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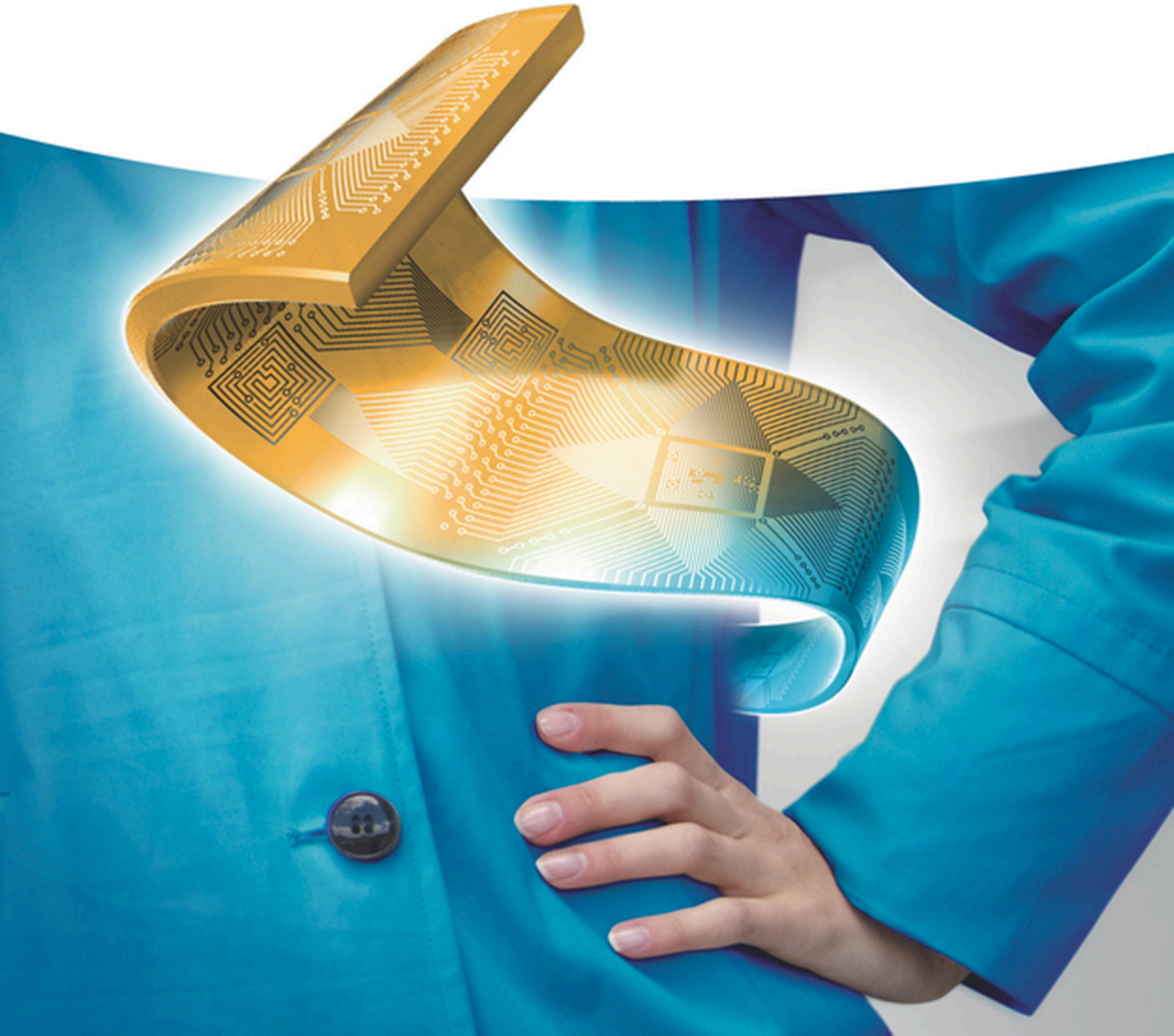
Flexible and Wearable Electronics for Smart Clothing



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Preface

When we study the history of clothing, we notice that its development depends on the revolution of materials and is relative to the industrial revolution. Materials development brings new functions to clothes and new opportunities to human society. We cannot help imagine what clothes will be like in the future. Many people have successfully taken forward the technology revolution in the clothing industry. For example, the so-called smart and wearable devices have emerged and are integrated into clothes; these devices are able to monitor our health conditions or charge mobile phones or displays, which takes us one step closer to the smart clothing that we expect. In the future, most functions that digital devices offer will be integrated into smart clothes; with all these functions together, as our second skin, the new clothes will be an intelligent interface between humans and nature.

How likely is it that it will become a reality? Be aware of this example – a fantasy shoe that can deform was demonstrated in a science fiction movie "Back to the Future" in 1989, and 17 years later, the exact same shoe was released by Nike.

To this extent, we shall believe that smart clothing, delivered by wearable technologies, is coming very soon.

Actually, wearable and flexible electronics have achieved considerable developments within the past decade and have now come to a point where they can be utilized in substantial applications, including energy conversion, artificial skin, health monitoring, and so on. In view of their versatility, ease of use, and the vast market of practical applications, wearable electronics have rapidly "exploded" in the United States, China, Korea, and all over the world. The research fields of wearable and flexible electronics are now covered from applied physics, chemistry, mechanical engineering, to material science, biomedicine, and clothing technology. Researchers and the public now pay increasing attention to wearable and flexible electronics, due to their tremendous achievement and vast potential.

This book will give an overview of recent developments in wearable and flexible electronics and their potentialities in smart clothing. The book will consist of an introductory overview followed by four sections: from Sensing (Part I), Energy (Part II), Interacting (Part III) to Integrating and Connecting (Part IV).

Sensing is one of the most typical characters of smart clothes. Part I looks first at the emergence of wearable organic nano-sensors (Chapter 1), and then moves forward to the stimuli-responsive electronic skins (Chapter 2) and flexible thermoelectrics and thermoelectric textiles for various sensing applications (Chapter 3).

Then, the next key step is to enable the wearable electronics function continuously, e.g. what is the energy supply for the smart clothes applications? Part II then moves on to energy-related topics. The first chapter in this part focuses on self-powered triboelectric nanogenerators for energy harvesting in smart textiles (Chapter 4). Besides the mechanical energy-harvesting techniques, solar cells and supercapacitors are also introduced for the smart clothes applications (Chapter 5). Lithium-ion battery is the most widely and well-commercialized energy supply for the current smart clothes industry; the development history, materials and microstructure design, and future prospects are well included in Chapter 6.

Then, how smart clothes interact with the human body is discussed in Part III. The first chapter in this section looks at the thermal and humidity management for the next-generation smart clothes (Chapter 7). The second chapter looks at the functionalization of fiber materials for washable smart wearable textiles (Chapter 8). The two chapters (Chapters 7 and 8) bring together how to make smart clothes behave humanization design and particle for the real commercialization. Microfluidics in wearable electronics is discussed in the next chapter (Chapter 9) – one of the most emerging techniques for wearable electronics in health-care applications, enabling the interaction between smart clothes and body fluids.

Even though many emerging technologies have been adopted for the development of smart clothes, only very limited real products are truly ubiquitous in current markets, compared with the conventional textile industry. How can the time-induced ultimate demise of laboratory-based wearable techniques be avoided? It is important to look at what end-users really need, the promising strategy of moving from the lab to fab for industrialization, and the future challenges that should be conquered.

Part IV considers the following themes: "how to integrate?"– the authors focus on flexible bio-integrated electronics for the health-care targeted smart clothes (Chapter 10). Then, "how to fabricate?" – flexible and printed electronics are well discussed (Chapter 11). Chapter 12 and 13 complete the picture by looking at the fabrication of the actual products that are available in the markets or the cutting-edge materials and processing for next-generation e-textiles devices.

Part I

Sensing

1

Wearable Organic Nano-sensors

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1.1 Introduction

The development of unconventional electronics, or the Internet of Things (IoT), which enables active connections between various electronic devices and massive information flows from both the environment and humans, will likely lead to another technology revolution in the near future [1]. To realize effective connections between factors such as environmental parameters and human vital statistics and electronic devices, sensors serving as an inevitable bridge that converts environmental/human body signals to electronic signals and their characteristics will determine the future of IoT [2].

Nowadays, numerous sensors, including optical, chemical, electrical, gas, heat, and mechanical, already play an important role in our daily life [3]. For instance, a typical smartphone contains an accelerometer, gyroscope, magnetometer, proximity sensor, ambient light sensor, microphone, touchscreen sensor, etc. These sensors enable us to live better, learn quicker, and work faster [4]. Even though enormous achievements have been realized with these state-of-the-art sensors, they continue to provide us with emerging applications, including humidity sensors that can be integrated into a cellphone and optical sensors that are able to recognize a human face. These successfully commercialized sensors rely on traditional inorganic mechanically rigid materials and complex fabrication processes, which are usually not compatible with flexible/stretchable substrates [5].

In recent decades, another kind of electronic material consisting of organic components has emerged as an attractive alternative [6]. Compared to its inorganic counterparts, organic materials, in theory, possess unlimited species, since the properties of organic materials can be manipulated by simply regulating the chemical structures and/or compositions [7]. Organic semiconductors (OSCs)

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have already accelerated the development of flat panel displays due to the incredibly high performance of organic light-emitting diodes (OLEDs). Organic thin-film transistor (OTFT) based back panel displays also give rise to the commercialization of the first ever bendable smartphone [8]. A plastic empire is on the rise, as a large fraction of the organic materials are polymers, and they are utilized in almost every aspect of daily life in the human society [8]. Polymers can be designed to be stronger than metals, as reliable as ceramics, and as soft as liquids. More interestingly, they can be constructed to be insulators, semiconductors, or even conductors. Unconventional properties, such as self-healing, and stretchable semiconductors/conductors can also be accomplished with organic materials [9].

Taking advantage of the wide range of properties of organic materials, multifunctional sensors with flexibility/stretchability are rapidly developing and as a result, the design of wearable sensors has become a major research target. The next-generation sensors should be low-cost, lightweight, low energy consuming devices, which together with capabilities such as being bendable or even stretchable, will ensure compatibility with wearable technologies. Wearable sensors can not only simplify the daily life routine but also provide a great tool for in situ monitoring of either external or internal parameters [10]. People have already partially benefited from wearable sensors; applications to monitor heart rate (or even electrocardiography) and the number of steps walked are already commonplace in smart watches. In the future, wearable sensors will enable real-time monitoring of the health of the human body, including blood pressure, oxygen levels or if someone has suddenly fallen, and will likely enable quick diagnosis of common diseases [11]. Furthermore, environmental conditions and hazardous atmospheric conditions can be monitored, which can act as information collection terminals in IoT, improving public safety [12].

1.2 Wearable Organic Sensors Based on Different Device Architectures

Owing to the boost in the area of organic electronic materials, different device architectures can be adopted to realize flexible and stretchable organic sensors for potentially wearable applications. Among various device architectures, resistors, transistors, electrochemical, and diode-based devices are intensively investigated, owing to their compatibility with traditional Si processing. While different device architectures have different advantages, they can all be designed to function as effective sensors. Sensing applications, including motion detection, hazardous gas monitoring, disease diagnosis, temperature recording, etc. will be summarized. Furthermore, the integration of wearable sensors with portable power sources and data processing hardware/software to enable real-time information collection and processing has been reported [13].

In the following sections, we will focus on different sensor device structures, illuminating the functional principles, popular organic materials, and practical applications. Representative examples for designing flexible/stretchable sensors and the strategies to enhance the sensing performance will be demonstrated.

1.2.1 Resistor-Based Sensors

1.2.1.1 Definitions and Important Parameters

One of the simplest electronic devices is the resistor, where resistance is the key parameter for any type of resistor. By utilizing resistors as sensors, the variation in resistance is recorded when the resistor is in contact with the analyte. Not only the value of the resistance is important for sensor applications, but several other parameters are also equally critical. These include response time and recovery time, which indicate how long the sensor will generate effective processable signals or recover to its original state, and sensitivity, which indicates the detection limit of a target analyte. As resistors are easily fabricated and characterized, they represent the most widely studied device structure for sensing applications, including sensors with stretchable and wearable properties.

1.2.1.2 Materials and Applications

Materials are the most important factor influencing sensor performance, contributing to the direct interaction with the analyte and electronic signal transformation. Among all the materials that can be used as active layers in a resistor-based sensor, graphene has exhibited emerging advantages due to its high surface to volume ratio, controllable conductivity by adjusting the composition/morphology/geometry, and excellent thermal conductivity. Wang and coworkers successfully demonstrated a highly conductive, flexible, and compressible all-graphene thin-film sensor [14]. This sensor can sense heat and cold, measure the dimensions of the heated/cooled area, discern human touch from other pressures, and enable human touch location and measurement of pressure level under zero working voltage. Graphene was also coupled with some organic materials to improve the sensing performance. The passive all-graphene flexible thin-film sensor (FTS) technology may pave new pathways for the development of electronic skin.

In another example, Zhu and coworkers fabricated highly sensitive graphene woven fabrics (GWFs) by using a crisscross copper mesh substrate with chemical vapor deposition (CVD) of graphene [15]. A flexible and wearable strain sensor was assembled by adhering the GWFs on polydimethylsiloxane (PDMS) and medical composite tape. The ultralight sensor exhibited features including relatively good sensitivity, high reversibility, superior physical robustness, easy fabrication, ease to follow human skin deformation without irritation, and so on. As a consequence of the piezoresistive effect of GWFs, the sensors were used as electronic skin covering the human body to detect body motions (Figure 1.1a,b). The signals of GWF resistance change depend on the deformation strain that is formed by the motions. The stronger the motion, the larger the strain, and the motion signals can be recorded more easily. Some weak human motions were chosen to test the notable resistance change, including hand clenching, phonation, expression change, blink, breath, and pulse. Because of the distinctive features of high sensitivity and recyclability, the GWFs–PDMS–tape based piezoresistive sensors exhibited wide potential applications in displays, robotics, fatigue detection, body monitoring, in vitro diagnostics, and advanced therapies.

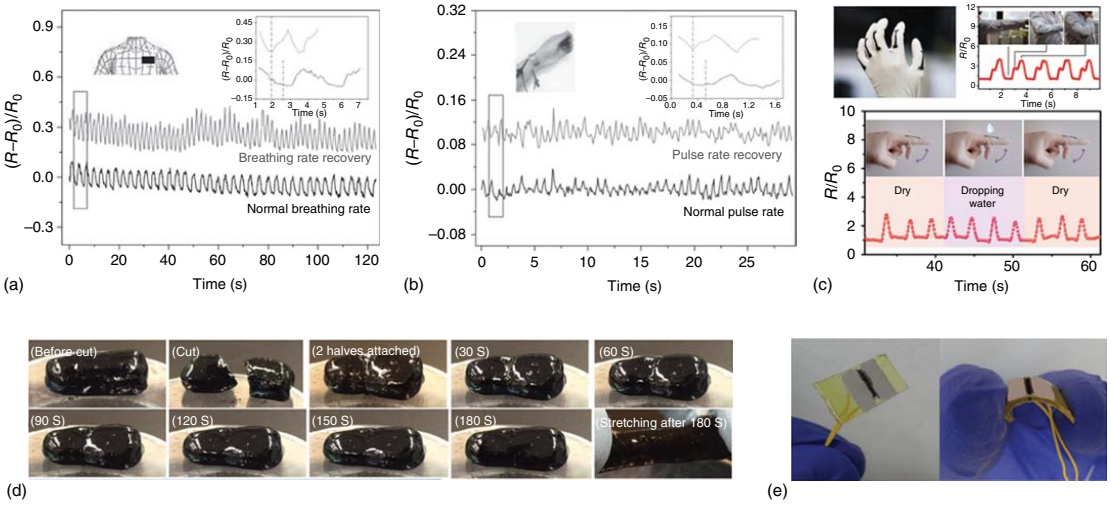

Figure 1.1 Relative change in resistance of respiration and pulse, in (a) and (b), respectively, at still state and exercise state. (c) Real-time human motion detection using superhydrophobic MWCNT/TPE-film sensors, including an optical photograph of a latex glove with five film sensors coated on each finger; normalized relative resistance as a function of time; and real-time variation of the normalized relative resistance. (d) Self-healing property of H2010h1 hydrogel. The hydrogel was cut into two halves and then brought together again; every 30 seconds, the hydrogel is shown enabling us to track the vestige of cut. (e) Photograph of the self-healing chemiresistor consisting of a transparent (yellowish) self-healing substrate, jelly-like self-healing electrode, and pliable induced self-healing AuNP film. Source: (a, b) Wang et al. 2014 [15]. Reproduced with permission of John Wiley & Sons; (c) Li et al. 2017 [19]. Reproduced with permission of John Wiley & Sons; (d) Darabi et al. 2017 [20]. Reproduced with permission of John Wiley & Sons; (e) Huynh and Haick 2016 [21]. Reproduced with permission of John Wiley & Sons.

Further, Lee and coworkers reported a flexible and transparent chemical sensor comprising reduced graphene oxide (rGO) coupled with organic dye molecules (bromophenol blue) [16]. This device possesses promising properties such as high mechanical flexibility (>5000 bending cycles with a bending radius of 0.95 cm) and optical transparency (>60% in the visible region). Stacking the water-trapping dye layer on rGO enabled a higher response in a large relative humidity range (up to 80%), and dual-mode detection capabilities of colorimetric and electrical sensing for NH_3 gas (5–40 ppm). These advantages were attributed to the flexible and transparent rGO sensor coupled with organic dye molecules, providing great potential for real-time monitoring of toxic gas/vapor in future practical chemical sensing at room condition in wearable electronics.

Carbon nanotubes (CNTs) are another attractive material [17]. As one of the most promising semiconducting materials that may replace traditional Si, CNTs, which can act as core active materials in next-generation electronics, have also been adopted in sensing. Karimov et al. designed a CNT-based Al/CNT/Al pressure sensor [18]. This sensor was fabricated by depositing CNTs on an adhesive elastic polymer tape and placing it into an elastic casing. The diameter of multiwalled nanotubes varied between 10 and 30 nm. The nominal thickness of the CNT layers in the sensors was in the range ~300–430 μm. The interelectrode distance (length) and the width of the surface-type sensors were in the ranges 4–6 and 3–4 mm, respectively. The resistance of the sensors decreased by three to fourfold as the pressure was increased up to 17 kN/m^2. Similar to graphene, researchers also mixed CNTs with other materials to enable enhanced performance. Zhang and coworkers fabricated a highly flexible multifunctional smart coating by spray-coating multiwalled CNTs dispersed in a thermoplastic elastomer solution, followed by treatment with ethanol [19]. The coatings not only endowed various substrate materials with superhydrophobic surfaces but also responded to stretching, bending, and torsion – properties useful for flexible sensor applications (Figure 1.1c). The coatings exhibited superior sensitivity (gauge factor of 5.4–80), high resolution (1° of bending), fast response time (<8 ms), stable response over 5000 stretching–relaxing cycles, and wide sensing ranges (stretching: over 76%, bending: 0°–140°, torsion: 0–350 rad/m). Moreover, multifunctional coatings with thicknesses of only 1 μm can be directly applied to clothing for full-range and real-time detection of human motions. These sensors also showed extreme repellency to water, acid, and alkali, improving the work stability under wet and corrosive conditions.

Polymers are another widely used material for resistor-based sensing, since most polymers are intrinsically flexible/stretchable and can be engineered to be either insulators or (semi)conductors. Most of the research concerning polymer sensors is realized by utilizing/incorporating active polymer materials. In recent years, self-healing polymers represent a highlight in wearable sensors, since the self-healing characteristics provide durability upon bending and stretching. Among all potential candidates, hydrogels with excellent biocompatibility and mechanical features close to human tissues constitute a promising avenue for realizing health-care-oriented electronic functionalities. Xing and coworkers reported the development of a mechanically and electrically self-healing hydrogel based on physically and chemically cross-linked networks (Figure 1.1d) [20].

Autonomous intrinsic self-healing of the hydrogel was attained through dynamic ionic interactions between carboxylic groups of poly(acrylic acid) and ferric ions. Covalent cross-linking was used to support the mechanical structure of the hydrogel. Establishing a fair balance between the chemical and physical cross-linking networks together with the conductive nanostructure of polypyrrole networks led to a double network hydrogel with bulk conductivity, mechanical and electrical self-healing properties (100% mechanical recovery in two minutes), ultrastretchability (1500%), and pressure sensitivity. The practical potential of hydrogels is further revealed by their application in human motion detection and their 3D-printing performance. Mixing self-healing polymers with other active materials was also adopted in sensors. Huynh and Haick synthesized a self-healing polymer and composite (with Au nanoparticles, AuNPs) and assembled a bendable and stretchable self-healing chemiresistor for pressure/strain, temperature, and volatile organic compounds (VOCs) sensing (Figure 1.1e) [21]. Pressure/strain and temperature sensitivity was highly comparable to available flexible sensors. The limit of detection for VOCs in the parts per billion range makes the device useful for sensing VOCs. Healing efficiency of this chemiresistor is high so that the sensor survived after cutting several times at random positions. Moreover, the sensor was environmentally stable, i.e. the sensitivity slightly decreased (<10%) after six months. Three different chemiresistive AuNPs were used for this chemical sensor, proving its versatile combination of self-healing polymers with different sensing materials. The reported self-healing sensor raises expectations that flexible devices might one day become self-administered, thus increasing their reliability in various applications, such as durable-transparent touch-screens, self-healing e-skins, and implantable health-care electronics.

On the other hand, biocompatible polymers are also of interest for wearable sensors. To date, most reported skin-like pressure sensors are based on nanomaterials and microstructured PDMS films, limiting their wide practical applications due to unknown biotoxicity and the redundant fabrication procedure. A cost-effective, large-area-capable, and biocompatible approach for fabrication of high-performance skin-like pressure sensors is highly desired. Silk fibroin (SF) is a natural protein that has recently drawn attention due to its application as a substrate for flexible electronics.

As shown in Figure 1.2, Zhang and coworkers demonstrated the fabrication of skin-like pressure sensors using SF-derived active materials [22]. Flexible and conformal pressure sensors were fabricated using transparent carbonized silk nanofiber membranes (CSilkNM) and unstructured PDMS films through a cost-effective and large-scale capable approach (Figure 1.2a–e). Owing to the N-doped carbon nanofiber network structure of CSilkNM, the obtained pressure sensor shows superior performance, including ultrahigh sensitivity ($34.47\,kPa^{-1}$) for a broad pressure range, an ultralow detection limit (0.8 Pa), rapid response time (<16.7 ms), and high durability (>10 000 cycles). Based on its superior performance, the applications in monitoring human physiological signals, sensing subtle touch, and detecting spatial distribution of pressure were also demonstrated. Not only can the chemical structure be modified to realize high-performance sensors, but the dimensional structural design can also lead

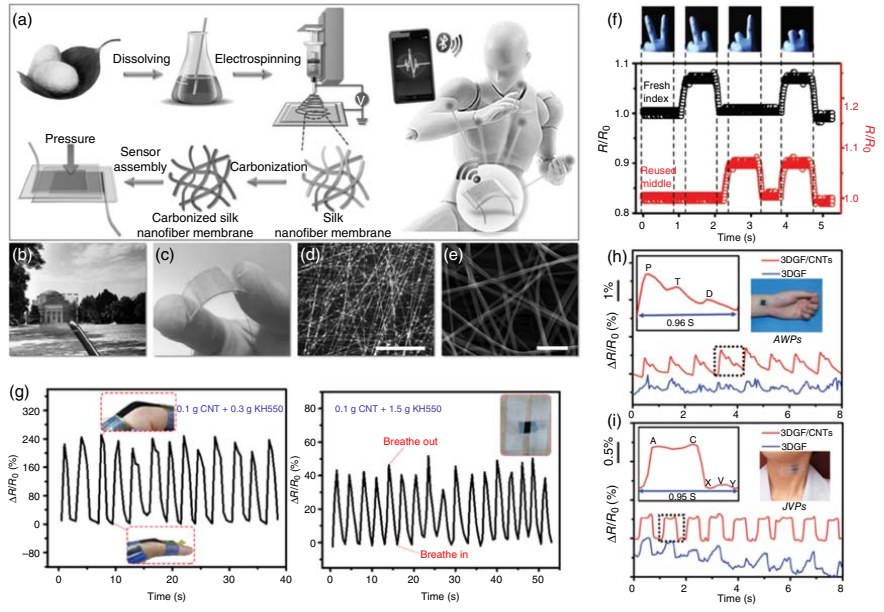

Figure 1.2 Fabrication process and structure of the CSilkNM pressure sensor. (a) Schematic illustration showing the fabrication process of CSilkNM pressure sensors. Photographs showing the (b) transparency and (c) flexibility of the obtained sensor. (d) Optical image of a silk nanofiber membrane. Scale bar: 100 μm. (e) SEM image of CSilkNM. Scale bar: 1 μm.(f) The dual sensing result from a fresh hydrogel sensor (index finger, black) and a reusable (after 12 drying–soaking cycles) hydrogel sensor (middle finger, red) reveals that the as-fabricated hydrogel electronics is able to simultaneously detect motions of multiple objects without cross-impact. (g) The relative resistance change of the sensor (0.1 g CNT/0.3 g KH550) in hand motion from stretch to curve, and the relative resistance change of the sensor (0.1 g CNT/1.5 g KH550) in response to breathing. (h) Real-time and in situ AWP measurement with the 3DGF/CNT and 3DGF networked skin-attachable strain sensor attached on the wrist. The inset shows the photograph and zoomed waveform. (i) Measurement of JVPs with strain sensors attached on the neck. The inset is the photograph and zoomed waveform. Source: (a–e) Wang et al. 2017 [22]. Reproduced with permission of John Wiley & Sons; (f) Liu et al. 2018 [23]. Reproduced with permission of John Wiley & Sons; (g) Zhou et al. 2018 [25]. Reproduced with permission of American Chemical Society; (h, i) Cai et al. 2017 [26]. Reproduced with permission of John Wiley & Sons.

to superior performance. Xu and coworkers proposed a simple paradigm to prototype stretchable electronics with an embedded three-dimensional (3D) helical conductive layout based on biocompatible and stretchable hydrogels [23]. Thanks to the 3D helical structure, hydrogel electronics presents satisfactory mechanical and electrical robustness under stretch. In addition, reusability of stretchable electronics is realized with the proposed scenario benefiting from the swelling property of hydrogel. Although losing water would induce structural shrinkage of the hydrogel network and further undermine the function of the hydrogel in various applications, the worn-out hydrogel electronics can be reused by simply casting it in water. Through such a rehydration procedure, the dehydrated hydrogel can absorb water from the surroundings and then the hydrogel electronics can achieve resilience in mechanical stretchability and electronic functionality. Also, the ability to reflect pressure and strain changes has revealed hydrogel electronics to be promising for advanced wearable sensing applications (Figure 1.2f).

One classical way using multiple active materials within a single device is widely adopted in resistor-based sensors. A mixture of graphene and stretchable polymers was investigated by Ren and coworkers, who demonstrated a mechanical sensor fabricated using a graphene porous network (GPN) combined with PDMS [24]. Using nickel foam as a template and a chemical etching method, the GPN can be created in the PDMS-nickel foam coated with graphene. The resultant material achieved both pressure and strain sensing properties. Because of the pores in the GPN, the composite sensor exhibited a wide pressure sensing range and highest sensitivity among graphene foam-based sensors. In addition, it showed potential for use in applications such as monitoring or even recognizing walking states, the degree of finger bending, and wrist blood pressure. Fu and coworkers reported a new method to realize control on the local conductive networks of strain sensors, and thus their sensing behavior [25]. They spray-coated a mixture of CNTs and 3-aminopropyltriethoxysilane (KH550) with various ratios onto PDMS to prepare multifunctional crack-based sensors. The conductive CNT/KH550 layer exhibited brittle mechanical behavior, which triggered the formation of cracks upon stretching. This is thought to be responsible for the observed electromechanical behavior. These sensors exhibited adjustable gauge factors of 5–1000, stretchability (ε) of 2–250%, linearity (nonlinearity–linearity), and high durability over 1000 stretching–releasing cycles for mechanical deformation. Washable, wearable, and water-repellent sensors were prepared through such a method to successfully detect human physiological activities (Figure 1.2g). Moreover, the variation in temperature or the presence of solvent could also be detected due to the thermal expansion and swelling of the PDMS layer. It is expected that such a concept could be used to fabricate sensors for multiple applications, thanks to its multifunctionality, adjustable and robust performance, and simple and low-cost fabrication strategy.

Separately, Dong and coworkers demonstrated epidermal sensors based on an all-carbon collaborative percolation network, which consists of 3D graphene foam and CNTs obtained by two-step CVD processes [26]. The nanoscaled CNT networks largely enhance the stretchability and signal-to-noise ratio (SNR) of the 3D microarchitectural graphene foams, endowing the strain sensor with a

gauge factor as high as 35, a wide reliable sensing range up to 85%, and excellent cycling stability (>5000 cycles). The flexible and reversible strain sensor can be easily mounted on human skin as a wearable electronic device for real-time and high-accuracy detection of electrophysiological stimuli and even for acoustic vibration recognition (Figure 1.2h,i). The rationally designed all-carbon nanoarchitectures are scalable, low cost, and promising in practical applications requiring extraordinary stretchability and ultrahigh SNRs. Lubineau and coworkers proposed transformation of an electrically conductive material from a sensor to a conductor using electrical welding (e-welding) [27]. This method is demonstrated in the case of a thermoplastic polymer sponge decorated with silver nanowires. The sensor-like behavior of the sponge was programmed by e-welding into conductor-like behavior, i.e. suppressing the gauge factor by 86%, without varying the density of the silver nanowires. An application of e-welding in the fabrication of a sensor-conductor hybrid material that may be applied as soft artificial skin in robotics was demonstrated.

1.2.2 Organic Field-Effect Transistor Based Sensors

1.2.2.1 Definitions and Important Parameters

The transistor, the base of modern electronics, is usually configured as a three-terminal device (including a gate electrode, and source and drain electrodes), where the gate electrode accompanied with a dielectric can effectively modify the carrier concentration of the semiconductor, leading to controllable drain current. Key parameters associated with transistor operation are mobility, threshold voltage, on/off ratio, and subthreshold swing. However, in a transistor-based sensor, the sensitivities and the response/recovery time are the dominant parameters for practical applications [28]. Compared with resistors, even though transistor-based sensors are more complicated in device structure, they have the advantage of multiparameter sensing capabilities [29]. All the key parameters, which include but are not limited to mobility, threshold voltage, turn-on voltage, off-current, and on-current, can be used to detect the influence of analytes on the device [30]. Moreover, since transistors can be operated under various gate biases and may be designed to amplify the current, such sensors have the potential to realize ultrahigh sensitivity [31]. Furthermore, since the active components in a transistor are richer than in a resistor, one can enhance the sensing performance by not only changing the semiconducting materials, but also the dielectric and electrode materials.

1.2.2.2 Strategy and Applications

Transistors based on OSCs are widely explored in the area of sensing [32]. Modifying the organic semiconducting layer is the most common way to improve transistor sensing parameters, where strategies including using thinner OSC films, organic nanowires, coupling with other analyte receptors are generally used. Perhaps the most common way to optimize sensor performance is to utilize an OSC that is intrinsically sensitive. As shown in Figure 1.3a, Noh and coworkers reported a highly sensitive printed ammonia (NH_3) gas sensor based on OTFTs fabricated with the fluorinated difluorobenzothiadiazole-dithienosilole

polymer (PDFDT) [33]. The sensor detected NH_3 down to 1 ppm with high sensitivity using bar-coated ultrathin (<4 nm) PDFDT layers in the absence of any receptor additives (Figure 1.3b,c). The sensing mechanism was confirmed by cyclic voltammetry, hydrogen/fluorine nuclear magnetic resonance, and UV/visible absorption spectroscopy. PDFDT–NH_3 interactions comprise hydrogen bonds and electrostatic interactions between the PDFDT polymer backbone and NH_3 gas molecules, thus lowering the highest occupied molecular orbital levels, leading to hole trapping in the OTFT active layer. Additionally, density functional theory calculations demonstrated that gaseous NH_3 molecules were captured via cooperation of fluorine atoms and dithienosilole units in PDFDT. They verified that incorporation of functional groups that interact with a specific gas molecule in a conjugated polymer presents a promising strategy for producing high-performance printed OTFT gas sensors. Sensitive organic semiconducting materials were also applied in photo-sensors.

Qiu and coworkers prepared flexible and low-voltage near-infrared organic phototransistors (NIR OPTs) with a low-bandgap donor–acceptor conjugated polymer as the semiconductor layer and *n*-octadecyl phosphonic acid modified anodic alumina (AlO_x/ODPA) as the insulating layer (Figure 1.3d) [34]. The phototransistors exhibited typical n-channel transistor characteristics at a voltage below 5 V. The photosensitivity can be enhanced by regulating the packing densities of the ODPA self-assembled monolayers and forming different trap states. The enhanced organic phototransistors (OPTs) exhibited good photosensitivity to 808–980 nm near-infrared (NIR) with the photocurrent/dark current ratio and photoresponsivity as high as 5×10^3 and 20 mA/W, respectively, benefiting from the charge-trapping effect at the AlO_x/ODPA interface, as shown in Figure 1.3e. The OPTs also presented a fast-optical switching speed of 20/30 ms and excellent mechanical flexibility. The outstanding performance of the NIR OPTs indicates that the development of wearable electronics is, indeed, possible.

Research on dielectrics has also been applied to the development of transistor-based sensors as a means to enhance performance. Huang and coworkers demonstrated a highly thermally stable organic transistor by applying a three-arm stereocomplex polylactide (tascPLA) as the dielectric and substrate material [35]. The resulting flexible transistors were stable up to 200 °C, while devices based on traditional polylactide (PLA) were damaged at 100 °C. Furthermore, the charge-trapping effect induced by polar groups of the dielectric was also utilized to significantly enhance the temperature sensitivity of the electronic devices. A skin-like temperature sensor array was successfully demonstrated based on such transistors, which also exhibited good biocompatibility in cytotoxicity measurements. By presenting the combined advantages of transparency, flexibility, thermal stability, temperature sensitivity, degradability, and biocompatibility, these organic transistors possess broad applicability in applications such as environmentally friendly electronics, implantable medical devices, and artificial skin. Good dielectric performance can enhance the sensitivity and lower the driving voltage at the same time. Zheng and coworkers developed controllable polyelectrolyte composites based on poly(ethylene glycol) (PEG) and polyacrylic acid (PAA) as a type of high capacitance dielectric for flexible OTFTs and ultrasensitive pressure sensors with sub-1 V operation (Figure 1.3f) [36].

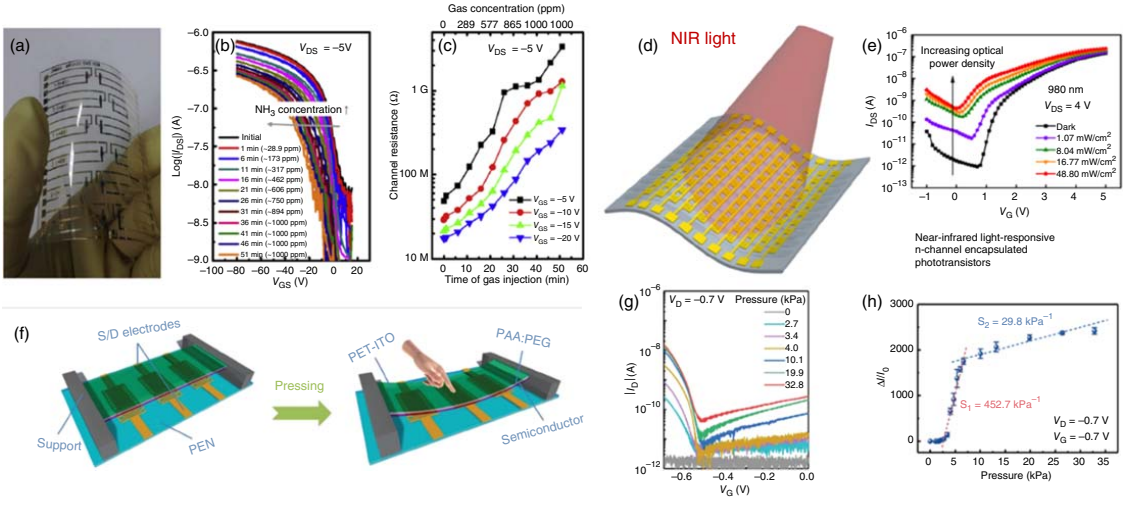

Figure 1.3 Various OTFT-based flexible sensors. (a) Image of P-29-DPP-SVS OFET showing the BG/TC geometry for the gas sensor, (b) transfer curves, and (c) channel resistance of P-29-DPP-SVS OFET. (d) Near-infrared organic phototransistors array. (e) Increased optical power density when exposed to different density of light. (f) Schematic illustration of the OTFT-based pressure sensor (gap: ≈310 μm) in the initial state (left) and pressed state (right). (g) Transfer characteristics of the OTFT sensor under different pressures. (h) Relative change of I_D in response to external pressure for the OTFT sensor at both constant V_D and V_G of −0.7 V. Source: (a–c) Nketia-Yawson et al. 2017 [33]. Reproduced with permission of American Chemical Society; (d, e) Wang et al. 2018 [34]. Reproduced with permission of American Chemical Society; (f–h) Liu et al. 2018 [36]. Reproduced with permission of John Wiley & Sons.

Flexible OTFTs using the PAA:PEG dielectrics showed good universality and greatly enhanced electrical performance under a much smaller operating voltage of –0.7 V than those with a pristine PAA dielectric. The low-voltage OTFTs also exhibited excellent flexibility and bending stability under various bending radii and long cycles. Flexible OTFT-based pressure sensors with low-voltage operation and superhigh sensitivity were demonstrated by using a suspended semiconductor/dielectric/gate structure in combination with the PAA:PEG dielectric, as shown in Figure 1.3g,h. The sensors delivered a record high sensitivity of 452.7 kPa^{-1} under a low voltage of −0.7 V, and excellent operating stability over 5000 cycles. The OTFT sensors were built into a wearable sensor array for spatial pressure mapping, which demonstrates the bright potential of flexible electronics for wearable devices and smart skins.

Apart from polymer and small molecule based transistors, CNTs have also been explored in transistor applications. Han and coworkers demonstrated a large-area high-performance flexible pressure sensor built on an active matrix of 16 × 16 carbon nanotube thin-film transistors (CNT TFTs) [37]. The active matrix exhibited superior flexible thin-film transistor (TFT) performance with high mobility and large current density, along with a high device yield of nearly 99% over a 4-in. sample area. The fully integrated flexible pressure sensor operated within a small voltage range of 3 V and exhibited superb performance featuring a high spatial resolution of 4 mm, faster response than human skin (<30 ms), and excellent accuracy in sensing complex objects on both flat and curved surfaces (Figure 1.4a,b). This work paved the road for future integration of high-performance electronic skin in smart robotics and prosthetic solutions.

Because of its narrow band gap, graphene generally does not exhibit semiconducting behavior. However, in the area of sensing, graphene-based transistors can be successfully fabricated as only the sensing functionality is needed. Also, graphene can be easily functionalized. Lee and coworkers demonstrated a flexible strain sensor based on a reduced graphene oxide field-effect transistor (rGO FET) with ultrasensitivity, stability, and repeatability for the detection of tensile and compressive strains [38]. The novelty of the rGO FET strain sensor is the incorporation of an rGO channel as a sensing layer in which the electrical resistance can be greatly modified upon application of an extremely low level of strain resulting in an intrinsically amplified sensing signal. The rGO FET device was ultrasensitive to extremely low strain levels, as low as 0.02%. Owing to weak coupling between adjacent nanosheets, therefore, upon applying small levels of strain into the rGO thin film, a modulation of the inter-nanosheet resistance is expected, inducing a large change in the transconductance of the rGO FET. Using a simple printing and self-assembly process, the facile fabrication of an rGO FET array over a large area was also demonstrated. In addition, the device was shown to be able to detect small and rapid physical movements of the human body.

A mixture of the organic semiconducting layer or dielectric layers is also a general strategy for improving sensing performance. Moreover, this approach can also impart mechanical stretchability leading to stretchable electronics. Yu and coworkers introduced an all solution-processed type of electronics and sensors that are rubbery and intrinsically stretchable as an outcome