Advances in the Study of Three-Dimensional Nanomaterials in Flexible Piezoresistive Sensors (FPS)

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Abstract. Due to the exponential growth of flexible pressure sensors that are used in electronic skin, wearable electronics, artificial intelligence, and other related fields, it has become important to study and create high-performance pressure sensors with high sensitivity, a low detection threshold, and a wide range of sensing capabilities. Flexible piezoresistive sensors are notable in the realm of pressure sensors for their straightforward fabrication technique and exceptional ability to conform to various environmental conditions. Conversely, there has been a change in attention towards the enhanced performance of nanomaterials due to their surface phenomenon, quantum size influence, and other related factors. Three-dimensional nanoparticles are a viable option for conducting sensitive materials for flexible piezoresistive sensors because of their distinctive composite structure, which makes up for some flaws in single nanomaterials. This review summarizes three common types of 3D nanomaterial piezoresistive sensors (graphene-based, Menxe-based, PDMS-based), introduces the innovation and development of 3D nanomaterial material properties and micro-nano structures, sensor preparation process and sensor performance, and then introduces the application of 3D nano sensors in health monitoring and motion state detection, and finally looks forward to their future development direction.

Keywords: Micro-nano structure, composite material, flexible piezoresistive sensor.

1. Introduction

Sensor is a kind of electronic devices that can collect and transmit information, and its working principle is to convert the external stimuli received by sensitive materials into electrical, optical and other directly measurable signals, and reflect the size and distribution of external stimuli through these response signals. As human beings pay more and more attention to their own health, and the rapid development of artificial intelligence leads to human desire for humanoid robots, the standards for sensor performance are rising steadily. The research of sensors has gradually developed in the direction of wide detection range, the desired attributes are a heightened level of sensitivity, rapid response time, exceptional stability, and optimal mobility. The popularity of flexible piezoresistive sensors has increased due to their simple fabrication process, high sensitivity, fast response, and significant potential for application in emerging domains which include electronic skin, wearable electronic devices, personalized medicine, and detective robots [1]. Compared with macroscopic materials, nanomaterials exhibit peculiar properties in terms of force, electricity, magnetism and heat because of their surface effect, quantum size impact, and other effect. In the field of sensing, zero-dimensional nanomaterials benefit from the significant effects brought about by their ultra-small size, resulting in excellent sensing performance in pressure sensors [2]. The utilization of one-dimensional nanomaterials in the construction of pressure sensors is highly advantageous, primarily owing to their inherent prominent aspect ratio structure and exceptional mechanical and electrical characteristics [3]. Two-dimensional nanomaterials have high mechanical flexibility, large specific surface area, and can be chemically modified or doped with materials to construct sensing layers with layered structures. It has been widely used in piezoresistive sensors [4]. Three-dimensional nanomaterials refer to materials composed of two or more kinds of the above three types of nanomaterials, and three-dimensional nanomaterials not only retain the properties of each component, but also produce special three-dimensional structures because of the process of recombination. Because it inherits the inherent advantages of the original material while making up for the defects of a single material such as poor oxidation resistance, poor mechanical properties, and poor conductivity, and has a special three-dimensional micro-nano structure, thereby improving the performance of the sensor.

For example, graphene has excellent mechanical and electrical properties, but its interlayer contact resistance is poor and its own structure is prone to defects, resulting in affected conductivity. Silver nanowires also have excellent electrical conductivity and mechanical flexibility, but silver nanowires are easier to be oxidized, and after oxidation, piezoresistive sensors will have measurement errors or even failures. If rGO covers the surface of silver nanowires, on the one hand, isolates silver nanowires from air to avoid oxidation, and on the other hand, it makes up for the shortcomings of insufficient conductivity of rGO itself, thereby improving sensor durability [5].

2. Application of Three-Dimensional Materials on Flexible Piezoresistive Sensors

2.1. Graphene-Based Sensors

Graphene is regarded as contender for the most promising conductive sensor layer because to its many attributes, including great electrical and mechanical capabilities, flexibility, and excellent transportability [6].

A loofah sponge (LS) was used as the framework by Cao et al. [6] who then prepared rGO-CB@LS by soaking the sponge in a solution of rGO modified with carbon black nanoparticles, cutting it into small pieces, coating two parallel surfaces with conductive silver paste, and assembling the pieces into piezoresistive sensors with conductive copper strip serving as the electrode (Fig. 1). The loofah sponge gives the sensor a three-dimensional, highly ordered structure that frees it from dependence on organic substrates. Meanwhile, the unique characteristics of carbon black nanoparticles, such as their tiny size and high conductivity, allow them to function as an intermediary reagent between reduced graphene oxide (rGO) sheets. This interaction results in an improved conductivity and sensitivity of the sensor (Fig. 2 and Fig. 3). The sensor exhibits a sensitivity of 0.66kPa-1 within the pressure range of 0~500 Pa, and a sensitivity of 1.89kPa^{-1} within the pressure range of 500-2000 Pa. It also has outstanding stability (>5000 pressure cycles and >3600 bending cycles) and its response time is 0.42 seconds, while recovery time is 0.29 seconds.

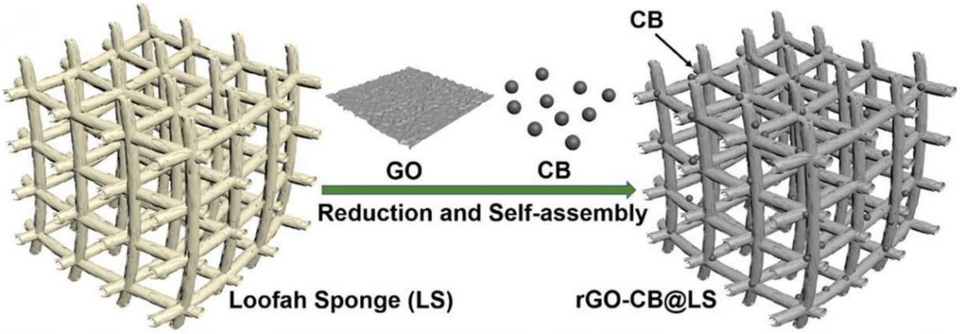

Figure 1. Schematic illustration of the production of rGO-CB@LS [6]

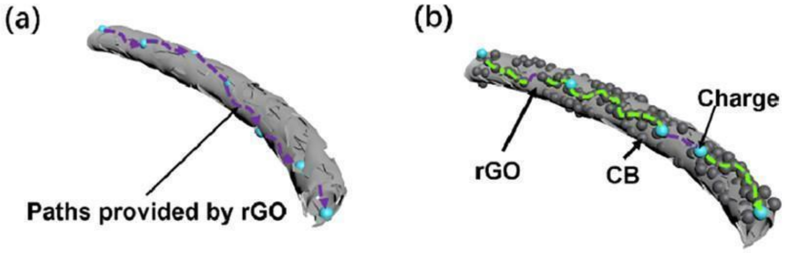

Figure 2. (a)A charge path provided by rGO on LS with no CB; (b)A charge path provided by CB on LS with the right amount of CB [6]

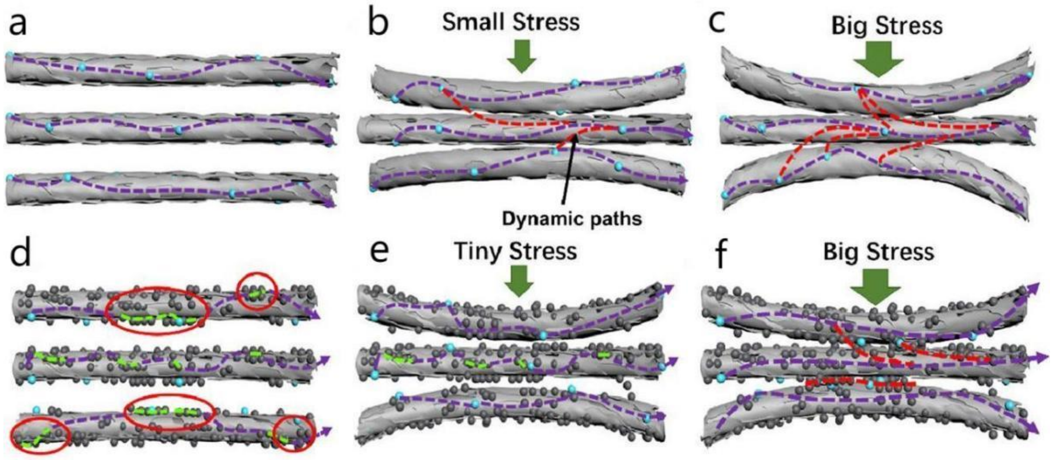

Figure 3. (a) (b) (c) Charge paths on LS with no CB in different stresses. (d) (e) (f) Charge paths on LS with the right amount of CB in different stresses [6]

By using the atmospheric pressure chemical vapor deposition (APCVD) method, Luo et al [7]. created a three-dimensional graphene network on nickel (Ni) foam. The number of graphene layers was maintained at 14 by manipulating the development time. Subsequently, PDMS was used to infiltrate the Ni foam covered with graphene (GNi foam). The final GP hollow structural film is created by immersing the GNi (GNiP) foam that has been penetrated by PDMS in hydrochloric acid after PDMS has been allowed to cure (Fig.4). With the help of this etching procedure, the GNi foam's pores may be entirely filled with PDMS, giving the material considerable mechanical strength. The pores of the foam are coated with polydimethylsiloxane (PDMS) on their upper surface, thereby maintaining an uneven surface topography. This deliberate modification is intended to facilitate rapid response times and enhance sensitivity of the foam. In a linear area of 60 kPa, the best-performing sensors sensor reaches 15.9 kPa^{-1} sensitivity. Additionally, with a measurement error of 6%, the GP sensor is still functional for various bending radii in the -25 to +25mm range (Fig.5 and Fig.6).

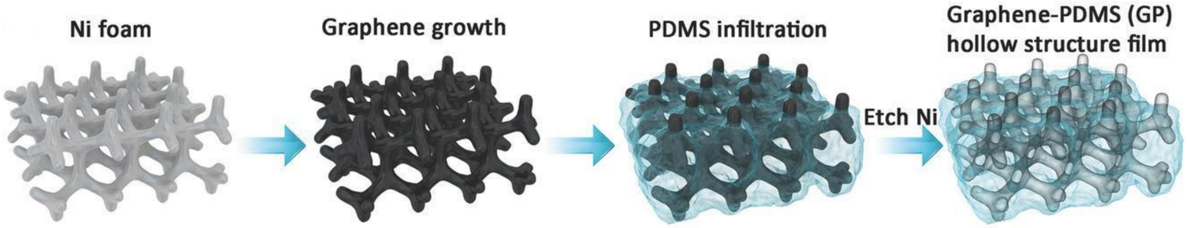

Figure 4. Schematic illustration of the production of GP hollow structure film [7]

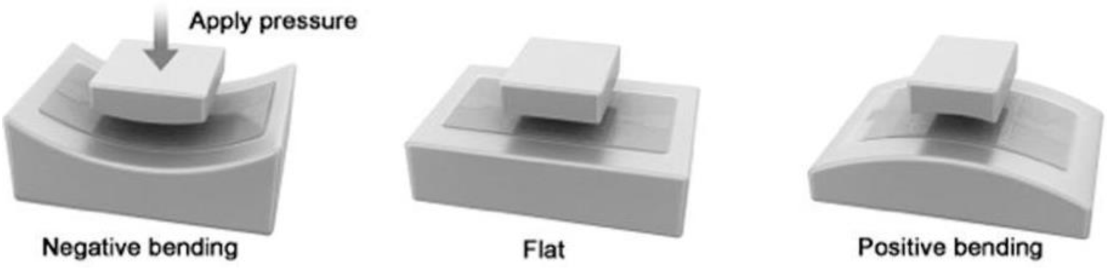

Figure 5. Three test situations for GP in bending tests [7]

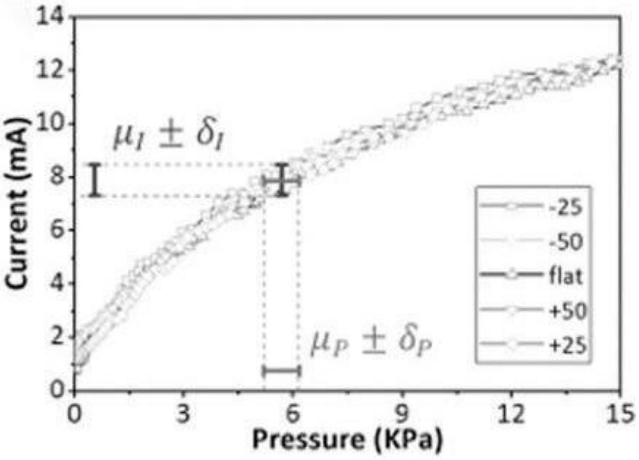

Figure 6. Pressure response curve of a GP sensor at different bending radii [7]

By using a PU foam block, Li et al. [8] are submerged in the created homogenous graphene oxide/aqueous solution before being put in a vacuum oven to dry. An immediate reduction process is then performed on the dried graphene oxide @PU foam. The achievement of switching behavior in ultrasensitive pressure sensor resistance variations was realized through the utilization of flexible composites consisting of polyurethane (PU) foam coated with graphene (Fig.7). The enhanced SPS sensor exhibits notable characteristics, including a high sensitivity of 0.67 kPa^{-1} within the pressure range of 1.5 kPa, rapid response and recovery times of 10 ms and 16 ms, correspondingly, exceptional stability demonstrated by a consistent response over 10000 compression cycles, and a facile material preparation process facilitated by the efficient transformation of the graphene network from an initially non-conductive condition to a conductive condition via electrically insulating porous layers.

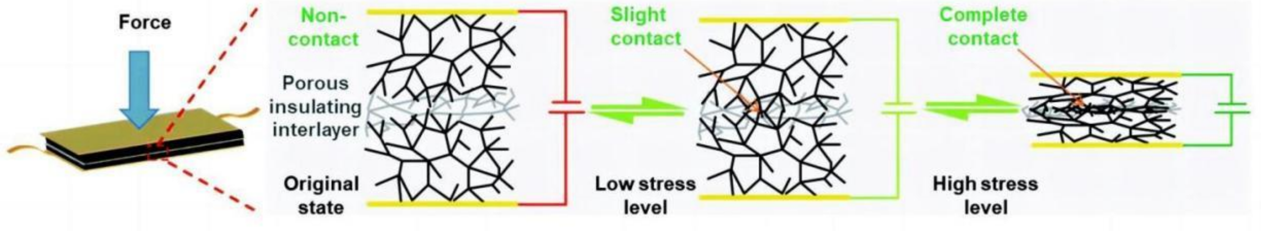

Figure 7. Principle of conductive path generation of SPS sensors [8]

2.2. Menxe-based sensors

MXene is a newly discovered 2D nanomaterial in which the A atomic layer in the $M_{n+1}AX_n$ phase commonly referred to as the MAX phase. In the MAX phase, M represents an early transition metal, such as Sc, Zr V, Ti and Nb; while A corresponds to main group elements III and IV; and X is C or N, n=1, 2, 3) is removed using a suitable etch agent to create a significantly separated multilayer MXene with a structure resembling graphene and the chemical formula is $M_{n+1}X_nT_x$ (M and X have the same meaning as above; The symbol "T" is used to denote the surface-located functional groups of MXene, which encompass chemical moieties such as hydroxyl, fluorine, and carbonyl.) [9]. The substantial possibility for MXene as an active layer for piezoresistive sensors has been proven, owing to its diversified chemistry, configurable surface terminations, improved metal conductivity, and advantageous surface hydrophilicity. [10].

Vacuum-assisted filtering was used by Fu et al. [11] to make a $Ti_3C_2T_x$@ZIF-67 film with interlayer delamination, which was then sandwiched between two Au/PET electrodes to create the sensor. ZIF-67 octahedral crystals with weak conductivity were placed between the highly conductive MXene nanosheets (Fig.8). To enhance the conductivity range of the conductive channel, augment the sensitivity and sensing range of the sensor, and establish a three-dimensional conductive network, the introduction of MOF crystals into the MXene layer is employed, therefore expanding the interlayer spacing of the MXene sheets. Each layer of MXene in the film is spaced too far apart when the sensor is not loaded for current to flow through the neighboring layers. The electrode deforms the film when the sensor is under stress, shortening the distance between each layer of MXene and creating a conductive route (Fig. 9). The sensor exhibits a broad pressure detection range spanning from 0.0035 to 100 kPa. It demonstrates a rapid response and recovery time of 15 ms each. Additionally, it possesses a sensitivity of 110.0 kPa^{-1} throughout the pressure range of 0.1 to 2 kPa.

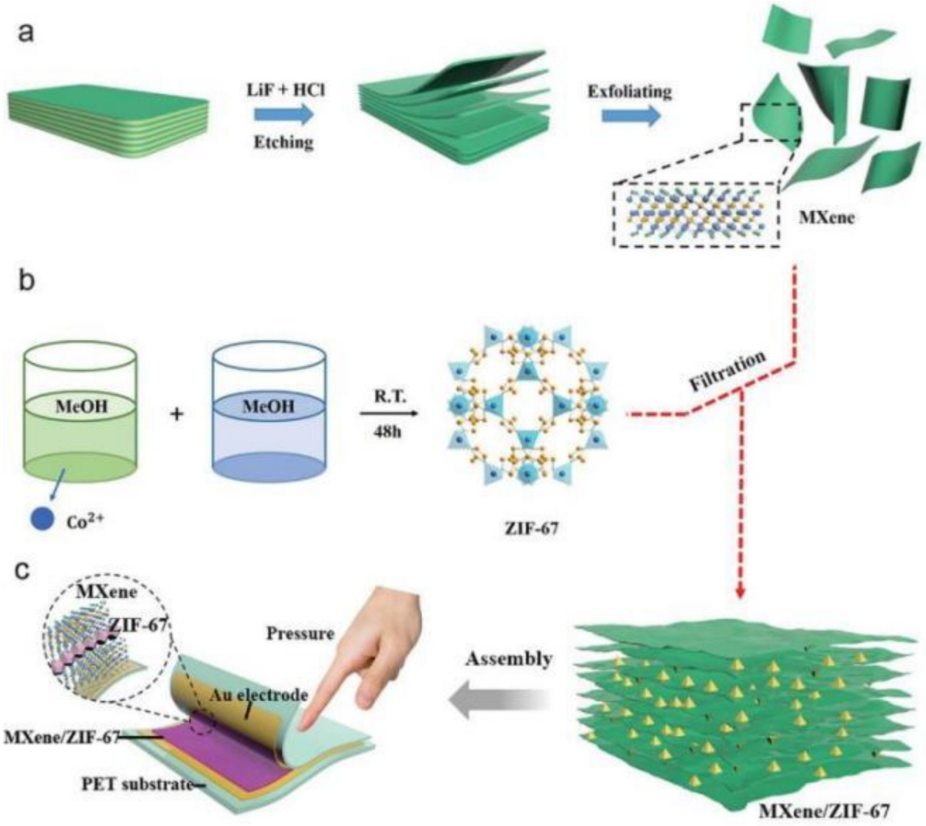

Figure 8. (a) Schematic illustration of the production of MXene; (b) Schematic illustration of the production of ZIF-47; (c) Schematic illustration of the production of MXene/ZIF-67 and the composition of the sensor [11]

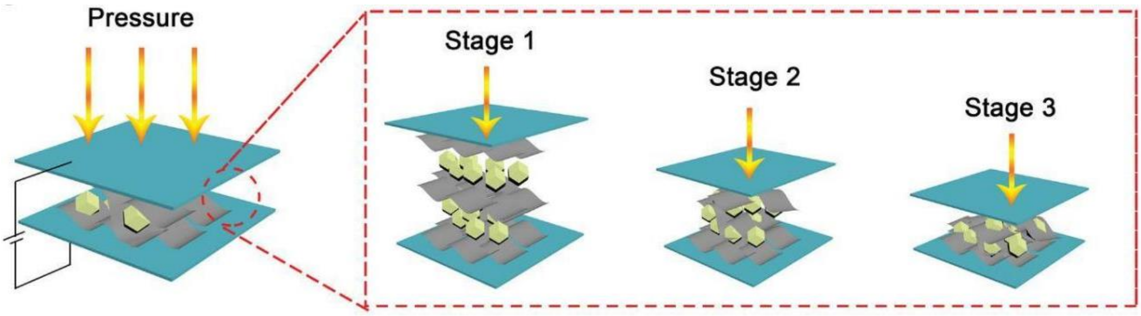

Figure 9. Schematic illustration of sensing principle of $Ti_3C_2T_x$@ZIF-67 sensor under pressure [11]

By combining MXene with CNTs using a layer-by-layer (LBL) spray coating process, Cai et al. [12] considerably improved the structure and orderliness of MXene's structure and conductive route (Fig. 10). CNTs link loose MXene sheets into a full network. Even under increasing strain, the Menxe sheets are connected by CNTs, retaining the integrity of the conducting channel, as the microcracks of MXene progressively develop as the tension rises throughout the stretching process. The achieved ultrathin sensor still does not show a huge measurement error after 5000 cycles, and it has a tunable sensing range of 30–130%, a LOD of 0.1%, and a GF which can be used to describe sensitivity of 772.6.

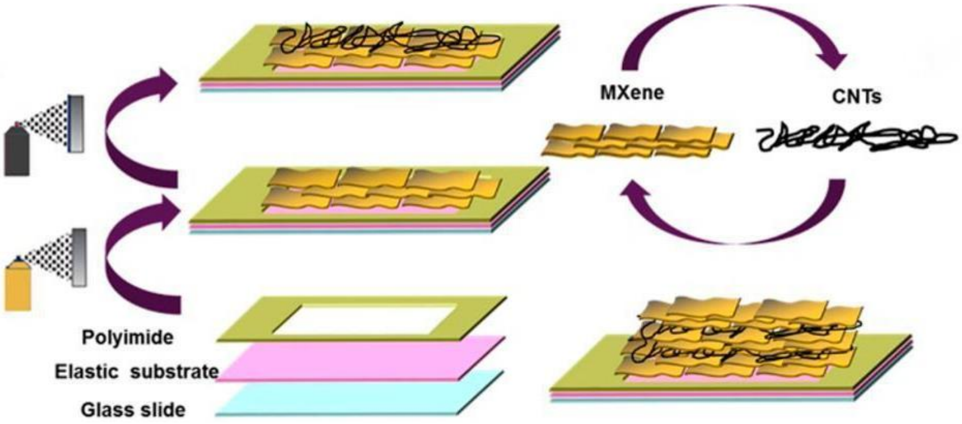

Figure 10. Composition of the MXene @ CNTs sensor [12]

2.3. PDMS-based sensors

Zhong et al. [13] incorporated one-dimensional carbon fibers (CFs) and zero-dimensional carbon nanoparticles (CNPs) into polydimethylsiloxanes. By using the template approach, the resultant mixture creates a sensing layer (P-HCF) with a surface microstructure (Fig. 11a) that attaches the patterned side to the electrode and puts together a piezoresistive sensor (Fig. 11b). A rapid and simple procedure produces a micro-nano hybrid structure conductive film with a variety of arching micropatterns, which is the sensing material P-HCF. In order to create a 3D conductive network in PDMS that transforms into multi-level sensing structures at the microscopic level, CFs and CNPs are utilized as conductive fillers (Fig. 11c). As a result, filler-matrix elastomer materials now have a substantially wider sensing range and greater sensitivity. As a result of the pressure from the outside altering the area of contact between the electrode and the surface microstructured sensing layer, contact resistance decreases as the sensor is loaded. The tunneling effect between CFs and CNPs is also improved, which reduces the distance between them inside the sensing layer and enhances the conductive path. The P-HCF pressure sensor has an extremely broad linear range of 20Pa–600kPa and a high sensitivity of 26.6kPa^{-1}.

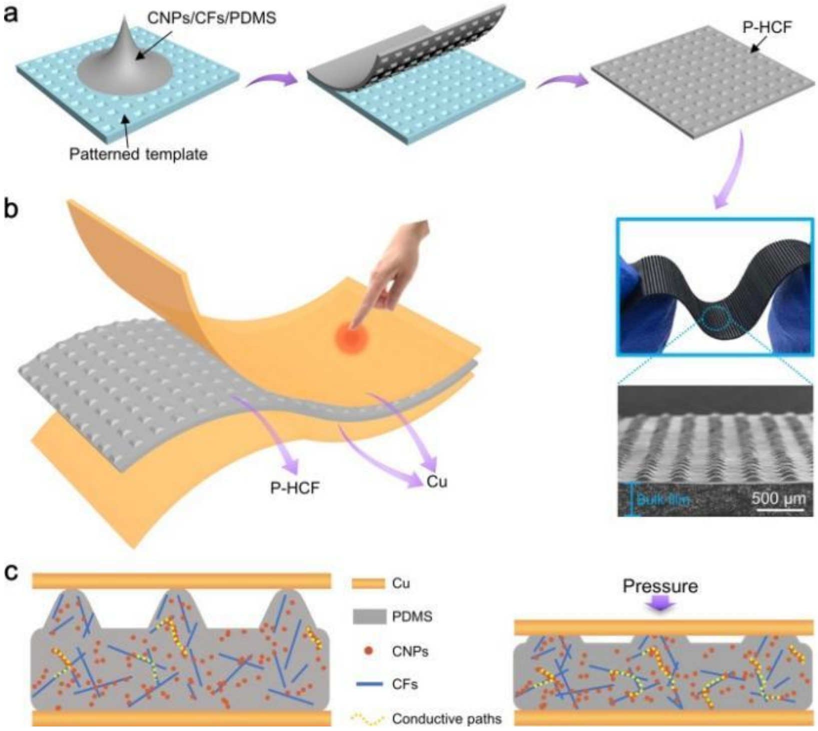

Figure 11. (a) Schematic illustration of the production of P-HCF layer; (b) Composition of the P-HCF sensor; (c) Schematic illustration of sensing principle of P-HCF sensor under pressure [13]

Li et al. [14] added liquid metal Ga (LM), nitrogen-doped graphene nanosheets (N-GNS), and NaCl to PDMS mixed slurry. In order to develop a pressure sensor based on a PDMS/LM/N-GNS sponge with a three-dimensional porous micro-nano structure, the PDMS mixed slurry is immersed in hot water after solidification in order to dissolve NaCl (Fig. 12). The contact area between LM and N-GNS and the conductive route continue to grow when the pressure sensor is compressed, thanks to the sponge's compressibility. The pressure sensor has a detection range of 0.0171–3.4kPa and a sensitivity of 476kPa^{-1}. The pressure sensor has outstanding stability (10,000 cycles of load) because to the extraordinarily high fluidity of liquid metal and the great flexibility of PDMS.

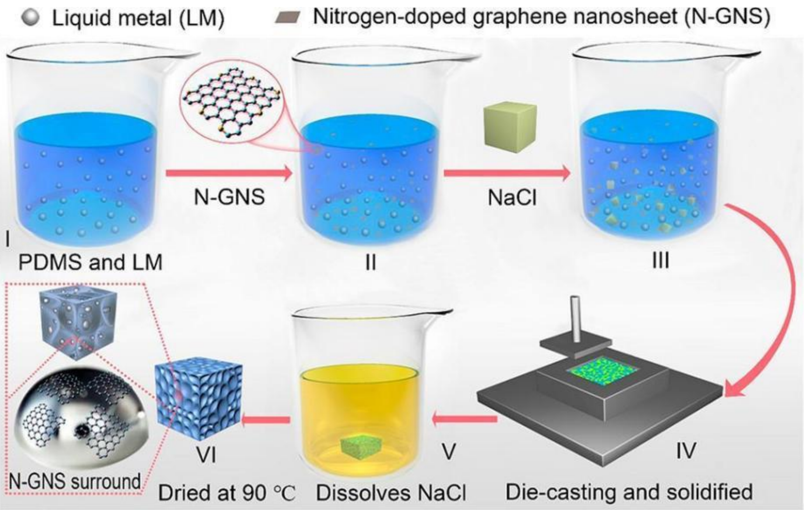

Figure 12. Schematic illustration of the production of PDMS/LM/N-GNS pressure-sensitive materials [14]

3. Application of three-dimensional nanomaterial piezoresistive sensors

3.1. Health monitoring

A person's heart rate is a crucial sign of their physical and mental health and the foundation for a doctor's diagnosis. In order to easily record wrist pulses in real time, Fu et al. [11] used an MXene@ZIF-67 wearable sensor mounted to the volunteer's wrist above the Raynaud's artery, which is the typical position for lie detectors and arterial tensiometers. The subject's health status can be ascertained by looking at the waveforms by carefully observing how the MXene@ZIF-67 sensor separates the various peaks of typical human body waveforms (Fig. 13).

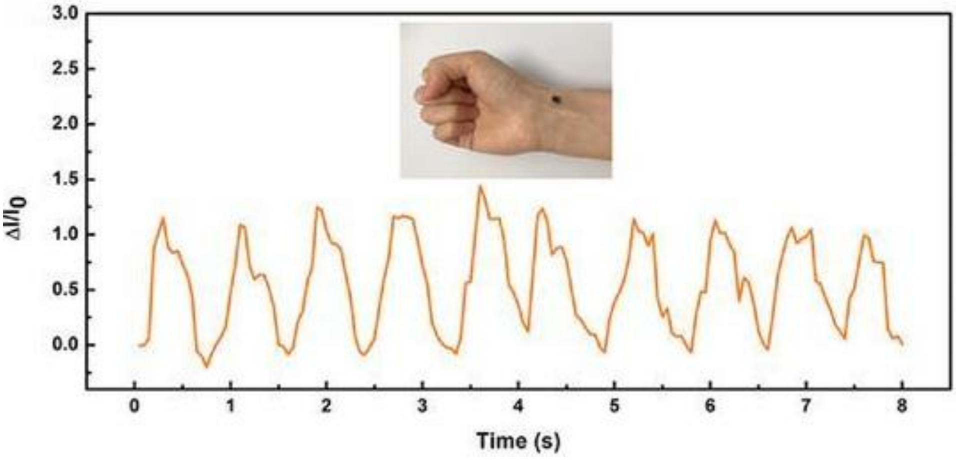

Figure 13. Pulse test by a MXene@ZIF-67 sensor [11]

Sleep apnea, one of the most serious diseases that has been diagnosed. A large range of practical applications are restricted by the employment of heavy, costly, and inconvenient equipment or heat flow sensors in current specialized biomedical approaches. A straightforward, efficient, and affordable method of tracking long-term breathing has been developed by Li et al. [8] utilizing graphene @ PU sensors that may be placed to the subject's chest to record the rise and fall of breathing (Fig.14).

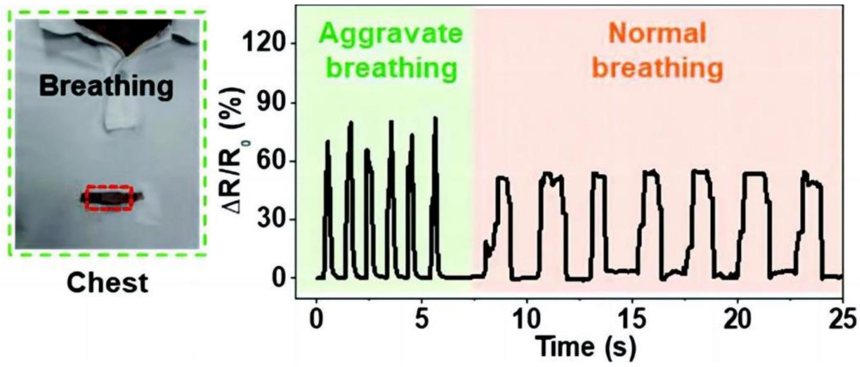

Figure 14. Breathe test by graphene @ PU sensors [8]

3.2. Motion state detection

In a study conducted by Cai et al. [12], piezoresistive sensors consisting of MXene/CNTs were affixed to the human knee. The researchers observed that during activities such as walking, running, and leaping (Fig.15), the resistance of the sensors exhibited variations that corresponded to the movements of the foreknee muscles.

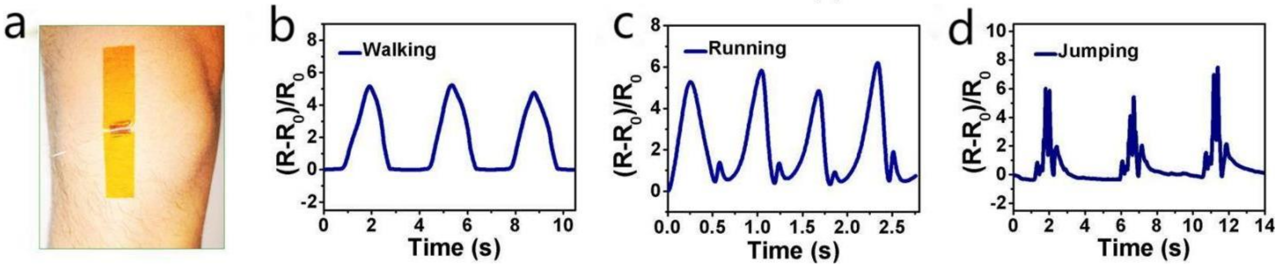

Figure 15. (a) A P-HCF sensor on the knee. Test data when the subject was (b) walking (c) running (d) jumping [12]

The researchers Zhong et al. [13] have developed a set of intelligent gloves that employ a CNPs/CFs/PDMS materials. These gloves have the capability to effectively capture and analyze bending signals from individual joints, enabling the control of manipulators for tasks such as gesture mimicry and object grabbing (Fig.16). By mounting these sensors on the insole, the continually collected data from 16 sensors is used to recreate pressure mapping changing with dynamic walking. The distribution of plantar pressure when walking often comprises heel impact, flat foot, middle standing, heel dropping off, and toe impact, which might indicate how the foot is moving at the moment (Fig.17). It can avoid sports-related injuries, the plantar force can also be studied.

Figure 16. A robotic hand controlled by P-HCF sensors to (i) open (ii) grasp the object (iii) move (iv) drop the object [13]

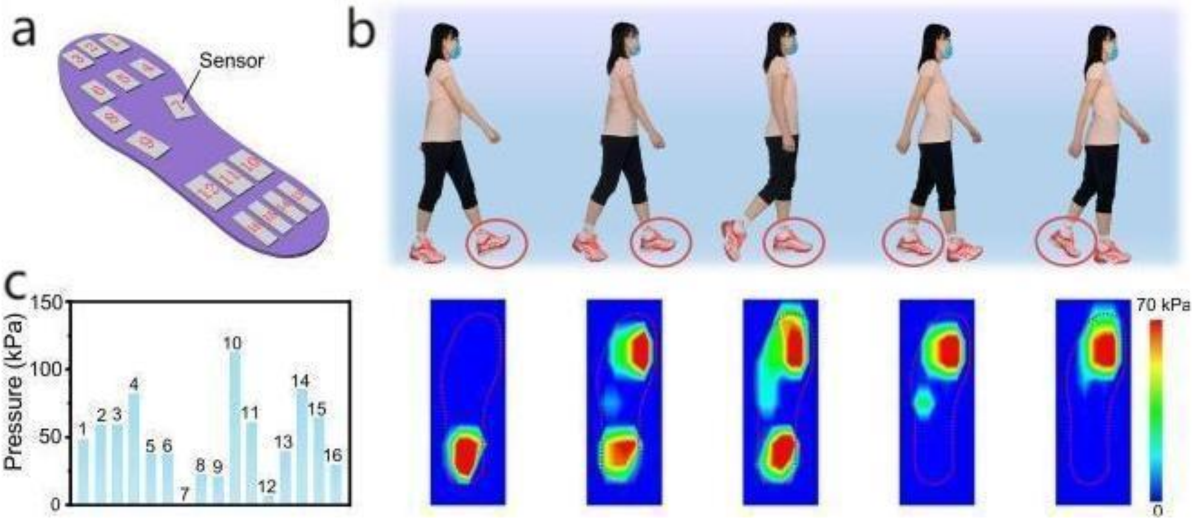

Figure 17. (a) Position of sensors on the insole. (b) Steps to move the feet of a person while walking. (c) Signals for different steps when a person walking [13]

4. Summary

In brief, enhancing sensor performance can be achieved by the utilization of conductive sensitive materials and the optimization of sensor microstructure design. Three-dimensional nanomaterials possess desirable characteristics, such as a substantial specific surface area, excellent electrical conductivity, and mechanical properties, which make them highly suitable for flexible piezoresistive sensors that require conductive sensitive materials. Additionally, these nanomaterials address the limitations of other nanomaterials, such as inadequate oxidation resistance, mechanical properties, and conductivity. In this paper, the applications of several three-dimensional nanomaterials in flexible piezoresistive sensors are reviewed, and the sensing performance and mechanism of three-dimensional nanomaterials flexible sensors with different micro-nanostructures are introduced. Nowadays, there is a gradual transition towards the era of flexible electronics due to the emergence of flexible electronic materials. The utilization of nanomaterials has significantly propelled the advancement of flexible electronic sensors to unprecedented levels. This review aims to enhance readers' comprehension of the role of three-dimensional nanomaterials in the context of flexible pressure sensors.

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