionic hydrogel dressing for simultaneously monitoring pH and glucose concentration in wound exudate. (b) Comparison of hemolysis rate upon incubation with different hydrogel dressings: ① PCB, ② PCB-PR, ③ PCB-E, ④ PCB-PR-E, and ⑤ DuoDerm. (c) Photographs of blood cells adhesion: hemolysis test about different hydrogel dressings. [86] John Wiley & Sons. © 2019 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (d), (e) Schematic diagram of the antimicrobial activity without and with 6-Cl Indole-doped Ca^{2+}-ISM against marine biofouling. (f) Comparison of the number of living and dead bacterial cells with and without 1 wt.% 6-Cl Indole-Doped Ca^{2+}-ISM. Reprinted with permission from [87]. Copyright (2020) American Chemical Society.

of exercise and human cancer markers [93]. These results indicate that silk-modified materials are a good choice for wear-resistant sensors.

6. System integration via printable strategies

For sensor manufacturing, it is necessary to adopt proper preparation methods to realize high sensitivity, flexibility, low cost and miniaturization. Printable technology has become a promising method because of its low cost, high precision and mass production, and it has been extended to the application of electronic equipment. Printing inks are usually composed of fillers, binders, and solvents. The performance and printing ability of the ink depend on the solid loading, the dispersibility of the particles, the specific surface area, and the density of particles. Conductive inks often contain materials like carbon, graphene, and metals (such as silver, gold, or platinum), while transducer functional inks incorporate oxides, polymers, nanomaterials, or enzymes to enhance sensor performance. Contact and non-contact printing are the two main methods in printed electronic equipment. Gravure printing and screen printing belong to the contact printing method because of the physical contact of ink and the substrate in the printing process. On the contrary, inkjet printing is considered a non-contact method. In the following section, the most commonly adopted printing technologies along with the conductor and transducer layer material preparation and ink formulations for wearable sensors fabrication and integration will be introduced. Table 2 provides a list of functional ink formulations for various printing technologies, which includes information on the binders and solvents used in each formulation.

Table 2. A summary of functional ink formulations for different printing methods.

Nanomaterial ink type	Printing method	Ink	Binder	Solvent	References
Conductor	Screen printing	Carbon ink	PVDF	N-methyl 2 pyrrolidone	[94]
	Gravure printing	Ag ink	PVP	Terpineol	[95]
	Gravure printing	Carbon ink		ECA	[95]
	Inkjet printing	Au/PEDOT-PSS ink		DI water	[96]
	Inkjet printing	CNT ink	SDS	DI water	[97]
	3D printing	CNT ink	Ethyl acetate	PDMS	[98]
Transducer	Screen printing	CuO ink	Poly (methyl methacrylate)-poly (butyl methacrylate) (PMMA)	Butyl carbitol acetate	[99]
	Screen printing	pH sensing ink	Silk fibroin	Glycerol	[100]
	Inkjet printing	PANI ink	SDS, acrylic resins	DI Water	[101]
	3D printing	ISMs ink	Bis(2-ethylhexyl) sebacate	Acrylate monomers, urethane dimethacrylate, photocurable resin	[102]

6.1. Screen printing

A widespread problem with wearable sensors is that the working electrode materials usually do not combine well with the flexible substrate. Screen printing technology is prominent because it can be applied to almost substrates, including paper, polymer materials, textiles, wood, metals, ceramics, glass, and leather. More importantly, the screen-printing process can not only apply ink to a flat surface but also print on a substrate with a curved surface, spherical surface and concave–convex surface, and the screen can consistently adapt to the shape of the substrate without deformation.

Screen printing can work by pressing liquid material with a scraper into a patterned mask/screen plate [103]. It consists of five parts: screen printing plate, scraping plate, ink, printing table, and substrate. The resolution of screen printing technology is mainly limited by mask manufacturing technology, and the quality of the pattern is highly dependent on the ink formulations and their affinity with the substrate. The composition of screen printing ink typically includes nanoparticles or compounds, binders (e.g. Nafion [103], polyvinylidene fluoride (PVDF) [103], thermoplastic polyurethane polymer [104]), solvents (e.g. dimethylsulfoxide (DMSO) [105], toluene [106], ethanol [107], glycerol [100]), and other components. The performance of the ink is usually controlled by adjusting the ratio of ink raw materials and additives. Additionally, various modifiers can be added to optimize the performance of the sensor. Notably, it can be used for large-scale printing because of its high speed of around 70 m min^{-1} [108, 109].

In recent years, various printable materials, such as metal (silver ink), carbon-based (e.g. carbon ink, graphene ink, and CNT ink), metal oxide and conducting polymer (e.g. PEDOT:PSS ink, polyaniline ink) composite materials, have been reported, showing wide applications in wearable electronic sensors [58, 99, 110, 111]. For instance, Ha *et al* prepared a multi-channel pH sensor based on nanocomposites of single-wall carbon nanotubes (SWCNTs) and Nafion printed by screen printing on flexible substrates, as shown in figure 8(a) [112]. Vinoth *et al* fabricated a wearable microfluidic sensor using a screen-printed carbon master for monitoring Na^+, K^+, pH, and lactate in sweat [94]. The sensor realized simultaneous health monitoring and reduced sample usage by printing a sensing electrode on a flexible polyimide substrate. Composite conductor layer ink is prepared by homogenizing silver paste with binder poly(styrene-co-methyl methacrylate) by ultrasonication and centrifugation. A smartwatch for sweat monitoring, which was used to monitor K^+ and Na^+ in sweat was presented by Ye *et al* [111]. Silver/silver chloride ink (for reference electrode), carbon ink (for ISE) and insulator ink were orderly arranged on PET substrate by screen printing technology. In addition, the high conductivity and two-dimensional layered structure of graphene make it a popular choice for creating conductive networks in screen-printing inks, thereby improving the conductivity of microelectronics [112].

In the screen printing process, the ink is pushed onto the substrate through the mesh. The grid serves as a support for the mold that defines the pattern. Therefore, a high-viscosity ink is required to obtain suitable thick film deposition. However, the printing of high-resolution features is limited by the grid, which requires

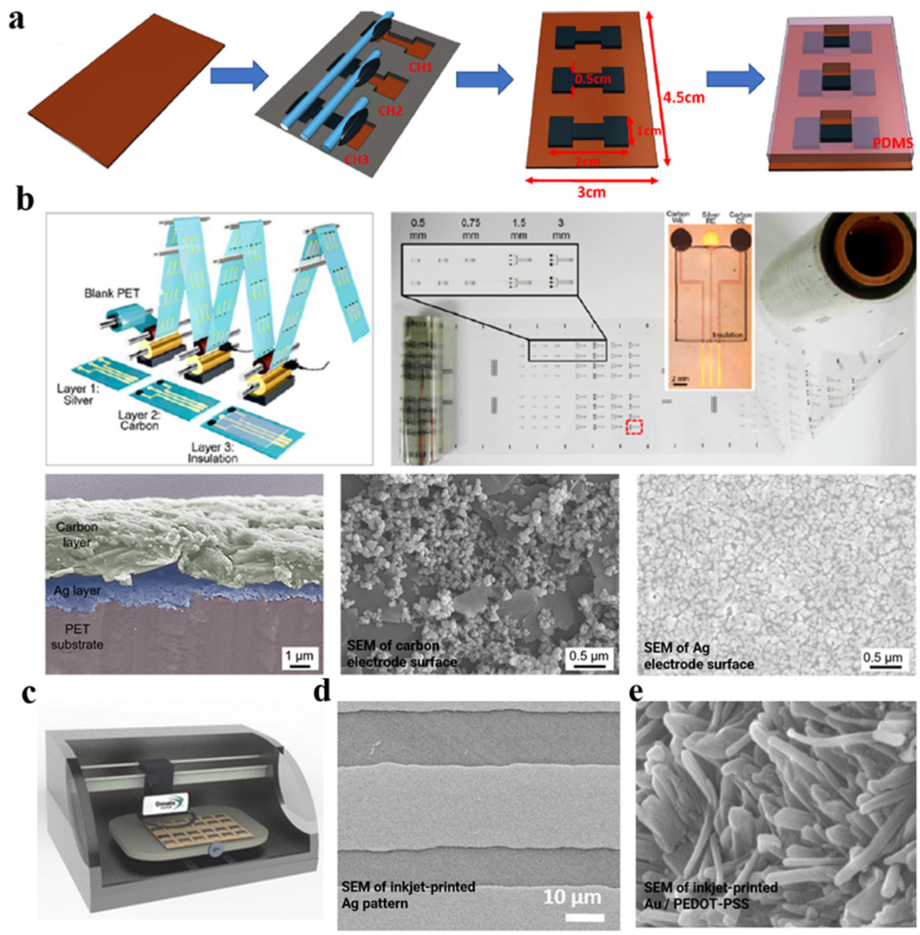

Figure 8. Printed electrolyte sensors. (a) Schematic process of the flexible pH sensor fabricated by a screen printing process in ambient air. Reprinted from [112], © 2020 Elsevier B.V. All rights reserved. (b) Roll-to-roll (R2R) gravure printed electrodes, distribution and nanostructure of carbon ink, silver ink. Reprinted with permission from [95]. Copyright (2018) American Chemical Society. (c) Dimatix materials printer and the printed SEM images of (d) Ag and (e) Au/PEDOT-PSS ink. [125] John Wiley & Sons.© 2017 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. Reprinted from [96], Copyright © 2013 Elsevier B.V. All rights reserved.

smaller openings to obtain fine graphics. This limits the amount of high-viscosity ink that can pass through the mesh, resulting in uneven structure [113]. Generally, the resolution of screen printing is limited to a few microns.

6.2. Gravure printing

Gravure printing is a widely used roll-to-roll (R2R) technique offering high throughput and low-cost sensing elements [114–116]. It has been regarded as a promising electronic technology because of its large-scale printing, fast speed, and ability to produce all kinds of shapes. Although R2R technology has been widely used in printing flexible electronic devices, it has not been fully utilized in wearable sensors. In short, gravure printing is to carve the pattern to be printed into the rotary printing cylinder as a discontinuous cavity. In the printing process, the engraving chamber is filled with ink through the ink pool, and the redundant ink is removed using the flexible scraper. The gravure printing process includes four sub-processes: unit filling, scraper wiping, ink transfer, and ink dispersion on the substrate. It has a resolution of fewer than 5 μm. However, the main challenge of gravure printing is to overcome the non-ideality of the wiping process of the doctor blade.

Javey *et al* used R2R gravure printing technology to manufacture electrode arrays on 150 m flexible PET substrate for various wearable electrochemical sensing, as shown in figure 8(b) [95]. In this process, several flexible electrodes with different sizes were printed, and the most suitable electrode was selected for comprehensive testing according to actual requirements. These electrodes can be fabricated as flexible sensors for sensing pH, Na^+, K^+, glucose, Cu^{2+}, and caffeine. To achieve a high quality ink, Javey *et al* adjusted the binder and solvent content to optimize viscosity and surface tension. Silver ink was produced by dispersing silver in a poly(vinyl butyral) binder solution and adjusting the viscosity and wettability with terpineol. Carbon ink was obtained by diluting the carbon paste with diethylene glycol monoethyl ether acetate (ECA), while an insulating ink was created by dissolving polyethylene in ECA. The above technology has an obvious advantage, the printed flexible electrode can maintain corresponding electrochemical performance under mechanical stress, which makes the physiological data reliable. Gravure printing is a prospective technology combining high resolution with high printing speed and can promote the development of fully printable sensors.

6.3. Inkjet printing

Inkjet printing has evolved from printing documents and pictures to a non-collision, addictive pattern formation, and maskless method for accurately depositing micro and nanomaterials into functional arrangements [117]. Among printing technologies, it is a popular and frequently-used printing method due to its non-contact, easy to control, and low cost in the working process. Whether it is a flexible or stretchable substrate or contains deep grooves [118], inkjet printing is also feasible. Just like the Dimatix materials printer, only need to import the pattern drawn by the drawing software into the software to print electrodes with different shapes. Conveniently, hardware properties or components do not need to be modified. Printers commonly have 1 pL and 10 pL ink cartridges, and their average dot diameters are 34.2 ± 1.9 and 65.4 ± 3.2 μm, respectively [119]. The printability of inks, which is defined by the ability of inkjet printers to produce well-formed single droplets without forming satellites, is typically within the practical range of approximately $2 < Z$ (the reciprocal of the Ohnesorge number) <20.

There are some differences between gravure printing and inkjet printing. For inkjet printing, the nozzle needs to scan the whole pattern gradually, and the volume of droplets is fixed so that the printing time may be several minutes to several hours, depending on the size of the pattern. However, it can easily print multiple layers or partial overlaps. For gravure printing, almost all patterns are printed at the same time. However, it is easier to control the volume of each droplet by changing the cell size.

Inkjet printing technology has been widely used in various fields, such as sensors [3, 120–122], food safety [123], health monitoring [124], and supercapacitors [125]. There are some limitations in different aspects of inkjet printing, such as printing speed and resolution. The use of a large number of nozzles in the printing process often increases the risk of clogging. When the size of the nozzle decreases, the deviation of the droplet increases, which leads to a decrease in reliability.

Common conductive inks include silver [119], gold [126], nickel [125], copper [127], graphene [128], carbon nanotubes [129], etc. Peltonen *et al* proposed a paper-based potential ISEs in which reference and working electrodes were printed using a stable suspension of gold nanoparticles as ink to detect K^+ [96]. Deen *et al* demonstrated the inkjet printing of functionalized single-wall carbon nanotubes for pH sensing [97]. The thick and dense SWCNTs film made the pH sensitivity reach 48.1 mV/pH. The resistance of the SWCNT electrode could be reduced by multi-pass printing, showing high pH sensitivity and stability. To create CNT ink, sodium n-dodecyl sulfate (SDS) is used to ultrasonically disperse CNT and decrease the surface tension of water. This results in optimized ink distribution to the cartridge nozzles. Conductive polymers, such as poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate) (PEDOT:PSS) [96], polypyrrole (PPy) [130] and polyaniline (PANI) [101], are well-suited for wearable electronics due to their mechanical properties, which are more compatible with flexible substrates. In many applications, the conductivity of conducting polymers is insufficient when compared to metal and carbon-based conductors. Based on this, DMSO and fluorosurfactant as additives are often required to enhance the conductivity. Figure 8(c) shows the appearance of the Dimatix materials printer and the scanning electron microscope images of the printed Ag and Au/poly(3,4-ethylenedioxythiophene) -poly(styrenesulfonate) (Au/PEDOT-PSS) ink. The aqueous dispersion ink of Au/PEDOT-PSS was synthesized by reducing tetrachloroauric acid with 3,4-ethylenedioxythiophene (EDOT) monomer in the presence of PSS. Monsalve *et al* utilized inkjet printing of PANI to prepare the pH sensor [101]. PANI was synthesized by oxidatively polymerizing aniline monomer with ammonium peroxodisulfate and hydrochloric acid. The dispersion of PANI was stabilized and its surface tension was reduced by adding SDS. A waterborne acrylic resin was prepared via semi-continuous emulsion polymerization, which allowed the acrylic acid to create a flexible film with strong adhesion to the polyester substrate after drying.

6.4. 3D printing

In recent years, another technology that has attracted widespread attention is 3D printing, a technology for manufacturing substrates by printing layer by layer using an adhesive material. Applications of 3D printing are rapidly expanding and are expected to revolutionize healthcare. Materials used in 3D printing, including elastomers, functional inks (such as nanosilver, polymer, carbon, and liquid metal inks), and hydrogels, presents opportunities for developing biosensors, particularly on non-planar substrates. The prominent advantage of 3D printers is that they can freely produce customized medical products and equipment cheaply. Traditional manufacturing methods are still cheaper for mass production; however, the cost of 3D

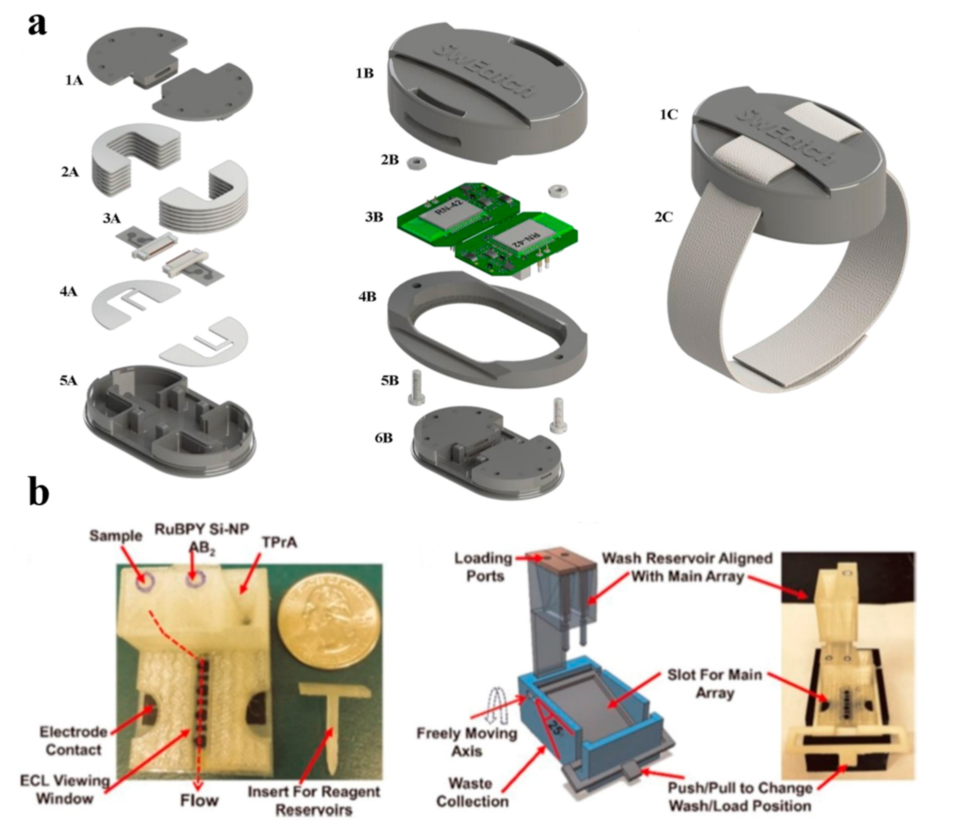

Figure 9. (a) The microfluidic unit, the platform body, and the fully integrated wearable platform. Reproduced from [131]. (b) 3D modeling and printing of the microfluidic immune array. Reprinted from [121],

printing is becoming more and more competitive for small batch production. 3D printing can also reduce manufacturing costs by reducing the use of unnecessary resources, and the production method is much faster than traditional. However, the resolution, accuracy, and reliability of 3D printing technology need to be improved.

At present, outstanding progress has been made in the medical field. For instance, 3D blood vessels, 3D chest cavity, and 3D heart machine pumps can be printed out using 3D printing technology. Besides, the technology can also be used in the field of wearable sensors. For example, McCaul *et al* prepared a wearable sensor by 3D printing technology to monitor Na^+ and K^+ in human sweat during exercise (figure 9(a)) [131]. The 3D printing platform was divided into three main components: the microfluidic unit, the platform body and the fully integrated wearable platform, which contained two independent Na^+ and K^+ electrode sample channels. Moreover, the microfluidic unit used a variety of materials for printing to show good capillary force. Kadimisetty *et al* developed an electrochemiluminescent protein immune array based on 3D printing, which was sensitive and powered by supercapacitors [132]. A commercial desktop 3D fusion deposition printer was used to print this microfluidic immunoassay (figure 9(b)).

In response to the demand for flexible and wearable sensors, stretchable conductive materials are frequently used for sensing device fabrication. Carbon-based conductive nanofillers [98, 133] are particularly well-suited for this purpose, as they can be readily combined with stretchable materials such as silicone elastomers, natural rubber, PU, and PDMS. This is due to their ability to reorganize the conductive network within the elastomer. Direct 3D printing methods can be used to fabricate stretchable electrodes. For example, CNTs are dispersed in ethyl acetate with sonication, followed by the addition of PDMS and another round of homogenization. After completely evaporating the ethyl acetate at high temperature, a PDMS-CNT composite ink is produced. Finally, PDMS curing agent is added to create the printing ink. This process enables the successful production of stretchable electrodes with high stretchability (>300% in PDMS) and excellent resistance stability (<5% increase at 100% strain). Bell *et al* developed a method for creating ISMs for potentiometric sensing using 3D printing [102]. Their 3D printable ISM hybrid ink consists of a photocurable structural support base (made up of acrylate monomers, urethane dimethacrylate, and photoinitiator), ion-exchange salts (composed of lipophilic anions paired with exchangeable cations to detect cationic species), and plasticizers (which enhance analyte mobility and solubility in the membrane mixture).

Table 3. Summary of the commonly adopted printing technologies for sensor fabrication and their characterizations.

	Screen printing	Gravure printing	Inkjet printing	3D printing
Resolution	>6 μm	>5 μm	>2 μm	>2 μm
Material requirement	High viscosity	High viscosity	Low viscosity	Quick solidification
Attractive factors	Facile operation and highly compatible with various functional materials	Scalable fabrication with high through-put and reproducibility	High resolution pattering and desired controllability on mass loading	Compatible with non-planar surface and versatile structural design
Printing speed	c.a.70 m·min^{-1}	Highly efficient and scalable	c.a.1 m min^{-1}	<4 m min^{-1}
Limitations	Mask designs required and low materials utilization efficiency	Mask designs required and low materials utilization efficiency	Limited printing speed and yielding due to easy nozzle clogging	Relatively lower resolution, accuracy, and reliability

The printed film is then formed using laser curing. ISMs for potentiometric sensing of bilirubin, benzalkonium chloride, and potassium were generated by changing ion-exchange salts in a 3D-printable ink mixture. 3D printing technology can assist in developing different sensors, thereby promoting the continuous development of more advanced sensors and increasing integration [117, 133, 134]. To better compare various printing technologies, different types of printing and their characterizations were summarized in the following table 3.

7. Conclusions and prospects

Undoubtedly, the emergence of wearable sensors opens a new perspective for personalized medicine, which is expected to achieve non-invasive and real-time health monitoring. Flexible materials have great potential in many applications, including wearable sensors. The analysis of electrolytes relies largely on the biomarkers tested and is usually carried out by potentiometers or colorimetry. It is necessary to manufacture sensors with stability, long life cycle, high mechanical strength, short response time, and low power consumption. With the great progress of manufacturing strategy, wearable electrolyte sensors will bring many exciting opportunities for continuous human monitoring across a broad range of biomedical and fitness applications through the combination of supercapacitors, solar cells, unlimited data transmission, etc.

However, further development is still needed through the proper selection and optimization of materials and manufacturing methods. Although wearable sensors have made great progress, many core issues, such as sensitivity, extensibility, lifetime, accurate quantitative analysis and simultaneous monitoring of multiple samples, still need to be improved. For example, a very serious problem is the stability of the wearable sensor, which is due to the poor adhesion between the flexible substrate and the material, which may produce wrong experimental results. The need for continuous optimization, such as the thickness of the evaporation material, ink formulation, ink viscosity, printing gap, and layer number, is widespread in biosensors and affects the life of biosensors. Therefore, it is necessary to design more stable sensor components to ensure more reliable data.

Additionally, although nanomaterials play an important role in improving the sensing performance of wearable sensors, biocompatibility, toxicity, and anaphylaxis should be considered. The application of devices in the field requires biocompatibility needs to be explored in depth, and the integration of fashion and wearable fields needs to be solved simultaneously to make wearable sensor technology more widely accepted. At the same time, it is necessary to use *in vivo* verification tests to verify the correlation between body fluid and blood measurements. Solving the problems and challenges in these fields is not only a symbol of the success of wearable sensors but also can shed light on next generation wearable sensors with improved sensing accuracy, multi-functionality and wearing comfortability.

Data availability statement

No new data were created or analysed in this study.

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