Application of nanomaterials in flexible sensors

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Abstract. Flexible electronic sensors have widespread applications in both traditional and emerging fields, particularly for human-computer interaction (electronic skins, wearable electronic devices) and physical and environmental monitoring for people. Flexible electronic sensors can be bent and folded readily without interfering with their detecting performance. However, researchers still face many difficulties. For instance, traditional flexible materials (such as organic materials) are less sensitive to external signals, and the production progress of flexible sensors is complicated. This review recapitulates applications of nanomaterials in flexible electronic sensors. Firstly, the working principles and applications of three common types of flexible electronic sensors, the piezoresistive sensor, the capacitive sensor, and the piezoelectric sensor, are introduced. Then, the paper summarizes methods for improving sensors' performance in health monitoring, disease diagnosis and biological detection by application of different nanomaterials to flexible substrates. Finally, the future development of flexible nanomaterial sensors prospects. It is found that nanocomposites of metal nanomaterials, carbon nanomaterials and other polymers with unique tuned photoelectrical properties show enhanced performance as flexible sensors and further research is needed to improve the material-substrate integration to promote the large-scale application as wearable sensors.

Keywords: flexible electronic sensors, nanomaterials, conductive composites, wearable electronic devices.

1. Introduction

In recent years, with the advent of the third-generation Internet era, scientists' demand for new sensors has become increasingly urgent. Flexible electronic sensors gained much attention recently because of their outstanding performance, such as high tensile properties, low modulus and excellent bio-compatibility. Flexible sensors can be bent and folded according to different application environments and other deformations that are difficult to achieve with traditional sensors and have shown good development potential in electronic skin, aerospace, environmental monitoring, and wearable devices (Figure 1) [1]. At the same time, with the development of flexible materials and nanomaterials and preparation processes, flexible sensors have greater development prospects in various fields. In the application of flexible medical equipment, the monitoring of pulse and other micro signals can be realized; Motion monitoring can be realized in applications in the field of wearable devices; In applications in soft robotics, robots can be given the perception of temperature and pressure.

Global shipments of non-degradable displays increased to more than 700 million in 2020, with a market share of 64% [1]. Smartwatches, bendable phones, and giant curved wall displays of flexible materials are changing human lives. According to the statistics, there are up to 3710 research branches in the field of flexible sensors in 2019 [1], which indicates that the research related to flexible sensors is a hot topic nowadays and in the future. It is foreseeable that people will make flexible sensors with more functions and application scenarios, and everyone will benefit from the convenience they bring.

Flexible sensors made of carbon nanomaterials can be used for temperature monitoring, for example, as wearable electronic devices that can monitor body temperature in real time to ensure the health of humans and animals [2]. In addition, the high surface area ratio of diamagnetic nanomaterials makes them highly utilizable, while their bendable nature makes them less susceptible to damage. Currently, nanomaterial-based flexible sensors are mainly used in human medical and health, biomonitoring and environmental monitoring [1]. In particular, flexible sensors made of metal oxide nanomaterials are relatively inexpensive to manufacture and are currently used in fields such as gas leak alarms [3].

Compared with traditional silicon-based materials, flexible materials have advantages such as flexibility. However, their disadvantage is poor conductivity, which can be solved by doped carbon nanomaterials and metal nanomaterials, which can greatly improve the conductivity and sensitivity of flexible, stretchable strain sensors while ensuring good flexibility. Due to their stretchable and elastic characteristics, flexible nanomaterials can capture high-quality mechanical information on curved surfaces and convert them into electrical signals to be widely used in various fields [4]. This paper first introduces common flexible nanomaterials and electronic sensors, then focuses on the advantages and disadvantages of flexible nanomaterials to construct sensors, proposes improvement measures, and finally looks forward to their future development.

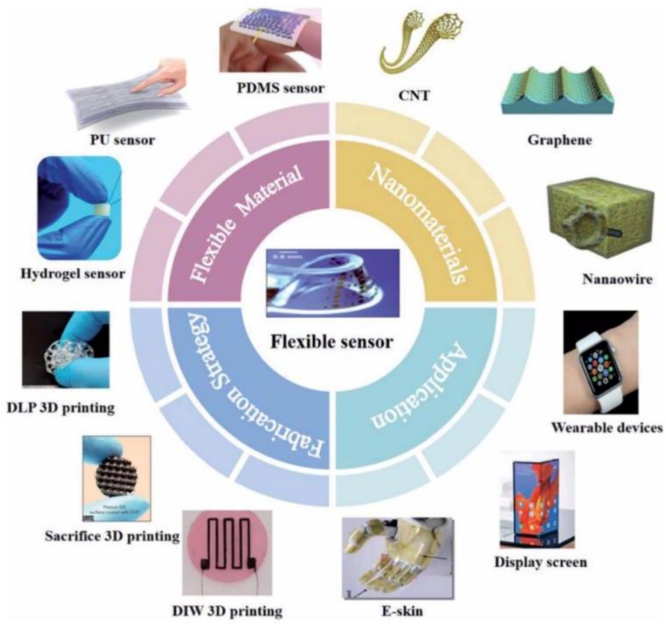

Figure 1. Applications of flexible sensors [1].

2. Sensor Fundamentals

The rapid development of the industry and industrial manufacturing automation brings opportunities and challenges in sensor development. At the same time, sensing technology in scientific research, agricultural production and industrial inspection are becoming more and more prominent. To meet the sensing needs of different application conditions, various types of sensors have been created. Flexible sensors overcome the shortcomings of traditional sensors, such as fragile, poor flexibility, and poor ductility. Due to their unique flexibility characteristics, stretchability, stability, etc., they are widely used in human physiological motion detection, health monitoring, clinical diagnosis, flexible touch screen, flexible electronic skin, and even industrial robots and other aspects. Common flexible sensors are primarily categorized as piezoresistive, capacitive, piezoelectric, and triboelectric based on the sensing method. Meanwhile, the triboelectric effect has been commonly used to make friction nanogenerators in recent years.

2.1. *Piezoresistive Sensors*

Piezoresistive sensors consist of nanomaterials that undergo deformation and change their resistance in response to an electrical signal change. Figure 2 shows the basic working principle of piezoeresistive sensors. Common preparation methods are integrating ultra-thin, advanced and high-performance sensing components on soft substrates or doping them onto elastic substrates. Common flexible substrates include polydimethylsiloxane (PDMS) and silver nanowires (AgNWs). The main preparation methods are the mechanical exfoliation method and liquid-phase exfoliation. Due to the excellent characteristics of this sensor, it is commonly used in human health monitoring and engineering applications.

Chen, Baodeng fabricated MXene based piezoresistive sensor successfully applied to human health pulse monitoring [5]. By using functionalized self-assembly as well as hydrothermal synthesis techniques, Shuaichao Chen's team has created the first carbon nanotube (CNT) films doped with different PVA parts (CNT/PVA) and nanowires made of ZnO on zinc sheets [6]. It holds considerable promise for applications in structural health detecting as well as tracking static/dynamic tensions on concrete structures because to its exceptional sensitivity and broad frequency response characteristics. Ramesh Ghosh developed a piezoresistive sensor using Si NR with a high sensitivity of 0.49 MPa^{-1} by enclosing vertical Si NR arrays with a large aspect ratio between two slim Au substrates [7].

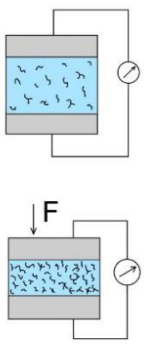

Figure 2. Piezoresistive conductionschematic diagram.

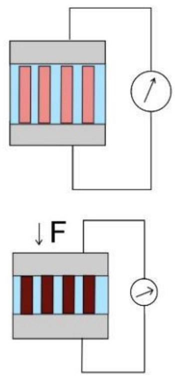

Figure 3. Piezoelectric sensors schematic diagram.

2.2. *Capacitive Sensors*

The capacitive flexible sensor is one of the most popular types of flexible sensors studied, which consists of upper and lower pole plates and a dielectric in between. It is caused by applying pressure to change the distance or relative contact area between electrodes or the change of dielectric permittivity, which causes the change of capacitance of the flexible sensor. These sensors have better temperature resistance than resistive sensors and sufficient frequency response. Different dielectric materials can control their sensitivity. The common ones are the ionic solution, SiO_2, air gap, polyimide and fabric [8]. In equation (1), C is capacity, ε is permittivity. The surface area is S, and the pole plate spacing is d. S and d are suspectable to changes in external pressure.

$$C = \frac{\varepsilon S}{d} \tag{1}$$

A extremely precise capacitive nanosensor for non-enzymatic measurement of glucose was invented by Tarun Kumar Dhiman's team. On indium tin oxide (ITO)-coated glass, capacitive assessments were carried out on copper oxide (PVA-CuO) films that were glued with polyvinyl alcohol using ARDUINO UNO [9].

Interfinger electrodes (IDEs) coated with a Nafion/Graphene Oxide layer were used to create Xiaoyu Li's capacitive humidity sensor. The sensor can translate changes in humidity concentration into variations in IDE capacitance. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) were used to study the morphology and nanostructure of the obtained Nafion/GOQD nanocomposites, confirming their effective fabrication [10].

2.3. *Piezoelectric Sensors*

The sensing mechanism of piezoelectric flexible pressure sensors is manifested by the internal polarization phenomenon caused by the deformation of the sensor when subjected to pressure, resulting in positive and negative charges on the sensor surface and the output of electrical signals (Figure 3). Piezoelectric flexible sensors generally have high sensitivity and fast response, do not require a power supply, and have high reliability. Piezoelectric sensors can detect sound vibrations or pulse beats and have great potential for wearable, flexible sensors such as electronic skin. Currently, piezoelectric flexible sensors are mainly prepared by dispersing piezoelectric materials in polymers to make flexible sensors with better mechanical flexibility, thus improving the performance of flexible sensors. Common materials by CNT and ceramic epoxy resin. Zhuo Wang's team used $BaTiO_3$ material to synthesize piezoelectric, piezoresistive and triboelectric principles to make a self-generating, highly sensitive nanosensor for detecting human motion, pressure and curvature [11].

2.4. *Sensors Based on Triboelectric Effect*

The triboelectric effect refers to the charge distribution and potential difference between two surfaces of different materials when they are in contact and moving relative to each other due to the charge transfer, recombination and polarization phenomena between the surfaces. Triboelectric nanosensors take advantage of this effect. When nanomaterials are subjected to changes in external parameters (pressure, deformation, etc.), they cause changes in the charge distribution and potential difference between the material surfaces, resulting in induced charge and voltage signals. The triboelectric effect is usually applied to build a nanogenerator that realizes a micropower supply. Triboelectric nanogenerators have a small size, lightweight and high energy density advantages and can be applied to micro-robots, wireless sensor networks, smart wearable devices and other fields. Dongyue Wang's team prepared an organ-like $Ti_3C_2T_x$ MXene/metal-organic framework-derived copper oxide (CuO) gas sensor powered by latex and PTFE-based triboelectric nanogenerator for the detection of ammonia (NH_3) at room temperature [12]. They have also developed a triboelectric nanogenerator based on polyvinyl alcohol/silver (PVA/Ag) nanofibers that can be used for human respiration, motion and harmful gas monitoring [13].

3. Flexible sensors in medical and health applications

3.1. *Self-healing flexible strain sensors*

Nanocomposites are used to create flexible electronic devices, one of which is self-healing and is easy to manufacture. With skin-like qualities like self-healing, stretchability, and sensing, flexible and wearable electronic devices offer a lot of potential for use in soft robotics, smart gadgets, and prosthetics. Different self-healing piezoresistive strain sensors have been created as a result of the combination of self-healing polymers with conductive elements, such as carbon nanotubes (CNTs), graphene, silver nanowires (AgNWs), gold nanoparticles (AuNPs), and liquid metals. Self-healing polymer nanocomposites with superior mechanical and electrical characteristics can be more effectively made possible by homogeneous dispersion of nanoparticles in a polymer matrix [14].

In wearable technology, strain sensors have a lot of potential, especially for this kind of skin that has smart skin characteristics like stretchability, robust mechanical strength, and high sensing sensitivity [14]. The researchers present a self-healing flexible strain sensor in this work for wearable technology that is flexible, resilient, and adaptive to detect human movements. It is made of an imine- and quadruple hydrogen-bonded dynamic cross-linked conductive nanocomposite. The nanocomposite has excellent self-healing properties and has a healing efficiency of up to 95% due to reversible interactions. Supramolecular interactions improve the interfacial compatibility between the nanofiller and the polymer network. Based on the piezoresistive effect, the strain sensor made of nanocomposite may be clearly shown to alter in resistance when subjected to various deformations such tension, bending, and twisting. With a measurement factor of 46, the sensor exhibits exceptional sensing sensitivity. The sensor exhibits tremendous promise in the development of intelligent wearables, healthcare monitoring, and human-machine interfaces due to its outstanding self-healing function, which can endure mechanical damage and restore the function of sensing human motion [14].

3.2. Physical applications of flexible sensors

By turning outside pressures into electrical impulses, flexible tactile sensors can detect stimuli. Real-time health monitoring and human motion detection are made possible by the examination of the electrical signal that is sent to a computer processing system. Piezo-resistive, capacitive, piezoelectric, and triboelectric tactile sensors are the four primary categories of tactile sensors, according to their operating mechanisms. Due to their lack of mechanical flexibility, conventional silicon-based touch sensors are frequently unsuitable for flexible electronics [15]. Polymer nanocomposites, on the other hand, are stretchy and flexible, making them good choices for flexible and wearable haptic sensors [15].

The resulting conductive polymer-based composites show promise as flexible haptic sensors by integrating conductive materials (nanometals, carbon nanomaterials, conductive polymers, etc. with a flexible polymer matrix, embedding them in the matrix or surface coating, or sandwiching them between thin films (Figure 4) [16]. Conjugated polymers (CPs), which exhibit great potential for flexible sensors and wearable gadgets due to their distinctive chemical structure and electronic properties that support their high electrical and mechanical conductivity, have been identified by researchers as among the promising polymers. Flexible sensors have been made possible because to polymers' remarkable flexibility. Due to their intrinsic delocalized -electrons, which can be regulated to vary from semi-conducting to metallic conducting, and their alternating single and double covalent bonds to conduct electrons, CPs in particular have exceptional electrical characteristics. Moreover, CPs are biocompatible and have good mechanical flexibility, making them great choices for sensors. In addition to these characteristics, they have increased stability, sensitivity, and detecting range, which increase their utility in pressure sensor applications [16].

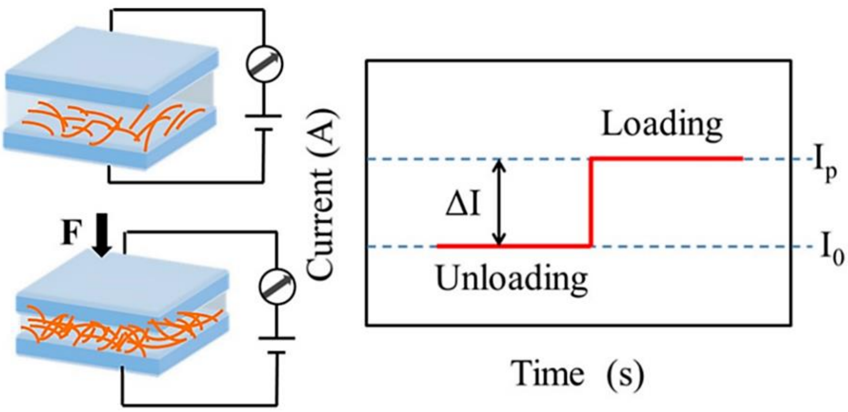

Figure 4. Operating principle of a piezoresistive pressure sensor [16].

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4. Application of flexible sensors in biological detection

Sunset yellow is a kind of food coloring. Appropriate use is conducive to the coloring of food and drugs, but excessive sunset yellow will harm human health. So the detection of sunset yellow is very important in production and life. In order to detect sunset yellow additive efficiently and sensitively, titanium carbide MXene-Gold nanocomposite (AuNPs@Ti_3C_2MXene) was prepared by in-situ reduction method, and the electrode was applied to sunset yellow electrochemical sensor with high sensitivity [17]. It was found that MXene has a unique accordion structure under optimal conditions (the square wave voltammetry peak current of the day setting yellow has a good linear relationship with its concentration in the range of 0.01 ~ 100 μmol/L), and this material has a good conductive synergism with gold nanoparticles. The electrochemical response of sunset yellow was significantly improved. As electrochemical detection is used in the experiment, the sensor has high detection speed and sensitivity. At the same time, because of the simple preparation method, the sensor has been successfully applied to the analysis of sunset yellow content in beverage samples, and the detection accuracy is high [17].

Ractopamine (RAC) is a synthetic accelerator used to increase lean meat content in livestock meat. It is often illegally added to animal feed to increase lean meat production. Excessive addition of RAC leads to long-term accumulation in meat, which causes great damage to human beings. In order to protect human health and accurately detect ractopamine, the specific interaction between streptavidin and biotin was used to amplify the color signal, and a magnetic separation competitive immune sensor based on a novel enzyme-linked gold nanocomposite probe (E-GNPs) was constructed [18]. After labeling RAC antibody, Horseradish peroxidase (HRP) was modified on the surface of gold nanoparticles by the electrostatic assembly method, and E-GNPs were obtained on the surface of the material. After signing a competitive reaction between magnetic beads coated with Ovalbumin (OVA) -RAC Hapten complex and the probe, quantitative analysis of RAC can be achieved through color reaction, that is, the color of the enzyme-catalyzed substrate changes linearly with the concentration of RAC. The content of RAC in the sample to be measured is indirectly reflected through the color reaction. Because each E-GNP can carry 11 HRP molecules, the immune sensor has high sensitivity. The sensor prepared in this study has excellent selectivity for RAC, not only the detection limit can be as low as 1.755pg/mL, but also the detection sensitivity is nearly 10 times higher than the traditional ELISA method. At present, it is considered that the sensor can be applied to the RAC detection of real meat samples of pigs, cows, sheep and so on, which provides a new idea for the rapid screening of RAC in the production and living animal food. This kind of sensor has high specificity and good sensitivity, and the equipment used is not expensive, so it has a great prospect for future research and development [18].

Diabetes greatly impacts human health, so efficient and rapid detection of glucose content in the body is conducive to early detection of the precursor of diabetes and timely treatment. In the experiment, a kind of CuCo-MOF bimetallic organic frame nanofiber material (CUCo-MOF) was synthesized by a one-step blending process under the condition of room temperature and water solvent [19]. Then the MOF material was calcined in the air at a high temperature. The product Cu (II) Co (II)@C was used to modify the glassy carbon electrode. The electrode can catalyze glucose directly in an alkaline solution to realize the ultra-sensitive detection of glucose without an enzyme sensor. Due to the uniform arrangement and inlaid CuO and CoO in the nanomaterials obtained by high-temperature calcination in the experiment, the agglomeration behavior of the catalyst can be prevented, and the catalytic specific surface area and the active catalytic site can be increased to a large extent, thus improving the stability of the material electrode. At the same time, due to the bimetallic structure of copper and cobalt in the carbon nanosheet, the two have a synergistic effect, so the enzyme-free glucose sensor has excellent conductivity, catalytic performance and catalytic performance and high sensitivity. Finally, the enzyme-free sensor for detecting glucose was successfully prepared in the experiment, and the sensor has similar effects to the current blood glucose detector on the market and is expected to be put into production in the future. However, due to the current electrochemical stability and the control of electrocatalytic performance is still a certain difficulty, this kind of sensor still needs more experiments to get research progress before it can be really used in people's production and life [19].

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Cadmium is one of the heaviest metal-polluted elements. Excessive intake of cadmium does great harm to the human body. And cadmium pollution is often found in water pollution. Rice is mostly grown and produced in water, so the detection of cadmium content is crucial. A nanoporous gold electrode (fGO/CS/IL/NPG/GCE) modified with functionalized GO/ chitosan/ionic liquid nanocomposites was prepared, and Cd^{2+} in rice was detected by anodic stripping voltammetry (ASV) [20]. The experiment found that the functionalized graphene had more active groups, and ionic liquid and chitosan dispersed the graphene, making the sensor achieve excellent conductivity and rapid detection effect. The lowest detection limit of the experiment was 100 μmol/L, and it was found that under the optimal detection conditions (5 μL of nano complex, enrichment potential -0.8V, enrichment time 100s, ABS buffer), the concentration range of 100 nmol/L ~ 10000 μmol/L, The dissolution peak current of Cd^{2+} has a good linear relationship with the concentration. It can be seen that this electrode has good repeatability and stability, which can be used for the preparation of cadmium sensors, and has good anti-interference and stability. At the same time, the detection speed is fast, so the result is more accurate [20].

5. Conclusion

Over the years, nanomaterials have gained more attention from researchers and scientists and have been widely applied to achieve high-performance flexible electronic sensors. In this review, cutting-edge research results on the application of nanomaterials to flexible sensors are presented. In particular, nanocomposites made from metal nanomaterials, carbon nanomaterials and other polymers greatly improve the performance of flexible sensors. Therefore, flexible sensors play a crucial role in medical treatment, health monitoring, food detection, etc. However, some key issues still need solving, for example, how to improve the integration of multiple functional devices, the resolution of different sensing signals, and how to establish a perfect intelligent sensor system. It is foreseeable that with the continuous progress of basic science and industrial technology, the use of nanomaterials will be more convenient in the future, and flexible sensors will better benefit human beings.

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