Flexible electronic skins based on piezoelectric nanogenerators and piezotronics

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Abstract

Electronic skins have received substantial attention in recent years and found great potential in prosthetics, robots, wearable devices, medical equipment, and many other areas. The development of the emerging field of nanogenerators and piezotronics unveiled new types of flexible electronic skins. These devices demonstrated high sensitivity, rapid response, and self-power capability. This review gives the research progress of electronic skins based on principles found in nanogenerators and piezotronics. The role of the piezoelectric effect and the piezotronic effect in sensors is explored, materials used in devices are discussed, and different sensors for electronic skins are provided in this review. The review concludes with an outlook of electronic skins enabled by nanogenerators and piezotronics.

Keywords: Electronic skin, Tactile sensor, Piezoelectric nanogenerator, Piezotronics, Pressure sensor, Strain sensor

1. Introduction

Skin is an important organ of human that can percept external stimuli or environmental changes such as temperature, pressure, and humidity. Electronic skin was known as “artificial skin” and proposed as early as 1980s by George Lucas via describing a vision of future [1]. The early electronic skins exhibited low resolution, limited flexibility, and poor sensitivity. The wearable technology, artificial intelligence, health monitoring and replaceable prosthetic devices often require electronic skins to be flexible, sensitive, and function independent of shape and size. In order to satisfy these needs, new sensing mechanisms have been discovered and new devices have been designed and fabricated.

Electronic skins based on piezoresistive devices and capacitive devices have been discussed fully in many review articles [2,3], and this review article is focused on devices based on new principles revealed in piezoelectric nanogenerators and piezotronics. A sensor array based on ZnO piezoelectric nanogenerators perceived both static and dynamic stimuli [4]. A piezoelectric GaN nanowire was used to fabricate a force sensor, and the piezoelectric effect enabled the sensor to have a transverse force sensitivity of 1.24 ± 0.13 ln(A)/nN [5]. Studies of piezoelectric nanomaterial-based devices are increasing in recent years [6–12] due to their high sensitivity, rapid response to dynamic stress, and relative ease of miniaturization. Triboelectric nanogenerator-based sensors have also been widely studied [13–17], and their application in electronic skins was discussed fully in a recent review article [18]. This review article is mainly focused on electronic skins based on principles revealed in piezoelectric nanogenerators and piezotronics. We provide a brief explanation of piezoelectricity and piezotronics, discuss in detail materials involved in device development and different sensors for electronic skins, and conclude with perspectives of the electronic skin enabled by piezoelectric nanogenerators and piezotronics.

2. Piezoelectricity and piezotronics

2.1. Piezoelectricity

Piezoelectric materials can produce polarization charges on their surfaces when a force is applied, such that mechanical stimuli can be measured from their electric responses. Electric fields applied to a piezoelectric material result in a mechanical response through the reverse piezoelectric effect. The unique energy transduction of piezoelectric materials enables their applications in fields of energy harvesting, actuators, sensors, photocatalysis, etc. The creation of strain-induced polarization charges in piezoelectric materials can be detected through electric measurements [19,20], making it possible for pressure/strain detection. Sensors have been fabricated using piezoelectric ZnO nanorod arrays [21]. Experimental results showed that the output voltage increased with the applied force, which enabled the sensor to detect pressure and bending action [21].
2.2. Piezotronics

Piezotronics is a new field that is focused on the study of the coupling mechanism between piezoelectricity and conductivity and the design and fabrication of new devices [11,22–24]. The piezotronic effect was first proposed by Wang and co-worker in 2006 and 2007 [25–27], and the field grew rapidly thereafter. The piezotronic effect shows the modulation of the band structure and the transportation of charge carriers through a deformed piezoelectric semiconductor [28]. When an external force is applied to a piezoelectric material, piezoelectric potential is created due to the piezoelectric effect. If the piezoelectric material is also a semiconductor and connected to a metal or another semiconductor, the free charge carriers redistribute and the band structure changes near the interface. Consequently, the current transport behavior reflects the mechanical deformation of the material and the external forces [29–31]. For example, a Schottky barrier can be formed at the interface of a metal and an n-type semiconductor. The carriers transport from metal to semiconductor across the Schottky barrier when a forward bias is applied. A compressive strain results in positive piezoelectric polarization charges at the interface and decreases the Schottky barrier height (SBH) [32], causing an increase of the current [20,30]. If a force is applied in the opposite direction, the piezoelectric material is stretched. Negative piezoelectric polarization charges are produced at the interface and the SBH increases, resulting in a decrease of the current (Fig. 1).

The piezotronic effect was used to fabricate piezotronic transistors in which the “gate” electrode in traditional transistors was eliminated and the “gate” voltage was induced by the piezoelectric potential [28,29]. The carrier transport process can be influenced by the piezoelectric effect and the piezoresistive effect, and it was found that the piezotronic effect played a dominant role in controlling the transport behavior in nanomaterials [33–36]. In 2006, Wang et al. [25] fabricated the first piezoelectric field effect transistor based on a ZnO nanowire. The working mechanism was adopted to fabricate sensors that detected forces in the nanonewton range [25]. The results showed a linear relationship between the force and the conductance, indicating a possible application for electronic skins.

3. Materials for electronic skins

3.1. Inorganic piezoelectric materials

Inorganic nanomaterials like BaTiO3 [8,37], MoS2 [38,39], lead zirconate titanate [40,41], ZnO [42] and their composites [43–45] have been used for electronic skins owing to their good piezoelectricity. Among them, ZnO exhibits a high piezoelectric constant $d_{33}$ along [0001] direction [30]. As a good piezoelectric material and a direct-bandgap semiconductor, ZnO is a popular material in the fabrication of sensitive devices and transistors [46]. ZnO nanostructures showed outstanding flexibility and could bear a strain as high as 5–7% without any obvious plastic deformation [47,48]. The flexibility, biosafety, easy process, and unique piezotronic effect make ZnO a good candidate for electronic skin applications [26].

ZnO nanostructures can be achieved through a hydrothermal synthesis method [49], vapor-phase synthesis [50] and solid-vapor growth process [51]. Hydrothermal growth combined with photolithography technology allowed the fabrication of patterns of vertically aligned ZnO nanowire arrays [4]. Many strategies have been developed to improve the properties of ZnO nanomaterials, such as doping [52–54] and composite structures [55,56]. Owing to their excellent property and simple synthesis processes, ZnO nanomaterials have been widely used in developing electronic skins [4,24,57–59].

3.2. Piezoelectric polymers

Poly(vinylidene fluoride) (PVDF) and poly(vinylidene fluoride-trifluoroethylene) (P(VDF-TrFE)) [60,61] are the most studied piezoelectric polymers and have great potential for electronic skins owing to their structural flexibility, biocompatibility, chemical stability, and piezoelectricity [62,63]. Four different phases, α, β, γ and δ phases, exist in PVDF, in which the β phase exhibits strong piezoelectricity and α phase is non-piezoelectric [64]. The α phase can be easily obtained through solution casting/solvent evaporation, and can be transformed into β phase through drawing or conventional stretching [64–66].

Electrospinning technology can be applied to produce β-phase or mixed-phase PVDF 1D nanostructures. The polymorphism and morphology can be controlled by voltage, solvent, electrospinning temperature, flow rate, and other process parameters [67]. For example, high pressure, solvent evaporation rate, high stretching ratio of the chain, and high rotation speed during the electrospinning process contributed to the production of β-phase PVDF [67–69]. The electrospinning combined with poling process enabled the synthesis of β-phase dominant PVDF nanowires with uniform polarization [71]. A fast-rotating collector was used to produce flexible and large area films that consisted of aligned P(VDF-TrFE) nanofibers for pressure/force sensors [61]. A rotating collector was used to produce flexible and large area films that consisted of aligned P(VDF-TrFE) nanofibers for pressure/force sensors [61]. The P(VDF-TrFE) textile with strong piezoelectric response and large contact area was used to detect a pressure as small as 0.1 Pa. Electrospinning was also used to fabricate PVDF composites like PVDF/BaTiO3 nanocomposite fibers [71]. Notably, the electrospray PVDF fibers/wires exhibited stronger piezoelectricity compared to PVDF films, making it suitable for the application of highly sensitive electronic skins [71,72].

3.3. Natural piezoelectric materials

Piezoelectricity has been found in both nature materials extracted from animal body and artificially synthesized counterparts [73–78]. Piezoelectricity was recently found in fish gelatin that was utilized to fabricate electronic skins to monitor human health [74]. Large-scale fish gelatin nanofibers have been achieved using electrospinning technology and successfully used for the fabrication of a self-powered contact interface between metal and n-type semiconductor (a) The increase of Schottky barrier height due to the depletion of major carriers by the negative polarization generated by the stretched piezoelectric material. (b) The decrease of Schottky barrier height by the increase of major carriers due to the positive polarization generated by the compressed piezoelectric material. Reprinted with permission from [20] © 2016 Macmillan Publishers Limited. All rights reserved.)
electronic skin for health care monitoring [74]. In this work, fish gelatin from Sigma-Aldrich was used to make gelatin solution, and electrospun fibers showed a piezoelectric coefficient ($d_{33}$) of ~ 20 pm/V. The fish gelatin nanofibers were used to fabricate into a piezoelectric strain sensor for an electronic skin that enabled the non-invasive detection of the blood pressure, muscle movements and epidermis deformation in real-time [74]. Alternatively, biowaste fish skin (FSK) was also achieved from *Catla catla* fish for the sensor fabrication [75]. The fish skin was washed, descaled, demineralized, and dissolved in EDTA (Merck, India). The demineralized FSK (thickness ~250 ± 30 µm) was further used to make a biopiezoelectric sensor that detected human physiological signals like wrist bending, swallowing motions, radial artery and carotid artery pulses.

3.4. Substrate and electrode materials

Flexibility and stretchability are important for electronic skin devices [59,79]. Polydimethylsiloxane (PDMS), polyethylene terephthalate (PET) and Kapton films have been broadly studied, and among them PDMS exhibits particularly good stretchability. Au is often used as an electrode material owing to its excellent conductivity and good mechanical property. A Au film was reported to survive a maximum strain of 32% after 101 cycles [80] and maintained a good conductivity after 250,000 cycles with a strain of 20% [70]. Reduced graphene oxide and carbon nanotubes have been used as electrodes or active materials in flexible sensors [81]. To improve the flexibility and stretchability of the device, several strategies have been developed, including the decrease of the thickness of substrates, net-shaped structural design, 3D architectures via compressive buckling, and so on [79].

3.5. Active sensing materials

Active materials can be fabricated on sensor substrates through hydrothermal growth or spin-coating methods. For example, ZnO nanowires/polystyrene nanofibers (PSNFs) hybrids were achieved through hydrothermal growth with ZnO seeds on flexible PSNFs [82]. The hybrid structure was used to fabricate a durable sensor that survived a strain as high as ~ 50%. Multifunction of a device can be achieved through integrating active materials with different properties.

For example, a sensor using PVDF and ZnO nanorod composite films as active materials detected pressure and temperature simultaneously [81]. A NiO@SiO2/PVDF nanocomposite film-based sensor realized energy harvesting and sensing of human body [83]. A multifunctional sensor was reported by He et al [59]. They used piezoelectric PVDF as binder materials to anchor various ZnO tetrapod fabrics to form a uniform network. The ZnO/PVDF hybrid material allowed tactile perception, atmosphere detection and self-clean function.

4. Different sensors for electronic skins

4.1. Piezotronic sensors

Since the demonstration of the piezoelectric field effect transistor based on ZnO nanowires in 2006 [25], the piezotronic sensors have attracted increasing attentions in recent years. The piezotronic sensor is based on a material with both piezoelectric and semiconducting properties, and its high sensitivity benefits from the dramatic change of current transport caused by the strain-induced piezoelectric potential [24,84,85]. Liu et al [86] reported a hybrid transistor in which the piezoelectric potential in a ZnO fine wire served as the gate voltage and the underneath single-walled carbon nanotubes provided a carrier transport channel, leading to the formation of electrical-power-free gate transistor. When a strain of 0.05% was applied, the drain-source current increased in the range of 10−40% (Fig. 2a). 3D large-scale ZnO nanowire arrays were fabricated to create piezotronic transistors [87]. The transistor arrays enabled tactile sensors with a taxel area density as high as 8464 cm$^{-2}$. The tactile sensor provided pressure distribution on a mapped geometrical pattern (Fig. 2b). Coplanar-gate graphene transistors and piezoelectric P(VDF-TrFE) nanogenerators were used to form an active matrix strain sensor [88]. The coupled structure of P (VDF-TrFE) as active materials and graphene as gate electrodes enabled the improvement of gate coupling performance and minimized leakage currents (Fig. 2c). The strain sensor detected a strain as low as 0.008%. Hand movement sensation was monitored by the sensor, suggesting the promising application of piezopotential-powered strain sensors in electronic skins.
4.2. Piezoelectric sensors

Piezoelectric ceramics and piezoelectric polymers have been widely used in conventional piezoelectric sensors. Piezoelectric sensors have been successfully demonstrated to detect dynamic stimuli [89–92], and piezoelectric material-based flexible electronic skins have been developed to detect wrist stretching, muscle movement, touch actions and other movements [40,72,93–95]. For example, PVDF and T-ZnO nanocomposites fabric was used to fabricate sensors to detect human elbow movements [59]. As shown in Fig. 3a, positive-charges and negative-charges were generated as a result of the bending and release motions respectively, and the elbow movement was thus detected from the output of the sensor. Wrist stretching and cheek movements, eyes blinking sensing, and breathing were measured through a fluorocarbon piezoelectret pressure sensor [96]. The measurements of wrist movements and facial muscle contraction are shown in Fig. 3b and c. Both of the wrist and facial muscle movements resulted in the change of the current of the sensor.

4.3. Multifunctional sensors

Earlier electronic skins were often used to detect one type stimulation only. Material development and technological advances resulted in multifunctional sensors that could perform different measurements simultaneously. The detection of both static stimulus and dynamic stimulus is crucial for human skin, and pressure sensors have been developed to detect these stimuli [97]. An electronic skin based on interlocked and hierarchical ZnO nanowire arrays was reported to detect static and dynamic pressure simultaneously [4]. The sensors showed a pressure sensitivity as high as $-6.8 \text{kPa}^{-1}$, and enabled the detection of a static pressure down to 0.6 Pa. The sensor could also detect the pressure varying at a frequency ranging from 0.5 to 3.6 Hz. The sensing of a pressure at a high frequency up to 250 Hz was demonstrated (Fig. 4a,b). A slow- and fast- adapting mechanoreceptor sensor was reported to detect various signals [98]. The sensor was composed of a PVDF active piezoelectric film, an aluminum foil/conductive carbon (AB) electrode, a polyaniline (PANI) electrolyte, and a porous polycarbonate track etched membrane (MB) (Fig. 4c). When a pressure was applied to the sensor, the PVDF piezoelectric film generated polarization charges on its surface and produced fast electric signals to measure rapid stimulation to the device. Strain-induced piezoelectric charges produced a large voltage across the Au/PVDF and PANI interface and promoted the movement of ions through the membrane. The slow adapting signal induced by the PANI and MB ion channel was used to measure the slow stimulation to the device. The electronic skin perceived vital signals such as heart beat and ballistocardiogram and other stimuli signals such as surface roughness, textures and slipping movement. The distance and direction of the pressure were monitored by a pressure and sliding sensing electronic skin [99]. The device had a fingerprint shape and was powered by a porous supercapacitor. It monitored sliding direction and speed with a triboelectric generator and various pressures with a hybrid porous microstructure sensor (Fig. 4d,e) [99]. The hybrid sensor demonstrated the abilities of detecting the pressure and the sliding movements without external power.

4.4. Sensor arrays for electronic skins

Multiple sensors with well-designed patterns are suitable for electronic skin systems. The pattern of sensors on a flexible substrate can be achieved with the photolithography [58,100–102] or molding process [4,103]. Metal electrodes can be deposited on substrates by electron beam evaporation [101], atomic layer deposition, and magnetron sputtering [94]. Photolithography technology allows the fabrication of sensors with sophisticated patterns for desired functions. A multistage sensation matrix based on piezoelectric nanogenerators was fabricated by Zhang et al [104]. The fabrication process is shown in Fig. 5a. Firstly, graphene was patterned on Cu foil with photolithography and reactive ion etching technologies, and then the graphene pattern was transferred onto a PDMS thin film as electrodes. Au electrode wirings were deposited to the ends of the graphene pattern. (PVDF-TrFE) was coated on the substrate serving as active materials. Finally, four PDMS thin films with a similar graphene pattern were laminated onto the bottom PDMS substrate to form strain sensor arrays (Fig. 5b). This sensor matrix allowed complex and multiple sensation of the strain and contact area. Interlocked and hierarchical ZnO nanoarrays allowed to grow on PDMS patterning substrates directly by molding (Fig. 5c) [4]. The molds were obtained through photolithography and a dry etching process. The ZnO array-based sensors enabled the static sensation and dynamic sensation.
5. Conclusion and outlook

The ability of our skin to sense the stimuli from the surrounding environment is essential for our daily life. The realization of an electronic skin to measure the external stimulus can find important applications in robotics, intelligent and artificial devices, and biomedical applications. The piezoelectric and piezotronic electronic skin materials can not only serve as the sensing material, but they can also harvest energy from the environment to form self-powered devices. The piezoelectric potential produced by piezoelectricity plays an important role in modifying output signals of sensors. Therefore, the investigation of piezoelectric nanogenerators and piezotronics provides a new approach for the development of electronic skins. Piezoelectric devices have shown very high sensitivity due to the new sensing mechanics, and the fast response can also benefit from the intrinsic piezoelectric property of materials.

Developing sensors with high sensitivity, multifunctionality, low-to-zero power consumption, and low cost is challenging in the development of the next generation electronic skin. The sensitivity of current piezotronic devices can be improved with the improvement of the conductivity and piezoelectric properties. Nanomaterials and micro/nanomanufacturing technologies enable people to design and fabricate electronic skins with high resolution and multifunctionality. The fabrication technology like electronic printing may hold hope to lower the cost and realize massive production of large area electronic skins. Further in-depth investigation of the working mechanism of
piezoelectric nanogenerators and piezotronics may facilitate the fabrication of electronic skins that even exceed human skins. Sensors with high spatial resolution, ultrasensitivity, fast responding speed, low-power consumption or self-power capability, and excellent durability are of research interests in coming years.

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Competing financial interests

The authors declare no competing financial interests.

References


Fig. 5. Multistage sensation matrix (a) Fabrication progress of piezoelectric nanogenerator-based sensors. (b) Schematic illustration of the multistage sensor arrays. Inset shows the enlarged sensing pixel. Reprinted with permission from [104] (© 2017, American Chemical Society) (c) Fabrication of metal-coated ZnO NWs on PDMS micropillars for pressure-sensitive electronic skins. Reprinted with permission from [4] (©2015 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim).

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