Flexible conductive polymer composites for smart wearable strain sensors

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Abstract

Wearable strain sensors based on flexible conductive polymer composites (FCPCs) have attracted great attention due to their applications in the fields of human–machine interaction, disease diagnostics, human motion detection, and soft robotic skin. In recent decades, FCPC-based strain sensors with high stretchability and sensitivity, short response time, and excellent stability have been developed, which are expected to be more versatile and intelligent. Smart strain sensors are required to provide wearable comfort, such as breathability, self-cooling ability, and so forth. To adapt to the harsh environment, wearable strain sensors should also be highly adaptive to protect the skin and the sensor itself. In addition, portable power supply system, multisite sensing capability, and multifunctionality are crucial for the next generation of FCPC-based strain sensor.

KEYWORDS

electrically conductive properties, flexible conductive polymer composites, multifunction, wearable strain sensor

Flexible conductive polymer composites (FCPCs) that can be stretched, bent, or twisted discretionally possess huge potential applications in the fields of tactile sensing, healthcare, human–machine interaction, and soft robotics.\textsuperscript{1} In 1977, the preparation of polyacetylene with excellent electrical properties, as reported by Hideki Shirakawa et al., opened the prelude to the exploration of conductive polymers.\textsuperscript{2} Subsequently, researchers have synthesized polythiophene, polypyrrole, polyaniline, and other inherently conductive polymers (ICPs). Nevertheless, ICPs show relatively poor flexibility and processability, restricting their prospects in the field of flexible electronics. Generally, FCPCs are achieved through combining flexible polymers with conductive fillers. The conductive network of FCPCs is designed and fabricated through melt blending, solution dispersion, and surface decoration (surface spraying, printing, etc.). Ecoflex, polydimethylsiloxane, hydrogels, thermoplastic polyurethane, etc., are frequently used as polymer matrix due to their excellent stretchability and processability. On the basis of different conductive mechanism and physical properties, conductive fillers for preparing FCPCs include ICPs (polyacetylene, polythiophene, polypyrrole, and polyaniline), metal fillers (metal particles and wires).

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carbonaceous fillers (carbon black, carbon nanotubes [CNTs], graphene, carbon fiber, etc.), and metallic oxide. As the conductive fillers affect the molecular chain structure of the flexible polymer very weakly, FCPCs can always acquire excellent electrical properties without sacrificing the intrinsic properties of polymer matrices. Moreover, the electromechanical performances of the FCPCs can be tuned by altering the polymer matrix, conductive filler, and the processing method to satisfy various requirements in practical applications.

FCPC-based sensors, converting the external stimulators (organic gas, temperature field, stress field, magnetic field, etc.) into electrical signals, have attracted wide attention of researchers owing to simple preparation, low production cost, and excellent mechanical performances and sensing capabilities. FCPCs cause deformation under external forces and also cause position change of conductive fillers in conductive networks, showing the sensing performance. FCPC-based strain sensors always possess high stretchability and acceptable biocompatibility, which can be safely attached to the surface of human skin as high-performance wearable strain sensors. In recent years, researchers have developed wearable strain sensors by exploring various conductive fillers and polymer matrices, distribution state, and conductive network structures. Universally, the performance of strain sensors is emphasized in superior sensitivity, high stretchability, fast response time, excellent stability as well as good durability. The response mechanism of FCPC-based strain sensors is mainly related to the resistance change caused by the destruction and reconstruction of the conductive networks toward strain (stress) stimulation based on the tunneling effect. In the past decade, researchers have achieved great accomplishments in high-performance FCPC strain sensors. For example, Lu et al. designed an FCPC based on CNTs and a polymer fiber, which has an ultralow detection limit (0.01% strain) owing to the design of double-leveled helical gaps and the CNTs with a high aspect ratio (Figure 1A). To adapt to the movement of large strain range, Shuai et al. fabricated highly stretchable conductive hydrogels (900% strain) for human movement monitoring, as shown in Figure 1B. Cao et al. used a network of multihydrogen bonds and nanoco nductive networks to achieve FCPC-based strain sensors with high sensitivity and excellent stability that can recognize facial expressions and vocal cord vibrations (Figure 1C). By perfecting the structure of polymers and conductive fillers, researchers have developed wearable strain sensors that are highly sensitive, stretchable, and extremely stable to monitor human movements.

Wearable and flexible strain sensors with large workable range and high sensitivity are desired to detect both subtle motions as well as large movements. Porous structure, crack structure, and segregated structure of FCPCs are widely concerned due to their high sensitivity. Although cracks as defects should be avoided in conventional materials, the sensitivity of strain sensors based on cracks is greatly improved. When the strain sensors are stretched, the porous structures and cracks expand with the increase of strain. Compared with strain sensors without cracks and pores, the number of conductive paths in sensors with cracks and porous structures decreases more rapidly, resulting in high sensitivity. For instance, Wang et al. fabricated crack-based wearable strain sensors for both subtle and large strain detection of human motions, which could detect up to 100% strain as well as a high gauge factor (GF) of 87.41. When the sensor is stretched, as shown in Figure 2A, the conductive fillers are damaged under minute strain due to the difference in elastic modulus between the conductive fillers and flexible polymer, resulting in a large number of broken conductive paths.
of tiny cracks and sensitive response to strain. With the increase of strain in a reasonable range, cracks propagation occurs regularly, which improves the stability and stretchability of the strain sensor. Inspired by the scorpion, Han et al.\(^8\) developed a high-performance wearable strain sensor with bioinspired crack arrays, achieving a high GF of 5888.89 (Figure 2B). The cracks prepared by the template transfer method have high stability, which can effectively avoid new cracks and physical damage. In general, the introduction of the crack structure greatly improves the sensitivity and stability of FCPC-based wearable strain sensors.

In summary, by tuning the structures of flexible substrates and conductive nanofillers, as well as constructing various sensitive conductive networks, scientists have built FCPC-based wearable strain sensors with high sensitivity, wide strain range, fast response time, and excellent long-term stability. However, the development of wearable comfort, environmental resistance, and portability of strain sensors remains important challenges, which limits their commercial application. Smart strain sensors with self-adaptive and multifunctional capabilities have attracted many researchers. Recently, scientists have paid extensive attention to endow these wearable electronics with additional features to address the necessary requirements of smart wearable strain sensors. Although many FCPCs are biocompatible, the FCPC-based strain sensors should be breathable to prevent bacteria growth. As shown in Figure 3A, Li et al.\(^9\) fabricated an FCPC with high elasticity and air permeability by electrospinning. To further improve the wearable comfort of FCPCs, Hu et al.\(^10\) fabricated polyurethane fibers with a porous structure. Due to the multiscale disordered porous structure, the fabric possesses self-cooling functions (Figure 3B). When the authors decorated graphene on the surface of the fibers, the resulted FCPC could not only sense deformation, but it was also capable of providing heat to the human body at low voltage, showing potential applications of smart strain sensors in human thermal management.

Wearable strain sensors attached on the human skin are vulnerable to physical and chemical attacks from the external environment such as sweat, oil, water, beverages, and tears, as well as strict washing cycle and mechanical wear. A smart wearable sensor system should have high performance, environmental stability, and mechanical stability under severe wear or washing conditions. Zhang et al.\(^11\) produced a self-protective super hydrophobic FCPC (Figure 3C), which can capture deformation normally even after being washed many times. Wearable strain sensors based on FCPCs with self-protective capability can effectively lower production and maintenance costs, demonstrating attractive applications in healthcare and man–machine exchange. With the rapid development of various electronics, information technology, and smart devices, serious electromagnetic radiation pollutions do great harm to human body and high-precision electronic instruments. In addition, with the development of space technology, astronauts may be exposed to harmful radiation in space. In general, metal layers are employed to cover the surface of the human

FIGURE 2 Crack-based wearable strain sensors. (A, B) An FCPC-based strain sensor with crack structure.\(^7,8\) Reproduced from Refs. [7,8] with permission from The Royal Society of Chemistry.
body and equipment to block electromagnetic radiation. However, metal materials increase the burden of the astronauts and restrict joint movement. To address the issues, Pu et al.\textsuperscript{12} designed the FCPC with high electromagnetic shield property and good sensitive responsibility toward pressure (Figure 3D), which can sense touch and protect humans from electromagnetic radiation, simultaneously. These FCPC-based smart strain sensors with self-protection and human-protection ability have attracted a lot of attention from researchers.

In addition, electric power supply is essential for smart wearable electronics. Traditional wearable electronics require extra batteries and power source to supply power, which greatly limits their portability and flexibility. To meet the portable and stable energy supply of wearable devices, a wearable strain sensor with energy harvesting is very attractive and necessary. Flexible energy storage devices, such as flexible lithium-ion batteries, lithium–sulfur batteries, supercapacitors, also play important roles in wearable electronics.\textsuperscript{15−17} However, the portability of energy supply devices based on FCPCs is developing rapidly. Pu et al.\textsuperscript{18} prepared a stretchable triboelectric nanogenerator that can convert mechanical energy into electrical energy by triboelectrification and electrostatic equilibrium, which has been proved to exhibit excellent performance in flexible power supply devices. Inspired by the triboelectric nanogenerator, Zhou et al.\textsuperscript{13} designed a self-powered wearable electronic device based on conductive polymer composite fibrous mats (Figure 3E) that can be used for harvesting energy and sensing pressure, proposing a new idea for energy supply advice of microelectronic equipment.

Nowadays, researchers have also endowed the FCPC-based smart strain sensors with many new features, greatly expanding the application ranges of the wearable strain sensors. Moreover, the movement of the human body is diverse and complex; the wearable sensors that can only collect a single point or several points toward the information have not been sufficient for the analysis for complex motion sensing. With the development of human–machine interaction and intelligent robots, the smart strain sensor that can sense the motion trajectory of pressure and the shape of pressure acting on the sensor is eagerly sought. Hua et al.\textsuperscript{14} presented a skin-like, flexible, conformable matrix network as a motion-sensing wearable sensor (Figure 3F), which realizes synchronous multipoint sensing and large area preparation. More impressively, the FCPC-based wearable sensors can also sense external temperature, magnetic field, relative humidity, proximity, pressure, and ultraviolet light stimuli simultaneously, which could potentially be used in prosthetics and disease care field. Finally, smart wearable strain sensors based on FCPCs are expected not only to possess high sensitivity, high stretchability, and excellent physical and chemical stability, but also to possess skin breathability, self-protection ability,
skin biocompatibility, and temperature management ability, besides being self-powered and conformable, which is crucial for the applications in motion monitoring, intelligent robots, and the Internet of things.

ACKNOWLEDGMENTS
This work was supported by the National Natural Science Foundation of China (51773183, U1604253, and U1804133), the Henan Province University Innovation Talents Support Program (20HASTIT001), and the Innovation Team of Colleges and Universities in Henan Province (20IRTSTHN002).

CONFLICT OF INTEREST
The authors declare no conflict of interest.

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How to cite this article: Zhou K, Dai K, Liu C, Shen C. Flexible Conductive Polymer Composites for Smart Wearable Strain Sensors. *SmartMat*. 2020;1:e1010. https://doi.org/10.1002/smm2.1010