Human skin is a remarkable organ. It consists of an integrated, stretchable network of sensors that relay information about tactile and thermal stimuli to the brain, allowing us to maneuver within our environment safely and effectively. Interest in large-area networks of electronic devices inspired by human skin is motivated by the promise of creating autonomous intelligent robots and biomimetic prosthetics, among other applications. The development of electronic networks comprised of flexible, stretchable, and robust devices that are compatible with large-area implementation and integrated with multiple functionalities is a testament to the progress in developing an electronic skin (e-skin) akin to human skin. E-skins are already capable of providing augmented performance over their organic counterpart, both in superior spatial resolution and thermal sensitivity. They could be further improved through the incorporation of additional functionalities (e.g., chemical and biological sensing) and desired properties (e.g., biodegradability and self-powering). Continued rapid progress in this area is promising for the development of a fully integrated e-skin in the near future.

### 1. Introduction to E-Skin: A Brief Chronology

Human skin is highly intuitive, making it easy to neglect the complexity of the largest sensory organ in our bodies. Our skin is the physical barrier through which we interact with our surroundings, allowing us to perceive various shapes and textures, changes in temperature, and varying degrees of contact pressure. To achieve such high sophistication in its sensing capabilities, several different types of highly specialized sense receptors are embedded within our skin. These receptors first transduce information generated by physical contact into electrical signals and subsequently send it to the central nervous systems for more complex processing. The collected signals are eventually interpreted by the somatosensory cortex, permitting us to successfully navigate our physical world with ease.

The effort to create an artificial skin with human-like sensory capabilities is motivated by the possibility of such large, multi-sensory surfaces being highly applicable for autonomous artificial intelligence (e.g., robots), medical diagnostics, and replacement prosthetic devices capable of providing the same, if not better, level of sensory perception than the organic equivalent. Endowing robots with sensing capabilities could extend their range of applications to include highly interactive tasks, such as caring for the elderly, and sensor skins applied on or in the body could provide an unprecedented level of diagnostic and monitoring capabilities.

An artificial skin with such sensory capabilities is often referred to in the literature as sensitive skin, smart skin, or electronic skin (e-skin).

Although the primary function of human skin is mechanical force sensing, electronic versions can be augmented with additional capabilities. In artificial platforms, researchers can incorporate chemical and biological sensors onto flexible substrates. Targeted species can be sensed in either gas or liquid media using such electronic noses (e-noses) or electronic tongues (e-tongues), respectively. Other sensing modalities (i.e., temperature) and other functionalities (i.e., biocompatibility, self-healing and self-powering) are also important and will be covered in subsequent sections.

#### 1.1. The 1970s to 1990s

The prospect of creating artificial skin was in many ways inspired by science fiction, which propelled the possibility of e-skin into the imagination of both the general public as well as the scientific community. One of the first science fiction books to explore the use of mechanical replacement organs was Caidin's Cyborg in 1971, on which the famed Six Million Dollar Man television series about a man with...
a bionic replacement arm and eye was later based (1974).\textsuperscript{[4]} Shortly after, at the beginning of the 1980s, George Lucas created a vision of a future with e-skin in the famous \textit{Star Wars} series. In particular, he depicted a scene showing a medical robot installing an electronic hand with full sensory perception on the main character, Luke Skywalker.\textsuperscript{[5]} Shortly after, in 1984, the \textit{Terminator} movie series depicted humanoid robots and even a self-healing robot.\textsuperscript{[6]} These fictitious renditions of e-skin took place against a real-life backdrop of vibrant microelectronics research that began bridging science fiction with scientific reality.

Early technological advancements in the development of e-skin were concomitant with their science fiction inspirations. In 1974, Clippinger et al. demonstrated a prosthetic hand capable of discrete sensor feedback.\textsuperscript{[7]} Nearly a decade later, Hewlett-Packard (HP) marketed a personal computer (HP-150) that was equipped with a touchscreen, allowing users to activate functions by simply touching the display. It was the first mass-marketed electronic device capitalizing on the intuitive nature of human touch. In 1985, General Electric (GE) built the first sensitive skin for a robotic arm using discrete infrared sensors placed on a flexible sheet at a resolution of $\approx 5$ cm.\textsuperscript{[8]} The fabricated sensitive skin was proximally aware of its surroundings, allowing the robot’s arm to avert potential obstacles and effectively maneuver within its physical environment. Despite the robotic arm’s lack of fingers and low resolution, it was capable of demonstrating that electronics integrated into a membrane could allow for natural human–machine interaction. For example, the robotic arm was able to ‘dance’ with a ballerina without any pre-programmed motions.\textsuperscript{[8]} In addition to the ability of an artificial skin to interact with its surroundings, it is equally critical that the artificial skin mimics the mechanical properties of human skin to accommodate its various motions. Hence, to build life-like prosthetics or humanoid robots, soft, flexible, and stretchable electronics needed to be developed.

In the 1990s, scientists began using flexible electronic materials to create large-area, low-cost and printable sensor sheets. Jiang et al. proposed one of the first flexible sensor sheets for tactile shear force sensing by creating silicon (Si) micro-electromechanical (MEM) islands by etching thin Si wafers and integrating them on flexible polyimide foils.\textsuperscript{[9]} Much work has since been done to enhance the reliability of large sensor sheets to mechanical bending.\textsuperscript{[10]} Around the same time, flexible arrays fabricated from organic semiconductors began to emerge that rivaled the performance of amorphous Si.\textsuperscript{[11]}

Just before the turn of the millennium, the first “Sensitive Skin Workshop” was held in Washington DC under the aegis of the National Science Foundation and the Defense Advanced Research Projects Agency, bringing together approximately sixty researchers from different sectors of academia, industry, and government. It was discovered that there was significant industrial interest in e-skins for various applications, ranging from robotics to health care. A summary of concepts outlined in the workshop was compiled by Lumelsky et al.\textsuperscript{[12]} In the early 2000s, the pace of e-skin development significantly increased as a result of this workshop, and researchers began to explore different types of sensors that could be more easily integrated with microprocessors.
1.2. The 2000s to Present

Significant progress in the development and advancement of e-skin has been achieved in recent years, in which particular emphasis has been placed on mimicking the mechanically compliant yet highly sensitive properties of human skin. Suo and coworkers have developed stretchable electrodes,\textsuperscript{[13]} and Rogers and coworkers have transformed a typically brittle material, Si, into flexible, high-performance electronics by using ultra-thin (100 nm) films connected by stretchable interconnects.\textsuperscript{[14]} Someya and coworkers have fabricated flexible pentacene-based organic field-effect transistors (OFETs) for large-area integrated pressure-sensitive sheets with active matrix readout,\textsuperscript{[15]} while Bauer and coworkers have investigated novel pressure sensing methods using foam dielectrics\textsuperscript{[16]} and ferroelectrets\textsuperscript{[17]} integrated with FETs. Our group has investigated the use of

microstructured elastomeric dielectrics for highly sensitive capacitive pressure sensors\textsuperscript{[18]} and has developed a composite conductive elastomer exhibiting repeatable self-healing and mechanical force sensing capabilities.\textsuperscript{[19]} Other groups have developed stretchable optoelectronics, including light-emitting diodes (LEDs)\textsuperscript{[20]} and organic photovoltaics (OPVs)\textsuperscript{[21]} for integration with e-skin. A timeline outlining the major milestones towards the development of e-skin is depicted in Figure 1.

In the following sections, we first discuss strategies and materials used in fabricating flexible and stretchable e-skins (Section 2), followed by a discussion of tactile sensors (Section 3) and flexible chemical and biological sensors (Section 4). We subsequently address other important qualities for e-skin applications (Section 5), describe some highly integrated demonstrations of e-skin (Section 6), and finally we provide an outlook for this field (Section 7).

2. Design Considerations for E-Skin

Human skin can be considered as a performance benchmark for the development of artificial tactile systems. Important considerations for the development of e-skin are the choice of materials used in its fabrication and the ability to confer the mechanical properties of human skin (low modulus, stretchability and flexibility) into its artificial counterpart. The following section will discuss some of the materials and techniques frequently used to accomplish these goals.

2.1. Materials

One defining characteristic of human skin is that it is mechanically compliant, allowing it to flex and stretch without incurring physical damage. The skin’s low mechanical modulus allows it to transmit the physical properties of the objects with which we interact to the myriad of receptors buried under the protective epidermis layer. Therefore, in the development of artificial skin, the materials chosen for its fabrication should reflect the flexibility and stretchability of natural human skin. Equally important is the ability of human skin to self-repair, and artificial skin should be imbued with this quality, allowing it to last a lifetime.\textsuperscript{[28]}

To achieve these properties, the choice of materials is critical, and technological advancements in e-skin have been largely possible through the development of new materials and processing methods for the fabrication of stretchable and flexible devices. In addition to mechanical compliance, good electrical performance and compatibility with large-area processing techniques are important to create highly functional, low-cost devices. Nanomaterials often provide an advantageous combination of physical properties and cost. Below, we survey several of the most commonly used materials for the fabrication of sensors and supporting electronics in e-skin. We also recommend several recent reviews that cover materials for stretchable electronics in greater detail.\textsuperscript{[29]}

2.1.1. Substrates

Polydimethylsiloxane (PDMS) has overwhelmingly been used for the fabrication of e-skin and other stretchable electronics owing to its commercial availability and well-researched properties. Its advantages include chemical inertness, stability over a wide range of temperatures, transparency, variable mechanical properties, and the ability to define adhesive and non-adhesive regions through exposure to UV irradiation, which is important for bonding electronic materials to its surface.\textsuperscript{[30]} Other substrates may be advantageous in particular applications; for example, polyurethane is compatible with stretchable printed circuit board technologies.\textsuperscript{[31]} Less conventional substrates, such as electrospun elastomeric fibers\textsuperscript{[32]} and common textiles,\textsuperscript{[33]} have also shown promise.

2.1.2. Dielectrics

Conventional elastomers, such as PDMS, can be effective dielectrics for FETs.\textsuperscript{[34]} However, there is significant opportunity to develop thin elastomer dielectrics with enhanced dielectric constants (k) and low leakage currents for use in intrinsically stretchable transistors and capacitive tactile sensors for e-skin. Three general routes towards developing high-k polymers are commonly pursued: 1) chemical design; 2) addition of high-k inorganic particles; and 3) addition of conductive fillers. Chemical design typically involves polymer chain modification to include polarizable entities such as cyano groups\textsuperscript{[35]} or fluorine atoms.\textsuperscript{[36]} A summary of elastomer dielectric constants is given by Shankar et al.\textsuperscript{[37]} High-k fillers for elastomers typically consist of rutile titanium dioxide (TiO\textsubscript{2})\textsuperscript{[38]} or ferroelectric nanoparticles (NPs), such as barium titanate (BaTiO\textsubscript{3}).\textsuperscript{[39]} Conductive fillers, such as metal particles,\textsuperscript{[40]} conductive polymers (CPs),\textsuperscript{[41]} and carbon nanotubes (CNTs),\textsuperscript{[42]} added at concentrations near the percolation threshold of the composite increase the dielectric constant by facilitating electronic polarization in the material\textsuperscript{[43]} and increasing the effective electrode area.\textsuperscript{[44]} Ion gels are composites of polymers and ionic liquids that demonstrate exceptionally high capacitance on the basis of the formation of an electrical double layer.\textsuperscript{[45]} The capacitance is largely insensitive to the thickness of the dielectric and is expected to be constant with strain, potentially making them suitable for strain-tolerant systems. Recent improvements in mechanical robustness have made ion gels a more viable option for structural applications.\textsuperscript{[46]}

2.1.3. CNT-Based Active Materials

CNTs have been remarked for their exceptional electronic and mechanical properties, as well as their chemical stability. Near ballistic transport can be achieved in defect free tubes, with reported charge carrier mobilities (µ) as high as 10,000 cm\textsuperscript{2} V\textsuperscript{−1} s\textsuperscript{−1}.\textsuperscript{[47]} Several recent reviews have discussed the properties of CNTs in more detail.\textsuperscript{[48]} Therefore, we highlight only the most important characteristics for e-skin below.

For e-skin applications, facile synthesis techniques that are reliable and scalable are of utmost importance for the production of large-area, low-cost devices. To this end, CNTs can be produced through various high-volume, low-purity techniques, including arc discharge\textsuperscript{[49]} and laser ablation.\textsuperscript{[50]} CNTs that are produced in bulk are compatible with large-area solution-processing techniques, which can be utilized to achieve purification as well as directly to deposit the CNT onto flexible
or stretchable substrates. Commonly used solution deposition techniques include vacuum filtration,[51] spin-coating,[52] spray-coating[22] and inkjet printing.[53] To optimize device performance, alignment of the tubes is necessary;[54] therefore, a number of techniques have been developed to achieve large-scale alignment, including the formation of Langmuir–Blodgett (LB) films,[55] mechanical shear techniques,[56] and contact and roll printing.[57] Additionally, we have developed a technique to sort and align CNT films simultaneously via spin-coating onto amine- or nitrile-functionalized surfaces.[52a,52c] CNTs dispersed in insulating elastomers have shown semiconducting properties,[58] but the performance of the system with strain has not been reported. A final consideration for CNT-based devices is the use of individual CNTs versus networks of CNTs. From a fabrication standpoint, networks are superior because they offer more uniform performance and are more compatible with conventional lithography and printing techniques.[86a]

2.1.4. Graphene-Based Active Materials

A second carbon allotrope, graphene, can be used as an active material in e-skin devices. Graphene consists of an atomically-thin layer of sp2-hybridized carbon atoms,[59] and possesses remarkable carrier mobility (μ~20,000 cm² V⁻¹ s⁻¹).[60] Depending on how it is processed, graphene can be used as a semiconductor or conductor. Recent reviews on graphene discuss its properties more thoroughly,[61] and we discuss only the properties relevant to e-skin below.

Graphene can be produced through a variety of high-yield techniques suitable for the fabrication of e-skin devices. These techniques include bulk growth with CVD and chemical exfoliation from bulk graphite. CVD growth of graphene on metallic surfaces[62] or epitaxial growth on SiC surfaces[63] allows for the high-yield production of large sized films[62b] with excellent electronic qualities. However, such films must be transferred to plastic substrates,[62a,63] which can introduce defects and contaminants[64] and limit device sizes,[65] although there have been recent reports of large-area transferred films.[66] Graphene can also be produced from the reduction of chemically exfoliated graphene oxide sheets[67] (reduced graphene oxide (rGO)) by chemical,[68] thermal,[69] photothermal,[70] or electrochemical[71] means. The rGO method leads to the low-cost, mass production of graphene sheets that are compatible with solution-processing techniques, such as spray coating,[72] vacuum filtration,[73] dip-coating,[74] spin-coating,[75] and inkjet printing[76] for direct deposition on large-area, flexible substrates for e-skin applications.

2.1.5. Nanowire (NW)-Based Active Materials

NWs of many materials (e.g., Si, zinc oxide (ZnO), gallium arsenide (GaAs), and cadmium selenide (CdSe), among others) form another class of active materials that has been pursued for the fabrication of e-skins.[83] However, the high cost associated with production of NW devices, either through top-down or bottom-up strategies,[77] limits their applicability in large-scale e-skin devices. Furthermore, the fabrication of NW-based devices has historically been restricted owing to the inability to integrate ordered arrays of NWs on the macroscale because of limitations with processing and assembly technology. While individual NW devices can be made through the lithographic deposition of electrodes,[78] this process is tedious and expensive and is not a viable approach for e-skin. Recent advancements in layer-by-layer (LBL) assembly,[79] LB films,[80] and contact printing[81] have allowed for the fabrication of integrated SINW devices on flexible substrates up to 1 cm² in size; however, there has only been limited demonstration of larger arrays[23a] that would be suitable for e-skin.

2.1.6. Organic and Polymer-Based Active Materials

Conducting small molecules (OSs) and polymers are flexible, carbon-based, π-conjugated materials that have demonstrated much promise for e-skin applications. Commonly used small-molecule semiconductors include acenes,[82] oligothiophenes,[83] and other molecules with fused aromatic rings, while common semiconducting and conducting polymers include regioregular poly(3-alkylthiophene) (P3HT),[84] polyaniline (PANI), polypyrrole (PPY), poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS), and their derivatives.[85] Several recent review articles on organic electronics exist,[82a,89] therefore, we will only highlight the properties that are relevant to e-skin.

While their electronic performance does not yet compare with that of inorganic semiconductors,[86] this class of materials has been touted for its ability to offer low-cost, large-area device arrays owing to the enhanced processibility of these materials over CNTs, graphene, and NWs. Additionally, although some OSs experience gate bias stress during long-term operation,[87] this issue has been alleviated through the incorporation of more complicated circuit elements (ring oscillators)[88] or through pulsed-gate bias application.[92] Despite these performance drawbacks, OSs are attractive in that their chemical and physical properties are highly tunable and can be controlled through altering their molecular structure by chemical synthesis.[90] Additionally, precise control over the deposition conditions has been found to affect parameters such as morphology, which has been linked to electronic performance.[91] Issues with light and water sensitivity can be addressed through manipulation of molecular structure, resulting in the fabrication of highly stable OS that are suitable for e-skin applications.[90a,91] The solubility of organic molecules can also be adjusted to allow for compatibility with large-area solution-processing techniques, such as spin coating, screen printing,[96] and inkjet printing.[93] As a result, these materials offer low-cost, large-area fabrication directly on flexible substrates.

One particularly attractive feature of OSs and CPs is that their mechanical properties are more comparable to human skin than their inorganic counterparts, making them ideal for implementation in e-skin. The degree of mechanical compliance depends on the molecular packing structure and intermolecular forces.[94] For instance, some small molecule semiconductors show very little tolerance for strain,[95] while some polymers can extensively deform,[94b,99] Poly(2,5-bis(3-alkylthiophen-2-yl)thieno[3,2-b]thiophene) (PBTTTT) exhibits a rigid 3D packing structure and cracks at low strains of ~3%, while P3HT can plastically deform to greater than...
150% while maintaining good electrical performance owing to the ability of its 2D packed planes to be pulled apart.\cite{94b,99a,100} The plastic deformation of P3HT could allow for one-time stretching, but reversible elasticity would require crosslinking the semiconductor to provide a restoring force.\cite{97} While P3HT itself is easily deformed, composites of P3HT with a small-molecule semiconductor for use in solar cells have demonstrated minimal strain tolerance.\cite{94u} P3HT homogeneously dispersed in PDMS has been reported as a stretchable dielectric,\cite{98} and similar methods for creating stretchable semiconductors could be considered. Compared to homogeneous dispersions, OS NWs\cite{103} dispersed in an elastomeric matrix\cite{119} may have improved electrical properties.

2.1.7. Stretchable Conductors

While conductive elastomers have been used for years as pressure sensitive elements,\cite{101} the rise in popularity of stretchable electronics has fueled the intense development of conductive elastomers with characteristics suitable for high-performance electronics. The ideal stretchable conductor would maintain high conductivity over a large range of strains, allowing reliable operation during stretching.\cite{103,105} Owing to the insulating nature of elastomers, conductivity is typically achieved through the introduction of conductive materials. The performance of composite conductors is intimately dependent on the morphology and interaction between the matrix elastomer and the filler material,\cite{104u} with large filler concentrations typically associated with enhanced elastic moduli and reduced strain at break.\cite{102,104a,105} In this respect, highly anisotropic fillers are advantageous because their low percolation threshold allows good electrical properties at low filler concentrations.\cite{113,102} In many cases, filler aggregation reduces conductivity,\cite{104d,106} although controlled aggregation into conductive pathways can reduce the required filler loading and improve conductivity.\cite{104a,107}

Compatibility with patterning methods is important for device fabrication, and stretchable conductors that can be printed\cite{20b,102,108} or photo-patterned\cite{111} have been developed. Park et al. demonstrated an innovative low-cost method of printing highly stretchable circuits using electrospun elastomeric fibers combined with metal NPs.\cite{32}

Owing to the exceptionally high conductivity of metals, metallic spheres,\cite{109} flakes,\cite{102,108} and wires\cite{110} have shown excellent performance in stretchable conductors. In general, metals can be incorporated into conductive matrices by mixing pre-formed particles with a matrix polymer,\cite{102,109a} or by growth of the metal particles in the polymer matrix using organometallic precursors\cite{32,111} or low-energy ion implantation.\cite{104b,109b} Liquid metals embedded in elastomeric channels have demonstrated some of the highest performances, but can be costly.\cite{112}

Carbon black (CB) is one of the least expensive conductive fillers available, but owing to its low conductivity (~0.5 S cm⁻¹), it is only suitable for limited applications, such as pressure sensitive rubbers and electrodes for artificial muscles.\cite{104u}

Owing to their high conductivity and large anisotropy, CNTs have been one of the most successful fillers for stretchable conductors.\cite{150,20b,102,109a,111} Aligned forests of CNTs embedded in an elastomer have been stretched up to 300% with only small changes in resistance,\cite{114} and composites of CNTs, AgNWs, and polymers have shown conductivity as high as 5710 S cm⁻¹.\cite{102} Since CNTs tend to aggregate strongly, composite preparation requires highly optimized mixing processes,\cite{20b,102,113c} or use of predetermined morphologies.\cite{113d,114} Aerogels\cite{115} and other low-density structures\cite{116} of CNTs and graphene\cite{117} can also exhibit conductivity and exceptional mechanical properties and have the potential to overcome the drawbacks of creep and relaxation that are inherent to elastomeric materials. CPs are attractive because of their compatibility with polymer matrices and low cost. CPs used in compliant electrodes have included PEDOT:PSS,\cite{104d,108} PANI,\cite{104a} PPY,\cite{105} and P3HT.\cite{120} CPs have demonstrated conductivities up to 1000 S cm⁻¹ at 0% strain and 100 S cm⁻¹ at 180% strain.\cite{104a} A challenge associated with the use of CPs is their sensitivity to environmental conditions, which results in the degradation of their electrical characteristics over time.\cite{118} However, this can be mitigated through chemical and morphological tuning.\cite{121} Overall, the field of stretchable conductors has progressed rapidly thanks to improved methods for optimizing the dispersion state of fillers.

2.2. Strategies to Achieve Stretchability

An important characteristic of human skin is its ability to stretch and flex with bodily movements without incurring damage. While arrays of flexible electronics have been developed by using very thin plastic substrates,\cite{112} stretchable devices have been more difficult to achieve, and new processes and materials are often required.\cite{112} In general, stretchable devices can be fabricated by developing devices comprised of intrinsically stretchable materials or by appropriate geometrical arrangement of conventional materials.

2.2.1. Intrinsic Stretchability

Intrinsically stretchable devices may have an advantage in applications where full area coverage and coplanar devices are desired. For example, stretchable displays with high pixel density could benefit from stretchable light emitters, which may require intrinsically stretchable drive transistors. Furthermore, intrinsically stretchable devices could realize a cost advantage by direct printing onto elastomeric substrates. Recent progress in stretchable materials development has enabled a number of intrinsically stretchable devices. Cao et al. developed transparent transistors that could withstand up to 3% strain using CNTs for both the electrodes and the active material and PDMS as the dielectric layer.\cite{124} Lee et al. demonstrated a transistor with graphene electrodes and active layer that showed reliable operation while stretching up to 5% for 1000 cycles.\cite{125} A more detailed description of issues relevant to stretchable graphene-based transistors is available by Ahn and coworkers.\cite{126} Intrinsically stretchable light-emitting electrochemical cells have been reported by Yu et al.\cite{20b} By replacing the traditional brittle active layer of LEDs with a liquid-like electrochemical emitter and using electrodes composed of CNTs embedded in a polymer, the light emitters
could stretch up to 45% while maintaining their performance. Carmichael and coworkers developed intrinsically stretchable light emitters by embedding electrochemically active emitters in a PDMS matrix and using a thin gold (Au) film as a semi-transparent electrode.[127] One challenge facing intrinsically stretchable devices is the difficulty of finding hermetic, stretchable encapsulants.[29b]

2.2.2. Geometric Structuring

Electronic devices have historically been developed using brittle high-modulus materials: namely, inorganic semiconductors and metals. These materials provide exceptional performance compared to currently available intrinsically stretchable materials, and their incorporation into stretchable devices leverages a rich history of technological development. Intrinsically brittle materials can be endowed with large-scale stretchability by appropriate geometrical patterning and device design.

Formation of Cracks and Patterns: While continuous plastic deformation can be promoted by adhesion to a compliant substrate,[128] large-scale reversible elasticity is achieved using discontinuous structures that can distort while retaining electrical conductivity. The discontinuous structures can be patterned at different length scales, but rely on similar mechanisms. At the microscopic level, discontinuous films on elastomeric substrates can be created by cracking a thin film while maintaining a percolating pathway (Figure 2a).[129] Wagner, Suo, and Lacour investigated Au films on elastic substrates[130] and found that they could be stretched up to 100% with reproducible cycling.[129e] Au is an attractive material because of its compatibility with standard patterning methods and high-density device fabrication.[131] In some cases, the stretchability of conductors can be improved by roughening the surface of the substrate[129c,132] to inhibit the propagation of cracks through the conductive layer and preserve the conductive pathways. In this manner, films of PEDOT:PSS on elastic substrates retain conductivity while being stretched far beyond the fracture strain of the pure material.[133] Lipomi et al. proposed that the deformation is accommodated by plastic deformation at low strains and cracking at high strains.[133c]

While cracking of a continuous film can create a randomly patterned conductor as described above, similar results can be achieved by depositing a network of 1D conductors.[134] The discontinuous, 1D nature of the conductors limits accumulation of stress in the network and allows contact to be maintained during stretching. During stretching, the long nanostructures bridge conductive regions, allowing electrical conductivity to be retained (Figure 2b).[134b-d] At a larger length scale, deliberate patterning of discontinuous structures can be used. To fabricate stretchable conductors on elastic substrates, convoluted pathways such as serpentine or horseshoe-shaped structures are effective,[24] and the strain reduction in the structures is strongly dependent on the patterned geometry and materials properties (Figure 2c).[135] Using optimized geometries of a single iteration of patterning, a serpentine structure embedded in an elastomer could be stretched to strains up to 100% with
minimal change in the conductivity,\(^\text{135a}\) and multiple iterations of serpentine patterning further improved stretchability up to 300%\(^\text{137}\). Patterning a flexible substrate into a discontinuous film is an attractive method of imparting stretchability on the device level because it requires minimal changes to established fabrication methods. With this technique, strain is accommodated by twisting out of the plane of the distortion (Figure 2d).\(^\text{15a,136}\)

**Buckling**: Depositing a high-modulus thin film onto a prestrained elastomeric substrate results in the formation of wrinkled (buckled) films upon relaxation of the system,\(^\text{118}\) as energy minimization induces the formation of sinusoidal wavy patterns in the film.\(^\text{119}\) Uniaxial prestrain leads to the formation of linear buckles (Figure 3a),\(^\text{21a,140}\) while biaxial prestrain results in a herringbone bucking pattern (Figure 3b).\(^\text{141}\) With buckles present, a device can be stretched to the value of the prestrain without inducing considerable strain in the active components. Similar results to buckling can be achieved by structuring an elastomeric substrate with waves prior to film deposition, eliminating the need for prestrain.\(^\text{132,142}\) Buckling has been applied to a wide variety of materials, including inorganic semiconductors, metals,\(^\text{143}\) composites,\(^\text{144}\) graphene,\(^\text{145}\) and CNTs.\(^\text{12,146}\) We demonstrated that simply straining and releasing a network of CNTs spray-coated onto elastomeric substrates can result in the formation of buckles (Figure 3c).\(^\text{22}\) Subsequently, the conductivity of the network remains constant during stretching. Buckled films of mechanically compliant materials such as porous copper (Cu)\(^\text{143}\) or silver (Ag) NWs\(^\text{134b}\) can sustain very large strains up to 460%\(^\text{114b}\). However, very brittle materials such as Si nanoribbons can withstand only \(\approx 20\)% strain.\(^\text{122}\) Larger stretchability can be achieved when the wavelength of the buckles can be controlled by rational design. Pop-up structures can be created using chemical patterning to selectively bind parts of the device to the substrate, allowing the unadhered sections of the film to buckle away from the substrate with a predefined wavelength (Figure 3d).\(^\text{147}\) Pop-up structures have allowed Si nanoribbons to be stretched to \(\approx 100\)% strain,\(^\text{147,148}\) many times higher than the buckled, adhered nanoribbons. Similarly, the selective adhesion of serpentine patterns to the substrate allows twisting and extension out of the plane of the substrate, reducing the strain in the material and affording a larger range of stretchability.\(^\text{144}\)

Buckling methods are attractive because of their compatibility with conventional high-performance materials. Recently, Chae et al. reported a hybrid method of making stretchable transistors in which stretchable electrodes were combined with a buckled alumina (Al\(_2\)O\(_3\)) dielectric layer, providing reproducible performance up to 20% strain.\(^\text{148}\) ZnO transistor arrays stretchable up to 5% have been fabricated by transferring ZnO transistors onto prestrained substrates.\(^\text{149}\) Although the stretchability of these devices lags behind what would be required for e-skin, the low-cost and good stability of oxide semiconductors make them an attractive option for further development.

The research group of John Rogers has pioneered many of the techniques to make buckled devices from traditional high-performance inorganic semiconductors and conductors. Many of their devices use inorganic NWs, nanoplatelets, and nanomembranes obtained by etching thin layers of material from multilayer\(^\text{141a}\) or bulk wafers.\(^\text{150}\) They have adhered inorganic nanostructures to stretchable substrates using transfer processing.\(^\text{151}\) Such transfer methods can achieve cost-effective large-area coverage by distributing active elements fabricated in a dense array over a larger area through successive transfer steps\(^\text{150a,151a,152}\) by automated systems,\(^\text{150a,152}\) and can be used to make three dimensional circuits by adding multiple layers.\(^\text{151b}\) The group has formed semiconductor devices into buckles,\(^\text{141a}\) pop-up structures,\(^\text{14a,147}\) and serpentine mesh layouts\(^\text{137}\) to demonstrate a range of functionalities. In Section 6, we describe several highly integrated devices based on this technology, and a more comprehensive discussion can be found in recent review articles.\(^\text{14a,154}\)

**Rigid Device Islands Linked by Stretchable Interconnects**: High-performance stretchable systems can be realized by connecting conventional rigid device islands with interconnects that have been made stretchable using patterning or buckling. The strain in the substrate is highly localized near the edges of device islands.\(^\text{155}\) As a result, interconnects experience greatly increased strains near the edges of device islands that can lead to failure of the devices.\(^\text{156}\) Interconnects that are not adhered to the substrate (that is, pop-up) can be used to alleviate this strain,\(^\text{157}\) as can grading the substrate's elastic modulus near the device islands.\(^\text{135d,158}\) Using low-modulus substrates is important for minimizing strain in the device islands, and patterning the substrate into mesas can further reduce the island strain.\(^\text{155,157}\) Wagner and coworkers have created functional device islands by fabricating amorphous Si FETs directly onto elastomeric substrates and connecting them with Au metallization.\(^\text{159}\) Lacour and coworkers have similarly fabricated OFETs directly on PDMS substrates.\(^\text{160}\)
substrate, the OFETs could be isolated from the strain. Shin et al. fabricated rigid islands of tin oxide ($\text{SnO}_2$) transistors connected with curvy metal interconnects.[161] The devices could stretch up to 40% with negligible change in performance but showed significant device-to-device variation. Vanlenten and coworkers have also reported impressive results in this area.[135d]

3. Tactile Sensors for E-Skin

Robotic technologies have found enormous utility in improving efficiency and reducing the cost of repetitive, well-defined tasks in manufacturing.[162] Recently, there has been intense interest in designing robots that can work in less-structured environments by collecting information about their surroundings to make appropriate responses.[12,162] Such capabilities would allow them to work in close quarters with humans and complete more complicated and dynamic tasks (e.g., providing basic services to elderly people or undertaking dangerous rescue missions).[2,163] However, highly functional tactile sensing will be required to improve the operation speed and effectiveness of current robotic technology.[164] In addition to robotic applications, efficacious tactile sensing arrays could transform the medical field. Tactile sensors integrated into prosthetics could allow amputees to regain considerable functionality, and touch-sensitive sensor skins could be useful in augmenting surgical gloves[165] or for continuously measuring the health of patients.[1]

The human tactile sensing system allows us to navigate our surroundings amply, and knowledge of its working mechanisms can be used as inspiration for effective design of electronic substitutes. Tactile sensing within the skin relies on neuronal sensor elements called mechanoreceptors, which are embedded at different depths below the skin surface and respond to forces on different timescales. Fast adapting (FA) mechanoreceptors sense dynamic changes in force and respond with intense signals during the application or removal of forces.[166] By contrast, slowly adapting (SA) mechanoreceptors are able to sense static forces by responding continuously during prolonged stimulation. The density of mechanoreceptors depends on the location in the body and ranges from approximately 241 cm$^{-2}$ in fingertips to 58 cm$^{-2}$ in the palm,[166b,167] resulting in a resolution of approximately 1 mm in the fingertips.[168] In humans, data processing starts in the individual receptors, where the stimulus is digitized.[169] Signals from groups of receptors are processed en route to the brain,[170] where final data interpretation occurs.[166b,169] This breakdown of tactile signal processing helps to reduce the brain’s data-processing requirements.[166b,169]

With this signal processing pathway, the body can sense pressures greater than $\approx 10$ kPa[172] with a temporal resolution of 20–40 ms[172] and vibrations can be sensed at frequencies up to 800 Hz.[166a]

The mechanical properties of skin have a pronounced effect on its tactile sensing capabilities. Mechanical compliance improves grip by promoting an understanding of an object’s shape and increasing contact area with the object.[173] The skin’s morphology has evolved to benefit tactile sensing, and the skin’s ridges enhance sensitivity[174] by concentrating forces into mechanoreceptors that are clustered nearby.[166b] These ridges are also essential for facilitating perception of slip, texture, and hardness. Many essential aspects of life are mediated by the multifunctional tactile sensing capabilities of skin, including:

- Normal force sensing for grasp control, object manipulation,[175] and orientation determination,[166a]
- Tensile strain monitoring for proprioception (essential for simple movements such as standing or walking)[169]
- Shear force sensing for grasp control and friction determination,[166b,175b,176] and vibration detection for slip detection and texture determination.[166b,174]

The characteristics outlined above should be considered as the minimum requirements for e-skin that would allow for its interaction with the world in a human-like way. In the 1990’s, a survey of robotics developers outlined desired parameters for tactile sensing skins.[163] In most cases, these requirements agree well with the capabilities of human skin, and both are summarized in Table 1. However, e-skin with enhanced capabilities, such as improved sensitivity,[18] higher receptor density,[230] and faster response times, could collectively endow robots and prosthetics with capabilities that surpass those of our own skin. While the skin provides an impressive range of tactile feedback capabilities, it is not a perfect system. For example, the hysteric nature of skin requires significant correction through cognitive processing, and is undesirable in electronic analogs.[166] Furthermore, its compliance and viscoelasticity also complicate pressure distribution analyses[163] and reduce spatial resolution.[166b] Tactile sensing has attracted significant interest, and development in the area has been rapid. An exhaustive description of tactile sensing is not practical within the limits of this review, and readers are directed to other excellent reviews on the subject.[166,177]

3.1. Transduction Methods

In order to measure the magnitude of a tactile stimulus, it must be converted into an electrical signal. Methods for accomplishing this conversion are described in this section.

3.1.1. Piezoresistivity

Piezoresistive sensors transduce a change in the resistance of a device into a measurement of strain and have been investigated extensively because of their simple structure and readout

### Table 1. Summary of the properties of human skin and corresponding requirements for e-skin.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Human Skin</th>
<th>Requirement for E-Skin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spatial resolution</td>
<td>1 mm[166]</td>
<td>1–2 mm[163]</td>
</tr>
<tr>
<td>Temporal resolution</td>
<td>20–40 ms[172]</td>
<td>1–10 ms[163]</td>
</tr>
<tr>
<td>Working range</td>
<td>$&gt;10$ kPa[177]</td>
<td>1–1000 g[143]</td>
</tr>
<tr>
<td>Hysteresis</td>
<td>High</td>
<td>Low[163]</td>
</tr>
</tbody>
</table>
mechanism. The change in resistance can be derived from several factors, including changes in: 1) the geometry of the sensing element, 2) the resistivity of a semiconductor owing to changes in band structure, 3) the contact resistance \( R_c \) between two materials, and 4) the resistivity of a composite owing to changes in interparticle separation.

The resistance \( R \) of a material is given by \( R = \rho L/A \), where \( \rho \) is the resistivity, \( L \) is the length, and \( A \) is the area. The effect of geometry on the piezoresistance is dominant when \( \rho \) remains constant, but \( L \) and \( A \) change with strain. The sensitivity of a strain sensor is referred to as the gauge factor (GF), and the ideal GF value for sensors based on a change in geometry is 2. Piezoresistivity derived from a change in the band structure of a material has been observed in Si, CNTs, and graphene. OS also possess piezoresistive properties, although through a different mechanism. Typically, \( \mu \) decreases with strain owing to an increase in the intermolecular or intergrain separation.

The \( R_c \) between two conductors changes with applied pressure owing to the change in contact area between the materials and is related to the force by \( R_c \propto F^{-1/2} \). This power law dependence between \( R_c \) and \( F \) is advantageous in that it provides high sensitivity at low pressures as well as a large working range. Sensors based on contact resistance have low temperature sensitivity, readily tunable ranges, fast response speeds, and are easily made flexible. However, they typically show undesirable drift and hysteresis.

To make large-strain sensors, several groups have pursued fibers coated with conductive materials. When woven into a fabric, \( R_c \) between fibers changes with tensile force. The incorporation of ZnO as a conductive material in fibers has led to large values of GF (GF = 116), which are comparable to those of traditional strain gauges based on piezoresistance in Si (GF = 200). The use of aligned films of CNTs have also shown exceptional performance as strain gauges, capable of measuring strains as large as 200%, as opposed to randomly oriented CNT films that cannot be strained past a few percent.

Piezoresistive polymer composites have been extensively investigated as strain- and force-sensitive materials because of their low cost and easy integration into devices. Piezoresistivity in composite materials depends on the composition, morphology, and strain range of the system. Mechanisms for piezoresistance in composites include: 1) the modification of filler resistivity owing to band structure changes, 2) the modification of tunneling resistance between fillers, and 3) the break-up and reforming of percolating pathways. Unlike stretchable conductors, piezoresistive composites usually show the highest performance near the percolation threshold of the filler material in the elastomer matrix. To avoid irreversible alteration of the sensitivity characteristics, the filler must be well dispersed and well adhered to the matrix. Generally, conductive composites exhibit large hysteresis and large variations in their electrical properties with temperature.

However, de la Vega et al. recently showed that the temperature sensitivity of CNT composites can be tuned by changing the concentration of CNTs, possibly leading to temperature stable sensors.

CB has long been used as a conductive filler in strain-sensing materials owing to its low cost and abundance, and its piezoresistive properties agree with developed models. CNTs and graphene have also attracted significant interest because of their unique electrical and mechanical properties, and anisotropic composites or films of CNTs have displayed exceptional sensing properties. Metal particles with sharp protrusions are highly effective as conductive fillers in piezoresistive composites, and the concept has been commercialized by Peratech Ltd. The protrusions concentrate the electric fields in the device, enhancing the effect of pressure on the tunneling current through the material. On application of compressive or tensile strain, the particles move closer together, thereby decreasing the resistance by up to 12 orders of magnitude. Piezoresistive components have been incorporated into highly flexible and stretchable devices using electrical connections made from liquid metal, stretchable helical electrodes, and stitched metallic electrodes.

### 3.1.2. Capacitance

The capacitance \( C \) of a parallel plate capacitor is given by: \( C = \varepsilon_0 \varepsilon_r A/d \), where \( \varepsilon_0 \) is the free space permittivity, \( \varepsilon_r \) is the relative permittivity, \( A \) is the area, and \( d \) is the distance between electrodes. Three of these variables \( (\varepsilon_r, A, d) \) are sensitive to changes in strain. The change in \( d \) is commonly used to measure normal forces, while changes in \( A \) are typically used to measure shear forces. The change in \( \varepsilon_r \) can be used to measure forces using specially designed materials, but this method has not been widely pursued. A major advantage of capacitive sensors is that their governing equation is simple, which simplifies device design and analysis. Capacitive sensors for tactile sensing have demonstrated high strain sensitivity, compatibility with static force measurement, and low power consumption. However, since \( C \) is proportional to \( A \), reducing the pixel size of these devices for miniaturization reduces the capacitance and the signal-to-noise ratio. Furthermore, capacitive sensors are susceptible to interference from external sources. Dobrzynska et al. have compared and commented on the characteristics of capacitive devices in a recent review.

When changes in \( d \) are used to determine normal forces, dielectrics with low moduli show improved sensitivity owing to increased deformation for the same applied force. Our group recently demonstrated stretchable and transparent capacitive sensors fabricated by sandwiching a PDMS dielectric between two sets of PEDOT:PSS or CNT-based electrodes. Ecoflex silicone was used as the dielectric material because of its exceptionally low modulus. Highly compliant capacitive sensors have also been reported by other groups using stretchable electrodes composed of CNTs, metal NWs, and Au thin films. Takamatsu et al. have also used an interesting fiber-based method to make compliant tactile arrays.

The sensitivity and response time of capacitive tactile sensors incorporating elastomeric dielectrics is limited by the incompressible and viscoelastic nature of rubbers. The performance of these sensors can be improved by using a highly compressible dielectric, and air gaps are commonly used to increase compressibility. However, forming air gaps typically requires complex patterning processes, and the low
Piezoelectricity refers to the ability of a material to generate a voltage in response to an applied force. The force causes a change in the length and separation between dipoles in the material, leading to the build-up of compensating charges on the electrodes. The ability of the material to convert normal forces into electrical charges is quantified using the piezoelectric strain constant \( (d_{33}) \). Owing to the high sensitivity of piezoelectric sensors to dynamic pressure and their fast response speed, they are often used to measure the vibrations associated with slip and their transient sensing capabilities resemble those of the RA receptors in human skin. However, piezoelectric materials exhibit drift in sensor response over time and have unreliable static sensing properties.

Piezoelectric behavior can occur in crystals that have anisotropic unit cells (piezoelectrics) or in macroscopically separated regions with different charges (piezoelectrets). Popular inorganic piezoelectric materials include lead zirconate titanate (PZT) and ZnO. Dispersing inorganic NPs in polymer matrices can achieve the mechanical compliance necessary for e-skin. Poly(vinylidene difluoride) (PVDF) and its copolymers are widely used owing to their flexibility and ease of processing compared to ceramics. While the \( d_{33} \) coefficient of PVDF is considerably lower than that of commonly used ceramics, additives can improve its performance. Although PZT and PVDF represent prototypical piezoelectric materials, many others have been demonstrated and the development of new materials and form factors is an active area of research. Piezoelectric materials are also pyroelectric, which means that a voltage can be induced owing to a temperature change. Pyroelectricity can be used to measure temperature, but it is a significant confounding factor in most piezoelectric tactile sensors.

In contrast to piezoelectrics, which rely on molecular dipoles, electrets and ferroelectrets utilize the change in fixed macroscopic dipoles in a material to generate a voltage. Charges are formed by the breakdown of gas in the voids during the application of large electric fields. The void volume can be tuned to optimize the \( d_{33} \) coefficient by reducing the Young’s modulus of the material. In contrast to molecular piezoelectrics such as PVDF, the temperature dependence of the ferroelectret response is very small. Furthermore, owing to the small transverse piezoelectric coefficients, devices can be flexed with minimal change in their functionality. Excellent reviews on ferroelectric systems provide more information on this subject and applications of piezoelectric materials in devices will be described in subsequent sections.

3.1.4. Optics

Optical sensors convert a tactile input into an electrical output using light as an intermediate. These sensors consist of a light source, transmission medium, and detector. The modulation of light intensity through force-sensitive waveguides or flexible optical fibers has been used to fabricate optical sensors. While these fiber-optic sensors had low wiring complexity, exceptional linearity, and negligible drift, they were not stretchable. The use of elastomeric waveguides enables...
stretchable devices to be created,[235] and our group has developed a stretchable pressure sensor based on a PDMS waveguide.[236] Light was produced by an LED positioned at one end of the waveguide and detected by a photodetector at the other end (Figure 5a). The device displayed excellent pressure sensitivity (0.2 kPa⁻¹), and the ability to distinguish the application of the waveguide and detected by a photodetector at the other end (Figure 5b).[237] Similarly, the pressure-induced coupling of light into a waveguide has been employed.[238]

Monitoring the deformation of highly compliant coatings can be achieved using arrays of light emitters and detectors. The orientation of an array of reflective chips[239] on the surface of an elastomeric covering changes on deformation, which modifies the amount of light collected by the array’s detectors. Rossiter et al.[240] used LEDs as both the source and the detector to simplify the design. Vision-based sensors have attracted significant attention owing to their low wiring complexity. They monitor the movement of reference objects, such as colored markers within a compliant material using a camera.[241] Maheshwari et al.[242] developed a sensor in which mechanical transduction occurred within the light source. With applied pressure, the local light emission from the material increased and was monitored with a photodetector array, attaining a resolution of 40 μm.[243] While optical devices have many promising characteristics, light generation is power-intensive,[166b,239b] and low-power devices may be difficult to achieve.

3.1.5. Wireless Antennas

The frequency at which a wireless antenna operates depends on the dimensions of the device, and strain can induce a change in resonant frequency as a consequence of deformations.[244] Antennas fabricated on elastomeric substrates using metals[244] and CNTs[245] have been used to measure pressures, and large tensile strains have been measured using stretchable microfluidic-based sensors with liquid metal conductors.[246] For example, Whitesides and coworkers demonstrated a wireless device that showed a change in frequency from 1.53 to 0.738 Hz as the device was stretched from 0 to 120% strain.[247] The robustness and compliance of these devices makes them inherently compatible with e-skin.

3.2. Device Structures and Functionalities

3.2.1. Fabrication Methods

The transduction methods described in Section 3.1 can be implemented using several fabrication methods. Si-based technologies have been well developed and show excellent sensing characteristics.[248] The challenges in fabricating large-area, flexible arrays can be mitigated by transferring devices to flexible substrates, allowing dimensional multiplication.[249] However, the drawbacks of high cost and fragility have yet to be addressed.[166b,250] Many groups have turned to polymer micromachining,[211,216,251] which is more cost-effective and provides flexible devices. Polymer micromachining typically involves using photolithography,[215a,250,251b,252] or molding[216,251a] to pattern device structures, such as air gaps for capacitive sensors[211,216] or resistive strain gauges.[252] Large-area solution processing[22] and printing technologies[200,253] have gained popularity as low-cost, high-throughput fabrication techniques.

3.2.2. External Interactions

In many cases, device arrays are encapsulated within an elastomer to protect them from mechanical harm and environmental exposure, as well as to provide conformal contact with stimuli. However, as with human skin, an elastic coating reduces the positional resolution and sensitivity of the array,[210,254] and introduces hysteresis into the measurements.[166b] Many sensor designs include a “bump” or force localizing protrusion (FLP) on the surface of a sensing system to modify or to localize a force distribution. FLPs act similarly to the ridges in skin that are essential for improving sensitivity and measuring texture.[177b] FLPs can increase sensitivity,[251a] convert normal forces into tensile forces (Figure 6a),[250,251a,252] and convert shear forces into normal forces for facile measurement (Figure 6b).[211,216b,251b,255]

3.2.3. Slip, Texture, and Hardness Sensing

In their simplest form, most of the transduction methods described in Section 3.1 measure tensile or compressive forces. However, human skin senses a multitude of tactile inputs, including normal, tensile, and shear forces, in addition to vibrations. To ascertain complex information about shear forces, hardness, and texture, device structures with additional functionalities are required. Dedicated shear sensors include resistive sensors made by embedding Si strain sensors in PDMS,[256] and capacitive sensors made by embedding a vertically-oriented...
3.3. Device Integration and Readout

3.3.1. Array Addressing

Our senses of vision and hearing are facilitated by a small number of localized sensors. By contrast, tactile sensing...
requires a multitude of sensors distributed over a large area, and developing methods to collect and process such a large amount of information has been a persistent challenge in the field. The simplest strategy for device readout is direct addressing, in which each device is contacted by a separate connection. Good temporal resolution can be achieved with this method, but large arrays quickly lead to an unmanageable number of connections.\cite{265} Passive matrices consist of two sets of parallel electrodes with the sensing elements located at the crossing points of perpendicular electrodes. Appropriate readout mechanisms can mitigate the tendency of passive matrices to produce erroneous readings\cite{266} but the disadvantage of slow readout speed persists. An active matrix uses transistors to address each pixel. While this design increases the complexity of the integrated array, it allows for rapid element addressing with relatively few wires. Additional benefits of active matrices include minimal crosstalk between sensor elements and low power consumption.\cite{265,177a} Complete elimination of sensor wiring requires wireless transfer of data and power\cite{267} and has been pursued by several groups.\cite{268} For example, Shinoda et al. wrapped a ground coil around a hard surface and wirelessly interrogated sensing elements that were distributed throughout an elastic skin.\cite{269}

3.3.2. Transistor Integration

Integration of tactile sensing with transistors is advantageous for making active matrix arrays and implementing local processing capabilities. For example, the ability of transistors to amplify signals may eliminate the need for signal amplification in the control system, reducing the required processing capabilities. Strain-sensitive transistors can be realized by integrating a strain-sensitive material as one of the components within the device.

A number of groups have investigated the effect of mechanical stimulation on pentacene OFETs and observed a repeatable change in the source-drain current ($I_{DS}$) with pressure.\cite{270} The mechanism of force sensitivity is likely related to a change in the trap states near the electrodes.\cite{270a,270b} The effect of applied force can be tuned by changing the morphology of the semiconductors, with larger grain sizes showing more pronounced sensitivities.\cite{95b,182a} Bonfiglio and coworkers have pursued cost-efficient, large-area arrays by developing printed devices.\cite{253a,271} However, these pressure-sensitive transistors have the drawbacks of long response times and significant hysteresis.\cite{270c,270d} On the basis of similar mechanisms, OFETs have also been investigated as active strain sensors that are capable of sensing strains in the range of several percent.\cite{272} The devices described thus far have utilized the strain sensitivity of the semiconductor active layer itself. The research groups of Someya and Javey have independently developed FETs in which piezoresistive rubbers have been integrated in series with the source electrode to create tactile sensor elements. Pressure applied to the resistive rubber directly modulates $I_{DS}$, and the voltage applied at the gate ($V_G$) provides the switching necessary for active-matrix readout. Both groups have exploited the use of low-cost processing methods with different active materials: Someya and coworkers have used pentacene OFETs (Figures 8a,b),\cite{15,26a,273} while Javey and coworkers have used NWs and CNTs (Figure 8c).\cite{23a,136b} A key consideration in pixel design is that the resistance of the pressure sensitive material must be larger than that of the transistor in the on state. Chao et al. reported the use of a vertical transistor, simplifying the process of integrating the pressure-responsive rubber.\cite{274} As described in Section 3.1.1, we have developed a microstructured dielectric layer showing exceptional pressure sensitivity. We further investigated the use of such a dielectric layer in an OFET with a single crystal of rubrene serving as the semiconductor (Figure 8d).\cite{18} On application of pressure, $I_{DS}$ increased proportionally to the change in $C$ of the dielectric. In addition to amplifying the signal, the

Figure 7. Detection of multiple stimuli with a device composed of interlocking pillars. a) Conceptual image of the flexible device fabricated using very thin elastomeric substrates. b) Multiple deformation modes of the device allow for sensing of normal, shear, and torsion forces. Adapted with permission.\cite{25} Copyright 2012, Macmillan Publishers Ltd.
device converts the signal from capacitance to $I_{DS}$ for simplified measurement. By replacing the rigid transistor with a flexible device, our group has recently demonstrated highly flexible OFET pressure sensors for medical applications.\cite{Kim2011}

Kim et al. used a similar concept to investigate the effect of different dielectric patterns.\cite{Kim2011}

Piezoelectric materials have been integrated with transistors using several methods. Bauer and coworkers developed flexible optothermal sensors by electrically coupling a discrete piezoelectric element to the gate electrode, the advantage being that the signal transduction and signal readout mechanisms could be designed independently.\cite{Bauer2011} By contrast, Lee and coworkers integrated piezoelectric films directly as the dielectric\cite{Lee2009} and have demonstrated pressure-sensitive transistors with an exceptionally high electromechanical coupling coefficient (Figure 9a).\cite{Lee2009} An alternating current (AC) biasing method was developed to decouple the pyroelectric and piezoelectric effects by exploiting the temperature sensitivity of the semiconductor.\cite{Lee2009} Hsu et al. reduced the parasitic capacitance to minimize crosstalk between adjacent devices.\cite{Hsu2011} By coupling a ferroelectric material to gate electrode of a transistor, Graz et al. created flexible transistor-integrated devices with the capability of measuring both static and dynamic forces, depending on the measurement mode.\cite{Graz2011} To overcome the temperature sensitivity of piezoelectrics, Graz et al. also integrated bifunctional composites that were sensitive to both temperature and pressure into the gate electrode (Figure 9b).\cite{Graz2011} To demonstrate the potential of high-throughput processes, Zirkl et al. fabricated arrays of PVDF copolymer sensors addressed with electrochemical transistors and connected to electrochemical displays (Figure 9c).\cite{Zirkl2013} All components of their integrated system were printed using only five materials. The devices were responsive to both pressure and temperature and could be used to track hand gestures.

3.3.3. Modular Designs

In addition to the signal conditioning that can occur at the device level in transistor-integrated devices, data processing can also occur at an intermediate level to reduce the volume of data reaching the control computer. This strategy is similar to human skin, where data collected from groups of neurons is processed en route to the brain.\cite{Zirkl2013,Lee2009} Modular approaches involve creating arrays that can be subsequently combined to create an even larger array. By implementing computing capabilities into each module, signal processing or data analysis can occur within the sensor network itself.\cite{Zirkl2013} Modularity also provides the ability to expand a sensor network to meet the needs of any application.\cite{Lee2009,Zirkl2013,Graz2011}

4. Chemical and Biological Sensors for E-Skin

We have discussed in Section 3 how e-skin can be endowed with tactile sensors. Here, we describe how the functionality...
of e-skin can be augmented beyond the capabilities of human skin through the integration of chemical and biological sensors. There is already high demand for miniaturized, portable, and inexpensive sensors for the monitoring of a broad range of compounds, including environmental pollutants, chemical and biological warfare agents, and medically relevant biomarkers. To meet this demand, electronically based chemical and biological sensors for gas (e.g., e-nose) and liquid (e.g., e-tongue) phase analytes have been demonstrated on rigid substrates using CNTs, graphene, inorganic NWs, and organic materials as the active sensor element. The continued production of low-cost chemical and biological sensors via high-throughput techniques and translation of this technology onto flexible substrates will be attractive for integration with e-skin.

In general, chemical and biological sensing with electronic devices relies on the direct transduction of a binding event or reaction into a change in the conductance of the device.

The introduction of particular chemical or biological species that are capable of interacting with the device (either nonspecifically through serendipitous interactions or, specifically through the use of receptor groups) perturbs the local charge environment, resulting in a change in conductance. These electronic-based sensors offer label-free, portable, and real-time detection without the need for bulky supporting electronics that are the status quo for optical detection methods.

Electrochemical electrodes, chemically sensitive sensors (i.e., chemiresistors), and transistors are the devices primarily used for chemical and biological sensing. Electrochemical electrodes are comprised of a single conducting layer in which a receptor element is typically encapsulated, and are sensitive to the generation of redox active species in solution. These electrochemical sensors operate using three electrodes (i.e., working, auxiliary, and reference) in solution. The large size of these electrode arrays makes them impractical for integration with e-skin unless subjected to significant miniaturization. Chemiresistors consist of a pair of electrodes (i.e., source and drain) deposited on a semiconductive material. Changes in resistance are measured on exposure of the chemiresistor to a targeted analyte. Transistors include an additional gate electrode that is capacitively coupled to the semiconductor via a dielectric layer and that acts as an electronic switch and signal amplifier. Since transistor-based sensors are a combination of sensing elements and amplifiers, they offer higher sensitivity than chemiresistors, as a small change of effective \( V_G \) owing to the presence of an analyte may lead to pronounced variation in \( I_D \).

Traditionally, chemical and biological sensors have been built on rigid substrates, which restricts their utility for flexible or stretchable e-skin applications. When the use of flexible interconnects allows for the possibility of transforming sensors built on rigid substrates into stretchable sensing networks, these devices are inherently fragile. Recently, chemical and biological sensors have been fabricated on plastic substrates. However, it should be noted that most studies have only demonstrated the flexibility of such sensors and not on their stretchability.

In this review, we will focus exclusively on sensors that have been demonstrated on flexible plastic substrates. The subject of chemical and biological sensing with CNTs, graphene, and organic materials on rigid substrates has already been extensively and recently reviewed, and we direct the reader to these sources for further information. Various NWs have also been used extensively for chemical and biological detection. However, in addition to the issues surrounding their macroscale integration and high cost, there are relatively few demonstrations of flexible NW chemical sensors and they will therefore not be covered in this review.

4.1. CNT-Based Sensors

On rigid substrates, CNT-based sensors have been utilized to fabricate extremely sensitive chemical and biological sensors. Their sensitivity results from their remarkably high surface-to-volume ratio and ability of each surface atom to contribute to the sensing response. CNT sensors for chemical and biological analytes can be broken down into two main categories: those for the detection of gas-phase analytes and those for the detection of liquid-phase analytes. As gas sensors, CNT sensors have been demonstrated as chemiresistors, transistors and capacitors. In aqueous environments, they are primarily used as transistors for the electrical detection of analytes and as electrochemical electrodes for the detection of redox-active species such as \( \text{H}_2\text{O}_2 \) and nicotinamide adenine dinucleotide (NADH). Here, we discuss several examples of flexible CNT sensors in both the gas and liquid phases.

4.1.1. Gas Phase Detection with CNT-Based Sensors

Chemiresistors: Flexible chemiresistive sensors with CNTs as the active sensing matrix have been demonstrated for the detection of gaseous analytes, including \( \text{NH}_3 \), \( \text{NO}_2 \), \( \text{EtOH} \), and organophosphonate nerve agents (dimethyl methylphosphonate (DMMP) and diisopropyl methylphosphonate (DIMP)) and the deposition of palladium NPs (PdNPs) has allowed for the detection of \( \text{H}_2 \) as well (Figure 10). The detection limit for these sensors is typically quite low (1–50 ppm), and their response time is rapid (<1 min), though it can vary with analyte concentration, leading to very slow responses for dilute samples. Additionally, recovery times can be quite slow (=several minutes), and regeneration is often incomplete unless elevated temperatures or UV irradiation are used. To implement these regeneration techniques in e-skin, it would be necessary to incorporate a microheater or UV light source, which would further complicate device architectures.

In general, these chemiresistive sensors have a nonspecific response to targeted analytes. This lack of specificity is undesirable for e-skin applications, as it is impractical to exclude all interferent analytes from the operating environment. However, several attempts have been made to increase specificity. Cattanach et al. used a chemiselective polymer barrier to enhance selectivity for nerve agents over other gaseous analytes for which their CNT films have previously demonstrated sensitivity. PdNPs have been used to enhance the sensitivity for \( \text{H}_2 \) over other analytes; however, such sensors still exhibit a low level of cross-reactivity to other gases at low \( \text{H}_2 \) concentrations. Furthermore, owing to the deactivation of the PdNPs by \( \text{O}_2 \), these sensors were operable only in...
Figure 10. Selective H$_2$ sensing via PdNP-decorated CNT chemiresistors. a) Schematic of flexible CNT device on a PET substrate. CVD grown CNTs are transferred to PET using dry transfer technique, followed by PdNP electrodeposition. b) Image highlighting extreme flexibility of fabricated devices. Adapted with permission.[294c] c) Bending fatigue and effect of bending on sensing. Device shows little change in sensitivity on being bent to a radius of curvature of 7.5 mm. Adapted with permission.[294a] Copyright 2007, American Institute of Physics.

inert environments as they demonstrated worse performance and lower sensitivity under ambient conditions.[294b,294c] These restrictions are impractical for e-skin applications, and the development of sensors that are capable of operation in air should be pursued.

Understanding the effect of strain on the sensing signal is quintessential to the development of gas sensors for e-skin applications. Most reports indicate a moderate (2–18%) change in sensitivity on bending.[290b,292a,294] The long-term stability of such devices is also important for e-skin applications. Su et al. reported little variation after 84 days of continuous analyte exposure.[294c] while Jeong et al. found that the resistance of their sensor had little change over a 6-month period.[290b] However, Parikh et al. found that the sensitivity and reproducibility of their sensors declined after repeated cycles of exposure and regeneration.[292a] Bending fatigue is another area of interest for e-skin applications. Sun et al. found that there was a 13% decrease in sensitivity after 1,000 bending cycles.[294a] The ability to maintain a stable sensing response despite long storage periods and mechanical stresses will be critical for the development of sensors that can be integrated into e-skin, and CNT-based devices show promise in these areas.

Transistors: Despite their enhanced sensitivity over chemiresistors, relatively few flexible CNT transistors for gas sensing have been reported. Chen et al. developed a CNT transistor for 2,4,6-trinitrotoluene (TNT) detection with a limit of detection of 8 ppm.[295] This detection limit was an order of magnitude better than corresponding transistors made from ZnO NWs, demonstrating the enhanced sensitivity of atomically-thin CNT sensors over metal oxides.[295] However, these CNT transistors also demonstrated nonspecific sensitivity for NO$_2$, as well as slow response and recovery times unless UV irradiation was used to accelerate regeneration. Another flexible CNT transistor was demonstrated for the detection of CO to 1 ppm.[296] By using two transistors fabricated from CNTs containing varying levels of defects, it was possible to discriminate the detection of CO from NO/NO$_2$.

4.1.2. Liquid Phase Detection with CNT-Based Sensors

Transistors: CNT transistors on flexible substrates have been demonstrated for a number of small molecules and ions, which include H$^+$,[297] glutamate,[298] and other biomolecular analytes.[297b,299] One particular application that CNT-based e-skin sensors could be particularly well suited for is blood glucose determination in diabetic patients. Several glucose sensors have been developed on flexible substrates[300] that are capable of detecting glucose down to 0.5 mM (linear range of 0.5 to 25 mM).[300]

The reported flexible transistors are comprised of CNT networks rather than individual CNTs and were fabricated entirely using solution deposition techniques. These allowed for facile and large-area fabrication approaches, which are highly advantageous for e-skin applications. Selective detection was demonstrated by incorporating bioreceptor groups on the CNTs through chemical grafting. However, the use of biological receptor groups limits the longevity of such sensors and mandates more stringent storage conditions and may not be feasible for e-skin applications. Furthermore, these sensors relied on solution gating, in which the gate electrode is suspended in an electrolyte. Unfortunately, these solution gates are not easily miniaturized, presenting a foreseeable obstacle for their integration in e-skin devices. Additionally, the effect of bending on the detection of aqueous-phase analytes has yet to be investigated. This parameter will be important in understanding the feasibility of using these sensors in e-skin applications.

Electrochemical Electrodes: Compared to carbon paste and glassy carbon electrodes, CNTs offer great advantages as electrochemical sensors owing to their ability to mediate fast and direct electron transfer with redox active enzymes, thus preventing overpotential and surface fouling.[282a] The most relevant molecules that could be monitored with flexible CNT electrodes are glucose (owing to its critical role in diabetes management) and H$_2$O$_2$ (owing to its role as a reactive oxygen species and a chemical messenger in biological processes). The electrochemical detection of glucose with flexible CNT electrodes has been achieved through the immobilization of glucose oxidase (GO$_x$), which can convert glucose into gluconic acid and H$_2$O$_2$.[301] The lowest detectable glucose concentration reported using GO$_x$ as the recognition element was reported to be 0.01 mM[301a,301b] however, these sensors demonstrated a linear detection range that was lower than the concentration relevant for diabetes monitoring. Chiu et al. reported a hybrid
CNT/PEDOT electrode that was capable of glucose detection to 0.1 mM (linear range of 1 to 10 mM) and of measuring glucose levels in human serum.[302]

For e-skin applications, high stability over time is necessary, and therefore enzyme-based electrochemical sensors may not be suitable for e-skin applications owing to restrictions on their storage conditions and limited lifetimes resulting from the use of enzymes. Rapid degradation of these “enzyme electrodes” would be an important issue requiring resolution before such sensors could be employed in e-skin. For example, Yan et al. reported a 20% decrease in activity in week, despite storage at 4 °C.[301b] By replacing the biomolecular recognition element (GO₃) with electrocatalytically deposited PdNPs to form a non-enzymatic electrochemical sensor, Pham et al. were able to improve the device stability without sacrificing sensitivity (detection limit of 0.003 mM).[303] Additionally, Bui et al. demonstrated the direct detection of H₂O₂ to 2.76 µM (linear range 0.02 to 18 mM) using flexible, enzyme-free CNT electrodes decorated with catalytic AgNPs.[304] They found that the sensors were relatively stable for long-term continuous operation and retained 90% of their original activity after 30 days without special storage conditions. This type of enzyme-free electrode would be more practical for e-skin applications, despite its intrinsically lower specificity for a particular analyte.

4.2. Graphene-Based Sensors

Like CNTs, graphene has exceptional electrical transport properties. As a planar sheet of sp²-hybridized carbon atoms, graphene exhibits the highest possible surface-to-volume ratio,[305] and a larger detection area than CNTs.[283a] Since each atom can potentially contribute to the sensing response, graphene’s electrical conductivity is incredibly sensitive to adsorption of chemical species on its surface.[106] This sensitivity, in combination with graphene’s extremely low intrinsic noise, allows such sensors to be capable of a wide sensitivity range, from the single-molecule level to high concentrations.[75,306,307] The extremely sensitive detection of a large number of analytes has been demonstrated with inflexible graphene sensors in both gaseous[75,306–308] and liquid[70,109] phases. Most early graphene sensors were chemiresistors,[306,307,310] but FET-based sensors for gaseous detection have also been developed.[311] The two primary types of liquid-phase graphene sensors are transistors[309e–g] and electrodes.[312] We review both gas- and liquid-phase flexible graphene sensors below.

4.2.1. Gas Phase Detection with Chemiresistive Graphene-Based Sensors

The field of flexible graphene sensors is still relatively young, with only a small number of flexible graphene chemiresistors existing for the detection of toxic gases. Due to its strong electron donating ability, NO₂ is one of the most prevalent analytes detected.[76,313] Additionally, it is of interest as a decomposi- tion product for certain explosives. NO₂ detection has been achieved to 20 ppm using a novel flexible 3D graphene foam architecture.[314] Alcohol detection has been demonstrated using a hybrid graphene/ZnO sensor, with a demonstrated detection limit of 10 ppm for EtOH.[315]

In general, gas phase detection with graphene chemiresistors is nonspecific, and cross-reactivity is common. In order to be used for e-skin applications, improved selective sensing will be necessary and can potentially be achieved through the use of chemoselective polymers or deposition of NPs. Chung et al. decorated graphene chemiresistors with PdNPs to enhance selectivity for H₂.[316] They reported a detection limit of 20 ppm, which is comparable to that reported on inflexible graphene sensors (40 ppm).[306c] In general, operation of these sensors occurs in either inert or vacuum atmospheres, as graphene is inherently sensitive to O₂ and other gaseous analytes present in the atmosphere.[76,314] Furthermore, sensors decorated with PdNPs operate with reduced sensitivity in an oxygenated environment owing to the deactivation of the PdNPs.[316] Despite these drawbacks, a number of flexible graphene chemiresistors have nonetheless been demonstrated to operate in air,[313] thus paving the way towards the development of sensors for practical e-skin applications.

The response time for detection of gaseous analytes with flexible graphene chemiresistors is rapid, although it is highly dependent on analyte concentration.[316] In addition, graphene chemiresistors typically experience slow recovery times (=several mins) owing to the strong association between the gaseous analytes and the defects on the graphene surface. While some studies have reported the use of UV irradiation[76] or elevated temperatures[290b,316] to assist sensor regeneration, these treatments would require the integration of additional components (such as microheaters and UV lamps) into the e-skin architecture. Regeneration could also be accelerated through the use of transistors rather than chemiresistors, which have been demonstrated to facilitate analyte desorption by applying a reverse bias; however, to the best of our knowledge, no transistor-based flexible sensors have yet been reported.

The effect of device bending on analyte sensing is a critical consideration for e-skin applications. Ideally, the performance of the device should remain unaffected under either compression or tension; however, a number of reports indicated have minor changes (<5%) in sensitivity during bending.[290b,313,316] The long-term operational stability of these sensors is also important for e-skin applications so that they do not require frequent replacement, though few reports discuss this important factor. Jeong et al. reported little change in the measured resistance over a 6-month period for their hybrid CNT/rGO sensors,[290b] which is encouraging for their integration into e-skin.

4.2.2. Liquid Phase Detection with Graphene-Based Sensors

Chemiresistors: McApline and coworkers recently reported a resistive graphene sensor that was printed on a bio-resorbable silk substrate. They demonstrated that the sensor could be mounted on complex surfaces (such as tooth enamel, muscle tissue, and plastic packaging) by dissolving the silk substrate (Figure 11).[317] Functionalization of the graphene surface with...
antimicrobial peptides made possible the detection of a single *Escherichia coli* bacterium as well as the wireless detection of *Staphylococcus aureus* bacteria on an intravenous bag. The detection of *Helicobacter pylori* in human saliva was also demonstrated by mounting the graphene sensor on a tooth. This work demonstrates the tremendous potential offered by the incorporation of chemical and biological sensors into e-skin.

**Transistors:** For liquid-based measurements using graphene transistors, the solid-phase back gate is replaced with an electrolyte solution and a solution gate. It has been demonstrated that such solution-gated graphene transistors (SGGFETs) are generally more sensitive than back-gated transistors owing to their more intimate electrical coupling. However, solution-gated setups have yet to be successfully miniaturized, making them less practical for use in e-skin. Flexible SGGFETs have been developed for the nonspecific detection of proteins as well as hormones. Additionally, Kwak et al. developed a glucose sensor that allowed for accurate detection between 3.3 and 10.9 mM, largely covering the relevant concentration range for blood glucose monitoring. Such sensors would be highly relevant for diabetes monitoring and management using e-skin.

The detection of cancer biomarkers is another important functionality that could be introduced into e-skins. Kwon et al. demonstrated the detection of vascular endothelial growth factor, a general angiogenic cancer biomarker, down to 100 fm. Zhang et al. detected prostate specific antigen, a prostate cancer biomarker, to 0.11 fm using a label free SGGFET. This flexible graphene-based sensor was three orders of magnitude more sensitive compared to a CNT-based sensor and a thousand times more sensitive than a graphene sensor on rigid substrates. Directly mimicking the human nose’s sensing capabilities is another concept that has been explored with SGGFETs. By functionalizing a transistor with human olfactory receptor (OR) 2AG1, Park et al. developed a flexible graphene bioelectronic nose for the detection of amyl butyrate to 0.04 fm with atomic level resolution between interfering analytes. This detection limit was four orders of magnitude more sensitive than that of similar CNT sensors which demonstrated graphene’s exquisite sensitivity. Despite being functionalized with OR proteins, the devices demonstrated stable performance for 10 days. The effect of bending on the flexible SGGFETs was studied and found to minimally increase resistance despite bending to a high radius of curvature. Finally, the sensing response of the device after a bending fatigue test revealed only a 9% decrease in sensitivity after 100 bending cycles.

For biodetection applications, passivation of the surface against non-specific adsorption is critical, especially in complex media and real-world samples, and can be accomplished using inert polymers or proteins (e.g., bovine serum albumin). Another important consideration for these sensors is long-term stability. The use of proteins and RNA aptamers as recognition elements inherently limits the lifetime of the sensors as they require special storage conditions and are prone to rapid degradation under ambient conditions. Kwon et al. reported a 5% sensitivity decrease after a single use, which they attributed to degradation of the RNA-aptamer recognition element. Replacing these unstable biological elements with more robust DNA aptamers could be a potential solution to increasing sensors stability and lifetime.

Sensor response and regeneration are both important parameters for sensors embedded in e-skin. Ideally, sensors would experience instantaneous response to allow for real-time detection, and regeneration could be achieved through simple means. The initial response of these flexible SGGFET sensors to analyte exposure was typically rapid (<10 s), but may not equilibrate for several minutes. Regeneration is another important consideration for e-skin applications. Kwon et al. found that they could regenerate their sensors with a simple buffer wash while He et al. reported that perfusion could be used to remove the nonspecific and noncovalently bound analytes from their sensor. These initial reports are promising, though the regeneration of a sensor with more specific receptor-analyte binding would be more predictive of the feasibility of using simple rinses for regeneration.

Due to the complex geometries associated with e-skin, elucidating the effect of bending on sensing is of the utmost importance. While He et al. reported a considerable increase in

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**Figure 11.** Biotransferrable graphene wireless nanosensor. a) Wireless sensor consisting of an inductor and interdigitated capacitive electrodes integrated onto a graphene/silk film. Graphene nanosensor transferred onto b) a cow molar, c) muscle tissue, and d) an intravenous bag. Adapted with permission. Copyright 2012, Macmillan Publishers Ltd.
resistance during bending (~25%). Other studies have found little variation (~1%). Additionally, Kwak et al. reported a decrease in $I_{DSS}$ and shifting of the Dirac point when their sensor was operated under strain but with no loss in sensitivity for glucose compared with the unstrained device. Bending fatigue is another practical concern for these flexible sensors. He et al. found that their sensors could withstand 5,000 bending cycles with only minimal increase in resistance (1%).

Sensor reproducibility is an important consideration for sensor development, which can be improved by the replacement of receptor groups, while Xiao et al. reported only 2.36% standard deviation for PtNP-decorated rGO paper electrodes. As movement is an important feature of e-skin, more reports studying the effects of strain on sensing is required owing to the large variation within the reported flexible SGGFETs.

**Electrochemical Electrodes**

Flexible graphene electrodes have been demonstrated for the detection of redox active species like H$_2$O$_2$, in addition to small molecules like lactate and nerve agents. Glucose monitoring is of particular interest for e-skin applications. Flexible graphene electrodes have been developed for the selective detection of glucose to 7.6 μM (linear range of 0.02 to 6.78 μM). Owing to the immobilization of GOx as the recognition element in these sensors, selectivity for uric acids was achieved. Impressively, a non-enzymatic flexible electrochemical electrode for glucose detection has been developed with comparable detection limit (5 mM) and a wider linear range (0.01 to 46 mM), while still exhibiting selectivity over sucrose and fructose, in addition to ascorbic and uric acids.

Typically, a redox active enzyme that has been immobilized onto the electrode serves as the recognition element. While the incorporation of enzymes increases selectivity, they are costly, and the electrodes suffer from stability issues and require special storage conditions owing to the sensitivity of enzymes to changes in temperature and pH. A better receptor for use in e-skin is catalytic NPs, as the elimination of enzymatic recognition groups dramatically increases the practicality of these sensors. Using this technique, Xiao et al. were successful in producing stable enzyme-free electrodes with long shelf lives; they have reported 90% activity after 48h and 60h days for PtNP- and AuNP-decorated rGO paper electrodes, respectively. These sensors have even detected H$_2$O$_2$ excreted directly from HepG2 liver cells.

Additionally, the ability of the sensors to operate continuously over long periods of time is important for integration into e-skin. Using their enzyme-free electrode, Xiao et al. demonstrated 98.6% activity to H$_2$O$_2$ after 200 successive operational cycles using AuNP-decorated rGO paper electrodes, as well as continuous operation over 1,800 s with little change in response for PtNP-decorated rGO paper electrodes. Sensor reproducibility is an important consideration for sensor development, which can be improved by the replacement of enzymes with non-biological groups. Qiu et al. demonstrated a 4.3% standard deviation in five sensors using CO$_2$ receptor groups, while Xiao et al. reported only 2.36% standard deviation during ten individual measurements from AuNP-decorated sensors.

Bending fatigue is another critical parameter for sensors used in e-skin applications. Most flexible graphene electrodes were reported to be quite insensitive to fatigue, typically demonstrating little degradation after many bending cycles. The most robust sensors were reported by Xiao et al., and demonstrated only a 5% resistance increase after 196 h (or 500 cycles) of bending for their AuNP decorated sensors, and a 5% increase in resistance after 24 h (or 100 cycles) for their PtNP decorated sensors. Other groups noted a 10% decrease after 100 bending cycles. However, Labroo et al. observed an 84% decrease in sensitivity with a single 180° bend, and 90% decrease after 10 successive bending cycles. The difference in performance could result from their use of their use of CVD-grown graphene rather than rGO graphene, but the cause of this variability should be further investigated. Overall, flexible graphene sensors show much potential for e-skin applications.

### 4.3. Organic-Material-Based Sensors

Organic materials, OSs and CPs, are attractive sensing materials owing to their compatibility with large-area, low-temperature solution processing techniques that allow for deposition onto flexible substrates, as well as the reduced material and fabrication costs compared to CNTs and graphene. These materials offer the advantage of synthetic versatility, which can be used to enhance not only sensitivity and selectivity for particular species but also the stability of the active material. Furthermore, variation of the deposition conditions can be used to alter the morphology, which influences the sensing capability of the devices. The role of grain boundaries on sensing has been investigated by a number of groups who determined that the sensing response is correlated with the number of grain boundaries present in the film. Another example of the interplay between morphology and sensitivity is the ability to deposit CPs as thin films or as NWs. Because the NWs have higher surface area, they demonstrate increased sensitivity. OOSs and CPs have already demonstrated tremendous potential for both e-nose and e-tongue applications.

For e-skin, the ability of sensors to operate in both ambient and liquid environments for real-time detection applications is critical. However, OSs may require large operating voltages, which is incompatible with liquid-phase operation. The dielectric layer can be manipulated in order to limit operating voltages, either through the use of ultrathin or high-k dielectrics. Additionally, many early OSs were inherently unstable on exposure to water vapor. To address this issue, Someya et al. used electrode encapsulation to operate a pentacene transistor in contact with water. Our group has also used the synthetic versatility of organic materials to develop an inherently water-stable OS, 5′,5′-bis-(7-dodecyl-9H-fluorene-2-yl)-2′-biothiophene (DDFTTF), which was used to fabricate transistors demonstrating stable, long-term operation underwater.

For sensing applications, OS and CPs can be fabricated into electrodes, chemiresistors, and transistors. Much emphasis has been placed on transistor-based detection, as it has been demonstrated to have superior sensitivity to chemiresistors. In addition, multiparameter measurements can be achieved with transistors, allowing for simultaneous measurement of changes in conductivity, threshold voltage ($V_{th}$), and $\mu$. It is also possible to expedite recovery time by desorbing weakly bound analytes by applying a reverse bias to the transistor.
which can preclude the need for harsher treatments (e.g., high temperatures, UV gas) and is therefore advantageous for e-skin applications. Organic transistors can be subdivided into organic field-effect transistors (OFETs) and organic electrochemical transistors (OECTs). OECTs are unique in that they can conduct ions in addition to holes and electrons.

4.3.1. Functionalization Techniques for Selective Sensing

OSs and CPs are inherently sensitive to a number of analytes, and Crone et al. have mapped the response of an array of eleven OSs exposed to sixteen volatile organic compounds in order to determine a sensing “fingerprint.” Liao et al. also developed an early e-nose based on the fingerprinting technique. The sensitivity of these early sensors allowed for detection to the part-per-million (ppm) level, but they lacked specificity, which is critical for e-skin applications since it is impractical to precisely regulate the operating atmosphere.

To achieve more targeted and sensitive detection, the incorporation of receptor groups is required. One advantage of OS and CPs is that they can enhance their selectivity through chemical structure manipulation. For example, Torsi et al. demonstrated enhanced sensitivity for compounds with a dipole moment by using alkoxy groups instead of alkyl groups in the side chains of an OS. Torsi et al. have also incorporated chiral groups to allow for enantiomeric selectivity. However, manipulation of the chemical structure may introduce trap states or alter the packing morphology of the semiconductor, which detracts from the electronic performance of the device. Several groups have proposed the use of OS bilayers to circumvent this issue. In this approach, an electronically optimized OS is first deposited to form the channel, followed by the subsequent deposition of an OS that has been chemically modified to incorporate recognition elements. The deposition of electrical insulators on top of pristine OS has also been used to provide functionalization sites for future covalent modification. Knoll, Bao, and coworkers grafted peptide nucleic acid residues onto a thin poly(maleic anhydride) layer deposited onto a DDFTTF OFET to demonstrate the detection of DNA with single-base pair discrimination. Torsi and coworkers have also pioneered the use of a functional biointerlayer to enhance detection selectivity. In this unique approach, the biological receptor molecules were deposited directly onto the dielectric layer, and physically separated from their analytes by the OS layer.

Other non-covalent functionalization techniques exist that allow for the incorporation of individual binding sites without interfering with the chemical structure of the OS. Our group has used thermally evaporated calix[n]arene groups to increase detection specificity in OFETs. These calix[n]arene receptors could be tuned via chemical synthesis to impart specificity for particular volatile organic species, such as ethyl acetate and isopropyl alcohol. We recently demonstrated that ordered arrays of AuNPs deposited onto OFETs can provide grafting sites for the integration of thiolated receptor groups (Figure 12a). By taking advantage of the self-assembly properties of a poly(styrene-b-vinylpyridine) (PS-b-PVP) polymer, we used a simple, low-temperature spin-casting technique to deposit ordered arrays of AuNPs onto a water-stable OFET. This functionalization strategy is particularly flexible owing to the vast library of existing thiolated receptor groups that are compatible with this sensing platform. Our group has used this platform to selectively detect Hg$^{2+}$ to 1 μM with selectivity over ten other interfering ions by functionalizing the AuNPs with a thiolated DNA aptamer for Hg$^{2+}$ (Figure 12b). The flexibility of this platform was highlighted by the interchangeability of the receptor groups; substitution of a different thiolated DNA aptamer allowed for the detection of thrombin, a model protein, to 100 μM (Figure 12c). In addition, the composition of these NPs can be varied to include other functional species further increasing the number of receptor groups that can be used with this sensing platform.

4.3.2. Gas Phase Detection with Organic Material-Based Sensors

Chemiresistors: For gas-phase detection, a number of flexible organic chemiresistors have been developed for the nonspecific detection of a variety of analytes, including strong oxidants, such as NH$_3$, H$_2$O$_2$, H$_2$, and O$_2$. Jang et al. demonstrated the selective detection of NH$_3$ over other compounds due to its unique ability to convert PANI between its emeraldine salt and base forms. Several techniques were used to enhance the sensitivity of these flexible organic chemiresistors. The use of PANI NPs and PANI NWs significantly enhanced detection for NH$_3$, as compared to a similar device made from a thin-film of PANI. Additionally, the use of CNT/organic hybrid materials was reported to increase sensitivity.

The response and regeneration of these flexible organic chemiresistor sensors was typically slow (~several mins), which is impractical for real-time e-skin sensing applications. However, recovery time could be improved through the use of thinner films or UV-treatments. Interestingly, while early reports suggested exposure to strong oxidants (such as NO$_2$, SO$_2$, and Cl$_2$) resulted in the irreversible chemisorption of the oxidants along the polymer backbone, Dua et al. were able to reverse the response by exposing their PT nanofibers to UV light. However, they noted that damage induced by UV irradiation could potentially limit the number of regeneration cycles that could be achieved with a single device and ultimately limit the lifetime of their sensors.

The issue of long-term sensor stability is critical for implementation in e-skin. Crowley et al. found that though their sensors could be regenerated initially, sensitivity declined over time. They further noted that the use of high temperatures degraded their sensors and therefore could not be used as a means of sensor regeneration. Rizzo et al. reported sensors that were stable over months of operation. Su et al. found little variation in sensing performance after 43 days, suggesting long-term potential for these organic sensors. Stable performance under ambient conditions is also critical for e-skin applications. While several groups have reported that operation in air is possible, Dua et al. reported that the sensitivity of their sensors decreased in air and others have only demonstrated the operation of their sensors in inert or vacuum environments. Since the operation of such sensors in controlled environments is not practical for e-skin applications, attention should be given to developing air-stable sensors with high sensitivity.
Transistors: Even though many gas-phase transistor sensors on rigid substrates have been reported, only a single report exists for flexible transistors: namely, a PEDOT:PSS OECT for relative humidity (RH) detection. This sensor was fabricated on both polyester and paper substrates using solution deposition techniques and was demonstrated to have a rapid response to 25–80% RH. The sensor showed tremendous promise for long-term sensing applications, as it could be stored for 6 months under ambient conditions with only a minimal (7%) decrease in sensitivity. Additionally, the OECT retained its performance after being bent to a radius of curvature of 5 cm, but the effect of bending on sensing was not thoroughly investigated.

The ability of e-skin to permit movement requires its constituent materials to be capable of bending and stretching. However, despite the critical role that bending plays in e-skin applications, its effect on chemical and biological sensor performance has received relatively little attention. Our group recently studied the effect of flexing on OFET performance in order to shed more light on this critical parameter for e-skin applications. We examined the response of two OSs (pentacene and 5,5′-bis-[7-hexyl-9H-fluoren-2-yl]-2,2′-bithiophene (DHFTTF)), and several polymer dielectrics to strain induced by flexing during operation. We found that both the active material and the dielectric can influence the device’s response to compressive and tensile strains (Figure 13). Importantly, we observed that $\mu$ was found to change during bending, and defined a mobility factor ($F_M$) parameter to describe the relationship between strain and OS performance. This $F_M$ was found to be generally positive for pentacene, but generally negative for DHFTTF. Furthermore, the composition of the dielectric was found to play a crucial role on $F_M$ for each OS. Importantly, we found that modification of the dielectric with a dense self-assembled monolayer of octadecylsilane (OTS) could significantly decrease $F_M$ for both pentacene and DHFTTF, thus diminishing the effect of bending strain on device performance and therefore sensing.

4.3.3. Liquid Phase Detection with Organic Material-Based Sensors

Transistors: A number of flexible OFETs have been developed for the detection of various small molecule analytes including explosives, cysteine, biotin, and sodium dodecyl sulfate (SDS). Lin et al. also demonstrated DNA detection using a flexible PEDOT:PSS OECT. They reported a detection limit of 1 nM for the complementary DNA sequence and were able to further increase their sensitivity to 10 pM using pulse gating. Interestingly, they reported that the device characteristics did not change significantly on bending and that the sensors were stable to measurement over a several-day period. These qualities are essential for e-skin applications. For all of the flexible transistors that were reported, response and

Figure 12. Selective analyte detection using an OFET patterned with an ordered array of AuNPs. a) Schematic of device fabrication depicting block-copolymer method used to deposit ordered arrays of AuNPs on the surface of the OFET for later functionalization with a thiolated receptor. b) Selective response of an AuNP-decorated OFET functionalized with an Hg^{2+}-binding aptamer to sequential addition of Hg^{2+}. Adapted with permission. Copyright 2012, American Chemical Society. c) Detection of thrombin using an AuNP-decorated OFET functionalized with a thrombin-binding aptamer. Adapted with permission. Copyright 2013, American Chemical Society.
regeneration occurred rapidly (∼secs), allowing for real-time detection in situ.

Organic active materials that are inherently unstable in water can be encapsulated to prevent their direct contact with aqueous solutions. A number of ion-sensitive OFETs (ISOFTETs) have been developed for pH detection while using pentacene as the active material and a chemiselective Ta_{2}O_{5} dielectric as the encapsulation layer. Knoll, Bao and coworkers used a different encapsulation strategy; they deposited a layer of copper phthalocyanine (CuPC) onto a pentacene OFET. Although the performance of these flexible OFETs was slightly reduced compared to similar devices fabricated on rigid substrates, they were still able to demonstrate the sensitive detection of biocatalysts to 200 nm and SDS to 1 μM. Alternatively, we reported the use of an inherently water stable OS (DDFTTF) to fabricate a flexible OFET sensor. The μ of these sensors was similarly depressed from that demonstrated on rigid substrates, but they were capable of the highly sensitive detection of both trinitrobenzene (TNB) and cysteine to the sub-ppm level. An interesting feature of the liquid-phase OFETs developed by our group is that they did not require a solution gate, unlike most CNT and graphene transistors that have been reviewed here.

Until liquid gates can be effectively miniaturized, the use of a solid-state back gate instead of a liquid gate is critical for successful incorporation into e-skin.

**5. Additional Desirable Properties for E-Skin**

E-skin can mimic the properties of human skin in its ability to sense tactile forces, as well as augment the capabilities of human skin through incorporation of chemical and biological sensing functionalities. Besides the sensing properties described in Sections 3 and 4, we highlight several additional desired properties which are actively being pursued for incorporation into e-skin in this section.

**5.1. Biocompatibility and Biodegradability**

Since e-skin applications require intimate association with biological interfaces, biocompatibility is an important consideration for such devices. Ideally, e-skin should be synthesized from highly biocompatible components; however, there are contradictory reports on the biocompatibility of many of the active materials used in e-skin fabrication. For example, CNTs have been found to show asbestos-like pathogenic behavior due to their small size and needle-like morphology and have been reported as highly toxic to cells at high concentrations. Other reports suggested that the immunogenic response elicited by CNTs incorporated into electronic devices was dependent on nanotopology. For example, Agarwal et al. compared cell growth on CNT networks and rGO surfaces, and found that morphological differences were the primary factors differentiating their biocompatibility. In particular, the atomically flat rGO was found to be biocompatible with various mammalian cell lines.
whereas the CNT surface impeded cell proliferation. Additionally, we have recently explored the effect of CNT morphology on cell cytotoxicity in vitro by comparing drop cast and spin cast CNT samples.\textsuperscript{168} We found that the increased roughness of the drop cast surfaces resulted in higher cytotoxicity as compared to the 2D morphology of the aligned, spin cast CNTs. In addition to morphology, other studies have suggested that concentration may influence biocompatibility; Wang et al. determined that both in vitro and in vivo, low concentrations of rGO did not elicit a toxic response, but higher doses had clear indications of cytotoxicity.\textsuperscript{169}

The biocompatibility of organic materials is also highly variable, and factors such as chemical composition, surface charge, and pH are responsible for influencing cytotoxicity. For CPs, additional factors such as monomer, solvent, and/or dopant leaching also influence biocompatibility.\textsuperscript{170} Despite the large number of factors governing biocompatibility, some materials, such as PPY and PEDOT derivatives, have generally been found to be biocompatible. For example, PEDOT:p-toluenesulfonate (PEDOT:TOS) OECTs have been used to control cell density gradients,\textsuperscript{171} while PEDOT:PSS OECTs have been used to monitor in vitro cell activities.\textsuperscript{172} Overall, these findings suggest there is a need to control the morphology of the active material, while limiting its concentration within devices in order to improve biocompatibility. More importantly, ensuring that these active materials do not leach from the electronic devices is critical for their implementation in e-skin.

Other strategies exist to improve the biocompatibility of the active materials used in e-skin. Immobilization of cell-adhesion peptides, polysaccharides, and growth factors, either through physical entrapment or covalent attachment, have been demonstrated to influence biocompatibility.\textsuperscript{170} The use of naturally occurring materials is another approach to increase biocompatibility. A number of naturally occurring materials, such as carmelized glucose, hard gelatin, and starches, have already been demonstrated as substrates for electronic devices.\textsuperscript{173} Furthermore, molecules such as DNA\textsuperscript{174} and sugars have also been used as dielectric materials, and naturally occurring OS such as indigo\textsuperscript{175} and its derivatives and carotenoid polyenes have separately incorporated the charge transfer salts tetrathiafulvalene (TTF) and tetracyanoquinodimethane (TCNQ) into poly(urea-formaldehyde) core-shell microcapsules.\textsuperscript{176} On fracture, the TTF and TCNQ components will mix to form a stable hydrogen-bonded $\pi$-stacked structure of natural dyes, hydrogen-bonded analogues of linear acenes have recently been demonstrated as substrates for electronic devices.\textsuperscript{173} Additionally, motivated by the need for self-healing materials, the use of naturally occurring molecules such as DNA\textsuperscript{174} and sugars has also been used as dielectric materials, and naturally occurring OS such as indigo\textsuperscript{175} and its derivatives and carotenoid polyenes have been used as active materials.\textsuperscript{173} Furthermore, molecules such as DNA\textsuperscript{174} and sugars have also been used as dielectric materials, and naturally occurring OS such as indigo\textsuperscript{175} and its derivatives and carotenoid polyenes have been used as active materials.\textsuperscript{173} Additionally, motivated by the stable hydrogen-bonded $\pi$-stacked structure of natural dyes, hydrogen-bonded analogues of linear acenes have recently been demonstrated as substrates for electronic devices.\textsuperscript{173} While the electronic performance of these devices will require considerable optimization to be useful for e-skin applications, they demonstrate a promising route to biocompatibility.

The concept of transient electronics, which dissolve or resorb into the body at a programmed rate, is an additional benefit offered by devices synthesized from natural compounds. We recently reported the development of a resorbable OFET fabricated from biocompatible and biodegradable polymers (Figure 14a).\textsuperscript{177} The device was fabricated on a polylactide-co-glycolide (PLGA) substrate, utilizing a poly(vinyl alcohol) (PVA) dielectric, DDFTTF active layer, and Au contacts. The PLGA substrate accounted for 99.89% of the device’s total mass and disintegrated completely over a period of 70 days in citrate buffer, indicating the feasibility of biodegradable electronics for e-skin applications. Moreover, the degradation products released through the breakdown of the OFET were naturally occurring byproducts of other cellular processes, so their decomposition would not elicit a cytotoxic response. Similarly, Rogers and coworkers have shown that ultrathin Si devices fabricated on silk substrates with magnesium (Mg) interconnects and a MgO dielectric were rapidly dissolved in water over a period of 10 min (Figure 14b).\textsuperscript{178} While these materials were not naturally occurring, each material was reported to be individually biocompatible. Furthermore, by encapsulating the devices in crystallized silk, a two-stage transience could be achieved, allowing for a programmed rate of degradation. Another route to tuning the degradation rate of devices is by adjusting the chemical structure of the constituent organic molecules. For example, Zelkin et al. demonstrated that biodegradable PPY derivatives could be fabricated through the incorporation of ionizable and hydrolysable side groups.\textsuperscript{179}

Resorbable substrates can also play a key role in interfacing e-skins with the body. Rogers and coworkers fabricated devices for electrocorticography\textsuperscript{180} and cardiac electrophysiology\textsuperscript{181} measurements on mechanically compliant substrates. The conformability of these devices was further improved by using biodegradable silk substrates to deposit them on the surface of the brain\textsuperscript{182} or implant them within the brain.\textsuperscript{183} Overall, much progress has been made toward developing biocompatible and biodegradable devices, allowing for the possibility of integrating e-skins with the human body.

5.2. Self-Healing

While naturally occurring human skin has the ability to repair itself after incurring mechanical damage, this property has yet to be fully realized in e-skin. For artificial skin, the ability to repair both mechanical and electrical damage would be highly advantageous for practical applications. There are two predominant strategies used to incorporate self-healing properties into materials, namely: 1) the use of materials loaded with healing agents,\textsuperscript{184} and 2) the use of materials containing dynamic reversible bonds.\textsuperscript{185} The incorporation of capsules containing healing agents was first demonstrated in self-healing, non-conducting polymers.\textsuperscript{184} However, for e-skin applications, it is necessary to use a system that is electrically active. To this end, Odom et al. have separately incorporated the charge transfer salts tetrathiafulvalene (TTF) and tetracyanoquinodimethane (TCNQ) into poly(urea-formaldehyde) core-shell microcapsules.\textsuperscript{186} On fracture, the TTF and TCNQ components will mix to form a charge transfer salt that restores the electrical conductivity to the composite material. However, this approach requires adequate mixing of the individually packaged TTF and TCNQ components. In order to overcome this requirement, White, Moore, and coworkers have pursued the incorporation of liquid metal healant capsules into conductive circuits.\textsuperscript{184a,184c} Specifically, the use of eutectic gallium indium (EGaIn)\textsuperscript{184} and Ag ink\textsuperscript{184c} healants allowed for rapid self-healing without the need for further mixing after the capsules have been mechanically ruptured. While this strategy allows for almost instantaneous (160 $\mu$s) return of the electrical conductivity,\textsuperscript{184d} the disadvantage of the healant capsule approach is that it is a single occurrence event: that is, the material no longer possesses self-healing properties after the first use.
To address this consideration, the use of reversible dynamic bonds for multi-use self-healing applications has been investigated. Williams et al. have introduced reversible crosslinking groups into CP networks; however, the demonstrated conductivity of their material (10⁻³ S cm⁻¹) was insufficient for use in e-skins. To increase conductivity, it is possible to use the conductive filler approach: that is, seeding insulating polymers with inorganic conducting materials. For example, Li et al. have incorporated AgNWs into a blended polymer membrane of branched polyethyleneamine and poly(acrylic acid)--hyaluronic acid (bPEI/PAA-HA). The structural and electrical integrity of the film was maintained thanks to reversible ionic bonds between the positively charged carboxylic acid groups decorating the bPEI/PAA-HA and pyrrolidone groups coating the AgNWs. However, the self-healing properties were dependent on exposure of the membrane to water. For e-skin applications, it is preferable to have materials that self-heal without the need for external stimulants (such as light, heat, solvents, water).

We recently demonstrated the first intrinsically self-healing conductive composite material (Figure 15). A composite material, formed with nickel microparticles (µNi particles) embedded in a hydrogen-bonded polymer matrix, was highly conductive (40 S cm⁻¹ at concentrations above the percolation threshold of µNi particles). Furthermore, this material was intrinsically self-healing and regained 90% of its conductivity within 15 s of incurring mechanical damage at room temperature and without any external stimuli (Figures 15a,b). The unique nanostructuring of the µNi particles facilitated the self-healing property of the composite; an analogous composite made with smooth µNi particles had low conductivity (10⁻⁶ S cm⁻¹). Furthermore, by maintaining the volume loading of the µNi particles just below the percolation threshold (15% vol loading), the composite material was made to be responsive to external forces, such as flexion (Figure 15c) and tactile pressure (Figure 15d). The compressive stress from flexion and/or pressure imparted from tactile stimuli brought the µNi particles into closer proximity, producing the sensing response. These results are quite promising toward the development of intrinsic, fully self-healing materials for e-skin applications. However, additional work to improve the stability and sensitivity of these materials is needed.

5.3. Temperature Sensitivity

Sensing temperature is a key functionality of human skin that helps to prevent injury and provides information about the surrounding environment. As previously mentioned in Section 3, most tactile sensors are inherently temperature sensitive, and their response must therefore be calibrated with a temperature sensor. Several groups have implemented piezoelectric/pyroelectric sensors that can discriminate between temperature and pressure inputs. Graz et al. used novel bifunctional composites while Trung et al. used a novel AC biasing method. Resistive temperature detectors (RTD) are attractive for e-skin applications owing to their flexibility, simple device structure, and compatibility with electronic readout methods.
Temperature region can be many orders of magnitude. In composites of a single polymer and filler, the change in resistance has little reproducibility because the material’s morphology can change during the melting and freezing processes. Composites comprised of multiple fillers and/or multiple polymers have shown improved reproducibility. Our group has demonstrated a wireless temperature sensor composed of polyethylene (PE), poly(ethylene oxide) (PEO), and μNi particles that possessed excellent sensing characteristics within tunable temperature ranges (Figure 16). The PE and PEO formed interpenetrating networks with the μNi particles segregated into the PEO domains. Large changes in resistance occurred at the melting point of PEO, which could be tuned by varying its molecular weight. The PE network maintained the morphology of the composite, thus improving reproducibility.

5.4. Self-Powering

Providing a long-lasting supply of power is a persistent challenge for mobile electronics. As the largest human organ, skin provides a large area for potential energy storage. Furthermore, as the body’s interface with the outside world, e-skins

Figure 15. Demonstration of an intrinsically self-healing conductive composite. a) Electrical and mechanical self-healing properties observed using an LED connected in series with the conductive composite: 1. Pristine composite; 2. Fully severed conductor; 3. Self-healing of conductor; 4. Healed film being flexed after 5 min healing at room temperature. b) Electrical self-healing as measured through resistance of the composite film. Inset is optical microscope image of damaged sample and complete scar healing (scale bar = 1 mm). Application of conductive composite as self-healing e-skin. c) A flexion sensor was mounted on the inner elbow region and connected to an LED mounted on the eye region. The LED intensity increased with increasing elbow flexion. d) A tactile sensor was mounted on the palm and connected to an LED mounted on the center of the body. The light intensity increased as a function of increasing tactile pressure. Adapted with permission. Copyright 2012, Macmillan Publishers Ltd.
be cycled to 18.5% strain at least 10 times without any degradation in the performance. We have subsequently characterized the effect of different semiconductors on the intrinsic stretchability of OPV devices. For more information, readers are directed to a recent, comprehensive review of stretchable materials for solar cells.

Technologies for harnessing mechanical energy include both dielectric elastomer generators and piezoelectric generators. Dielectric elastomer generators consist of an elastomeric dielectric coated with two highly compliant electrodes, and their stretchability makes them attractive for use in e-skin. The electrodes are charged by applying a voltage in the compressed state. Relaxation of the elastomer increases the voltage, producing higher energy charges that are harvested. Dielectric elastomer generators can achieve very high efficiencies, but have historically been limited by the complexity and weight of the associated electronics. Recent reports have demonstrated that the circuit complexity can be reduced using systems that are self-primed or primed by electrets. An excellent review of the fundamentals of dielectric elastomers and their applications to energy generation and soft machines is available by Anderson et al.

Mechanical energy harvesting devices based on nanostructured piezoelectric materials have also been developed, and stretchable versions have been fabricated by buckling the active materials.

Fueled by the development of new soft materials, the field of mechanically compliant energy storage technologies has recently emerged. Supercapacitors store energy in the form of double layers of charged species residing at the electrode–electrolyte interface and provide very high power densities. Buckled CNT electrodes on prestrained substrates have been used to...
make supercapacitors that are stretchable up to 30%. Cui and coworkers developed a method for making highly conductive and porous electrodes by printing a CNT ink onto commercially available substrates such as paper and fabric. Niu et al. have also fabricated supercapacitors that could stretch to 120% with little change in performance. Additionally, compressible supercapacitors have been reported using graphene-based electrodes. While reports on stretchable supercapacitors have been relatively limited so far, the popularity of CNTs and graphene in both supercapacitor electrodes and stretchable electrodes suggests an excellent overlap in their properties.

The first intrinsically stretchable batteries were demonstrated by Kaltenbrunner et al. using conventional materials (in a paste form) embedded within an elastomer. Lateral separation of the electrodes permitted stretching to values of 100% strain while retaining functionality. The same group recently reported an improved version that could be recharged and had electrical properties that were nearly strain-insensitive. Gaikwad et al. have developed stretchable batteries using commercially available electrodes, and several groups are developing stretchable electrodes for battery applications. Rogers and coworkers have recently demonstrated a battery composed of an array of small pouches of lithium ion batteries connected with stretchable metal interconnects (Figure 18). The battery was able to function with an applied biaxial strain of up to 300%, and could stretch reversibly to 200%.

Radio frequency (RF) antennas have become popular as transient power supplies. Carta et al. demonstrated that an RF antenna incorporated into flexible device islands with stretchable connections could charge a battery. Intrinsically stretchable RF antennas have been produced using liquid metals embedded in stretchable microfluidic channels that could stretch up to 200%. Stretchable antennas have been reported using solid metals patterned into either meandering or serpentine patterns. Rogers and coworkers have incorporated RF antennas into epidermal electronic systems (EES) that could be directly integrated with skin and demonstrated their feasibility to charge stretchable batteries.

6. Highly Integrated E-Skin Devices

Using the technologies described in previous sections, highly integrated systems of mechanically compliant sensor arrays possessing multiple functionalities have been reported. A select number of recent advancements will be described in this section, along with some of their demonstrated applications in the fields of biomedical devices, robotics, and optoelectronics.

6.1. E-Skin for Biomedical Devices

Active electrode arrays have been demonstrated by Rogers and coworkers for measuring electrical activity in both the heart and brain. The mechanical compliance of these arrays was essential for achieving conformal interactions with these irregularly shaped organs. For measuring electrocardiogram signals, an array of 2016 transistors was used to achieve good temporal resolution at 288 contact points, thus allowing for high-resolution spatial mapping of electrical characteristics. A similar flexible array of active electrodes was used to measure brain activity with unprecedented spatial accuracy.

Rogers and coworkers also demonstrated multifunctional balloon catheters (Figure 19a) with the capability to collect data on temperature, pressure, and tactile stimuli during surgical procedures, as well as emit light through incorporated LEDs. Stretchability up to 130% with these catheters was achieved using serpentine-patterned metal lines. RTDs were implemented using serpentine-patterned Pt electrodes, and a piezoresistive rubber was used to design tactile sensors that responded selectively to normal forces. Exposed electrodes were used for ablation of tissues and collection of electrocardiogram signals.

Rogers and coworkers have also incorporated stretchable arrays of sensors and electrodes into a conformal “finger tube” that could be used to augment tactile feedback in applications such as surgery. Pressure sensing was implemented using electrodes...
first flexible and highly multifunctional skin-like systems was reported by Engel et al. using polymer micromachining technologies.\[259b\] An array of several sensor types allowed the measurement of numerous desired parameters such as contact forces, object hardness, temperature, thermal conductivity, and surface curvature. However, the system lacked multiplexing for large-scale implementation.

Over the last decade, Someya and coworkers have reported a series of increasingly more complex stretchable circuits with multiple functionalities. A flexible active matrix of pressure and temperature sensors was first reported in 2004,\[26a\] and stretchability was subsequently added by the selective removal of periodic sections of the flexible substrate.\[15a\] To increase the device's stretchability, stretchable interconnects were implemented by developing a highly conductive and stretchable material comprised of a fluorinated elastomer and ionic liquid with long CNTs (Figure 20a).\[15b\] The stretchable material was later formulated to be printable, thus improving the throughput and cost effectiveness of the device's manufacturing process.\[20b\] The adopted active matrix technology has subsequently been used to drive a range of devices, including pressure sensors, temperature sensors, electromagnetic interference sensors,\[418\] and actuators for tactile feedback arrays.\[419\] By integrating a floating gate into their OFETs, pixels with memory capabilities were created that could locally store information from piezoresistive elements.\[15c\] For device readout, local memory is important to capture transient events that may be shorter than the readout time of the sensor array and to provide a “snapshot” of an instantaneous distribution of the stimulus.\[166b\] The work of Someya and coworkers has been comprehensively reviewed elsewhere.\[136d,273\]

Javey and coworkers have also developed high-throughput fabrication methods for e-skin applications as well.\[420\] They have produced active matrix arrays of pressure sensors using inorganic NWs and CNTs as the semiconductor. The use of

on either side of a soft PDMS membrane, and strain sensing was accomplished using piezoresistive Si strain gauges with geometrically tunable responses. Electrotactile information could be communicated via electrodes situated inside the finger tube.

Using thin, breathable substrate materials, Rogers and coworkers developed an EES that could be transferred onto the skin in a manner akin to a temporary tattoo (Figure 19b).\[390a\] This system could stretch reversibly to 30% without damage or delamination, which is sufficient to accommodate natural movements. Temperature, strain, and electrical measurement capabilities were demonstrated, as well as active and passive components for signal readout. Solar cells and wireless devices were later integrated for self-powered applications.\[390a\] and both the mechanics and capabilities of the device were characterized in a subsequent report.\[417\]

Using transistors with highly compressible dielectrics, our group has made flexible pressure sensors for healthcare monitoring. The devices were operated in the subthreshold regime, resulting in low power consumption and exceptionally high sensitivity (8.4 kPa\(^{-1}\)).\[3\] The devices were patterned into an array that could detect the pressure distribution created by a 46 mg weight. Patterning the dielectric avoided the bulk viscoelasticity of the elastomer and provided a response time of \(\approx 10\) ms, which was fast enough to measure arterial pulse shape with good resolution and could be used to assess a patient's cardiovascular health (Figures 19c,d). Furthermore, these solution-processed devices provide a more economical alternative to conventional Si MEMS technology.\[153\]

6.2. E-Skin for Robotics

Compliant devices with integrated tactile functionality could be used as skin-like sensors for intelligent robots. One of the
Additionally, Rogers and coworkers have demonstrated stretchable and twistable GaAs-based arrays of micro-LEDs (μ-ILEDs) and micro-photodetectors (μ-IPDs) (Figures 20 c) and integrated them into gloves.\footnote{20c} These devices were fabricated by transfer printing arrays of devices onto elastomeric substrates and connecting them with stretchable interconnects. The μ-ILEDs and μ-IPDs could be used to monitor the proximity of objects based on the detection of backscattered light. Javey and coworkers very recently described a user-interactive e-skin capable of spatially mapping pressure stimuli through integrated OLEDs.\footnote{424} Someya and coworkers have also fabricated stretchable arrays of OLEDs using flexible OLED islands connected with stretchable printed conductors.\footnote{20b}

7. Conclusions and Outlook

In the past decade, the pace of e-skin development has accelerated dramatically owing to the availability of new materials and processes. As a result of this progress, the capabilities of e-skin are rapidly converging on those depicted in science fiction (Figure 1). Interest in e-skin has been driven by its potential to: 1) enable highly the development of interactive and versatile robots that are capable of performing complex tasks in less structured environments; 2) facilitate conformable displays and optical; and 3) revolutionize healthcare by providing biomimetic prostheses, constant health monitoring technologies, and unprecedented diagnostic and treatment proficiency. Sensors and circuits have already exceeded the properties of biological skin in many respects. Electronic devices have been fabricated that stretch many times further than skin,\footnote{117} flexible tactile sensors have been demonstrated that possess vastly superior

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**Figure 20.** Highly integrated e-skins for robotics and optoelectronic applications. a) Stretchable active matrix devices reported by the Someya group including biaxial stretching of an integrated, encapsulated device demonstrating a conformal coverage of a non-planar surface (left), and a depiction of an individual organic transistor in the array (right). Adapted with permission.\footnote{15b} Copyright 2008, AAAS. b) Depiction of piezoelectric NWs used as an array of active tactile sensors with unprecedented spatial density. Adapted with permission.\footnote{23b} Copyright 2013, AAAS. c) Stretchable and twistable LED arrays. Adapted with permission.\footnote{20c} Copyright 2010, Macmillan Publishers Ltd.
spatial resolution to human skin,\textsuperscript{23b} and tactile and temperature sensors are available with enhanced sensitivity over their natural counterparts.\textsuperscript{18,192}

Despite rapid progress, there is a continuing need for further development before the goal of integrating multiple functionalities into large-area, low-cost sensor arrays is realized. From a design standpoint, e-skin requires active circuitry to address large numbers of devices with minimal wiring complexity and fast scan rates. Furthermore, the ability to mimic the mechanical properties of human skin (e.g., flexibility and stretchability) is critical in order to accommodate the various movements of the user. This can be accomplished through the use of intrinsically stretchable materials or rigid device islands tethered together through flexible interconnects. While the latter leverages the extensive optimization of rigid devices, the former may have advantages in terms of cost and robustness.

One of the most important functions of skin is to facilitate the sense of touch, which includes normal force sensing for grip optimization, tensile strain sensing for proprioception, shear force sensing for object manipulation, and vibration sensing for slip detection and texture analysis. While the commonly used transduction methods (such as piezoresistive, capacitive, piezoelectric, optical, and wireless) are readily available, advancements in device structures and materials have produced dramatic improvements in tactile sensor performance. For example, improvements in processes to create microstructured and nanostructured materials have presented exciting opportunities for smaller devices suitable for high-density arrays\textsuperscript{23b} with low power consumption and excellent performance.\textsuperscript{18} However, further optimization of materials and device configurations is still necessary. For example, the piezoresistive composites that are currently used in some integrated systems\textsuperscript{15b,23a} display viscoelasticity that may potentially be overcome using matrix-free structures of nanomaterials.

Different transduction methods provide different sensing capabilities, thus allowing integrated systems to mimic the multifunctional nature of human tactile sensing capabilities. For example, large strains can be reliably measured using piezoresistive devices,\textsuperscript{188} capacitive devices can provide high sensitivity to normal forces, and piezoelectricity can measure vibrations. Integration and readout is one of the most important development areas for large area sensor arrays. Active matrices have been developed that provide a method of multiplexing large arrays with fast addressing and minimal cross-talk between pixels.\textsuperscript{13b,136b} Future work will probably involve continuing efforts to improve the performance and reduce the cost of tactile devices integrated with transistor matrices. Furthermore, integrating multiple functionalities (such as temperature, shear, and vibration sensing) with active matrix arrays is an area of tremendous opportunity.

Concomitantly, the properties of human skin can be augmented by incorporating both chemical and biological sensors into e-skins. Several flexible chemical and biological sensors have been reported for the detection of both gas- and liquid-phase analytes. Flexible chemiresistors and transistor-based sensors for gas detection have sensitivities on a par with their flexible counterparts. However, most sensors have to be operated in controlled, inert environments owing to cross-reactivity with species present under ambient conditions (such as O\textsubscript{2} and H\textsubscript{2}O). A handful of techniques have been developed to increase specificity for particular analytes, the most promising of which are the use of chemiselective films and the deposition of catalytic NPs. The ability to quickly regenerate these sensors is also important for e-skin applications, but unfortunately, most chemiresistors are plagued by lengthy recovery times. To implement this technology in e-skins, it may be necessary to incorporate a microheater or UV light source in order to accelerate regeneration times, which adds additional complexity to the device. Recovery times could also potentially be accelerated through the use of transistors rather than chemiresistors for gas sensing.

For flexible sensors operating in aqueous media, a wide variety of biologically relevant analytes have already been detected. A solution gate is commonly used to increase sensitivity in these devices; however, little progress has been made in miniaturizing these gate electrodes, making them unsuitable for e-skin applications at this time. Additionally, the use of protein-based receptor groups limits the shelf life of these sensors and imposes restrictive storage conditions, although immobilizing them on polysaccharide supports have been shown to slow device degradation.\textsuperscript{425} Otherwise, the replacement of protein-based receptors with more stable organic molecules such as DNA aptamers or inorganic catalytic NPs can be used to increase the lifetime of the device. Finally, the ability to accommodate bending fatigue is crucial for practical e-skin applications, but has yet to be thoroughly investigated.

Other desirable properties, including biocompatibility and biodegradability, self-healing, temperature sensitivity, and self-powering are also currently being developed for implementation into e-skin. The use of bio-resorbable materials would allow for the fabrication of transient electronics with programmable lifetimes. By contrast, e-skin with self-healing capabilities would allow for the ability to repair mechanical and electrical damage, allowing such electronics to last a lifetime. Temperature sensors, often incorporated in conjunction with tactile sensors, would be highly useful in e-skin. Finally, the prospect of self-powering e-skins made possible through the incorporation of devices such as solar cells, mechanical energy harvesters, supercapacitors, batteries, and wireless antennas would allow a degree of autonomy not possible with an immobile power source.

While tremendous effort has been concentrated on developing e-skin hardware, its true value is derived from effective digitization, which requires software to provide a communication interface with the user. The signals produced from sensors in e-skins are analog, and signal digitization is required for interfacing with modern digital microprocessors. Ideally, digitization would be performed at the sensor device level in a manner that does not require considerable power consumption in order to integrate a large density of sensors (>100 cm\textsuperscript{-2}). After digitization, software algorithms could be used to process, interpret, and act on the large amounts of data in a coherent fashion. Further integration of other signal processing methods (such as wireless technologies) could be used to create super skins, such as implantable biofeedback devices for healthcare applications. Future work in the development of e-skin will most certainly require concentrated and multi-disciplinary
research efforts, using the human skin and other living organisms as excellent example models.

Several highly integrated e-skins demonstrating multiple functionalities for applications such as biomedical devices, robotics, and optoelectronics have been recently reported. One particular challenge in the future of e-skin will be neural interfacing.[14] Work has already begun to overcome this obstacle, and recently, a neurally controlled robotic arm capable of 3D reach and grasp movements was reported.[15] Additionally, a bionic ear has been demonstrated with the capability to receive RF signals beyond that of the human ear.[16] The rapid pace of progress in e-skin technology suggests that the fabrication of a more complex e-skin with properties far surpassing those of their organic equivalent will soon be possible.

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