Carbon Black/Multi-Walled Carbon Nanotube-Based, Highly Sensitive, Flexible Pressure Sensor

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ABSTRACT: Flexible piezoresistive pressure sensors have promising applications in wearable devices, artificial intelligence, and other fields. However, developing low-cost and high-performance pressure sensors still poses a great challenge. Herein, we utilize low-cost carbon black (CB) and multi-walled carbon nanotubes (MWCNTs) mixed in porous polydimethylsiloxane to assemble a flexible piezoresistive pressure sensor combined with interdigitated electrodes. Simultaneously, the COMSOL Multiphysics simulation analysis was performed to predict the sensing behavior of the pressure sensor, which was verified by experiments; the preparation of the pressure sensor was guided according to the prediction. Additionally, we studied the effects of the mixed conductive filler’s weight ratio, the shape of the interdigital electrode, and the line width and spacing of the interdigital electrode on the performance of the sensor. Based on the interaction of the 3D porous structure and the synergistic conductive network of CB/MWCNTs, the prepared pressure sensor exhibits a high sensitivity of 3.57 kPa$^{-1}$ ($\sim$21 kPa), a wide detection range of 0–275 kPa, fast response time (96 ms), fast recovery time (198 ms), good durability (about 3000 cycles), and good flexibility. Moreover, the fabricated sensor can monitor and recognize human activities (such as finger bending and mouse clicking), indicating that it has great potential in flexible wearable devices and other fields. It is worth noting that the preparation process of the entire pressure sensor was simple, low cost, and environmentally friendly, which provides a certain basis for industrial and commercial applications.

1. INTRODUCTION

Due to their applications in human health monitoring, motion detection, electronic skin (e-skin), human–machine interfaces, and smart medical electronic devices, flexible pressure sensors have received extensive attention from researchers in recent years.$^{1-9}$ To date, according to different sensing mechanisms, flexible sensors can be divided into piezoresistive,$^{10-12}$ capacitive,$^{13-15}$ piezoelectric,$^{16}$ and triboelectric sensors.$^{17,18}$ Among these, piezoresistive pressure sensors, which can transform a variety of pressure signals into a variety of resistance signals, have become ideal for high-performance flexible sensors. This is mainly due to their simple device structure, easy signal processing, high sensitivity, wide detection range, and low manufacturing cost.$^{19,20}$ To obtain piezoresistive pressure sensors with excellent performance, the selection of conductive materials and the construction of sensor microstructures are two effective strategies.

In the past few decades, researchers have chosen a wide range of materials such as carbon nanotubes (CNTs),$^{21,22}$ MXene,$^{23}$ graphene,$^{24}$ Ag nanowires,$^{25}$ polyaniline (PANI),$^{26}$ and polypyrrole (PPy)$^{24,27}$ as active materials. Various sophisticated microstructures, including single uniform micro-nano structures,$^{28}$ biomimetic structures,$^{29}$ porous structures,$^{31}$ and so on, have been used to enhance the performance of sensors. For instance, Zhong et al. fabricated e-skin devices by two-interlocking elastic patterned nanofibrous membranes using in situ oxidative chemical polymerization, a replication imprinting method, and a solvent evaporation method.$^{30}$ This patterned electronic skin-like sensor exhibits ultra-high sensitivity (1.24 kPa$^{-1}$) in the ultra-low range (<150 Pa). Han et al. prepared multifunctional 3D carbon nanofiber networks (CNFNs) via electrospinning and heat treatment.$^{31}$ The sensitivity of the prepared pressure sensor is 1.41 kPa$^{-1}$.

Sun et al. proposed a high-performance flexible tactile sensor composed of a composite material with a pyramid and double-sided rough structure.$^{32}$ The fabrication of the tactile sensor involves spin coating and photolithography to jointly prepare a square array, wet etching to obtain an inverted pyramid

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structure, and coating to obtain a nanocomposite thin film. The tactile sensor has good reliability and high sensitivity (3.2 kPa⁻¹, ~1 kPa). Ko et al. prepared an AgCNT composite film via tip sonication, spraying, and dip coating processes. The developed sensing material demonstrated good sensitivity (0.02 kPa⁻¹, ~11.67 kPa). Although the above-mentioned sensors achieved good performance, the fabrication cost is relatively expensive. Moreover, the fabrication process is relatively complicated; this greatly limits the sensor’s practical application. Thus, the fabrication of high-performance flexible pressure sensors by simple and low-cost methods still faces great challenges.

In recent years, researchers have been trying to find low-cost materials and simple fabrication methods to realize high-performance pressure sensors. For instance, Zheng et al. prepared PANI/polydimethylsiloxane (PDMS) composites with hollow structures and micro-protrude surface structures by cyclic voltammetry and foam template methods. The results showed that the sensor achieved a sensitivity of 0.641 kPa⁻¹ in the linear range of 0.05–60 kPa, excellent stability (6000 cycles), and fast response time (200 ms). Wu et al. prepared CB@PU sponges using sonication and water-based layer-by-layer assembly. The CB@PU sponge can monitor various deformations from 91 Pa to 16.4 kPa in real time. Zhan et al. prepared single-walled carbon nanotube (SWNT)/tissue flexible sensors using dip coating and heat treatment. The sensor exhibited high sensitivity (2.2 kPa⁻¹, 35–100 Pa; 1.3 kPa⁻¹, 2.5–11.7 kPa) and ultra-low energy consumption (about 10⁻³ W) due to the unique structure of SWNTs interconnects in the paper. Duan et al. combined polyester conductive electrodes and cellulose paper that both have inherent microstructure surfaces to form a double-sided microstructure interface for sensors. The fabricated piezoresistive sensor was not only of low cost (far less than 0.01 USD per sensor), but it also demonstrated high-pressure sensitivity (5.54 kPa⁻¹, 0.5–5 kPa; 1.61 kPa⁻¹, 5–60 kPa) and excellent durability (5000 cycles under 2 kPa). Although some achievements have been realized, two problems remain: first, to achieve a good performance, one must compromise the materials’ low cost and the design’s simple fabrication process. Second, for one to cut the materials’ cost and simplify the fabrication process, one must compromise the sensor’s good performance. Therefore, a flexible piezoresistive pressure sensor with economic benefits, a simple fabrication process, and excellent performance is urgently needed and is of great research value in practical applications.

In this work, we propose a simple and low-cost fabrication method of high-performance, flexible piezoresistive pressure sensors. The porous structures were constructed with Ni foam as a sacrificial template. The conductive networks were constructed by the synergistic effect of carbon black (CB) and multi-walled carbon nanotubes (MWCNTs). Finally, the flexible piezoresistive pressure sensors were assembled with interdigital electrodes. Compared with graphene and noble metal conductive materials, CNTs are one of the most promising materials for flexible pressure sensors because of their flexibility, outstanding electrical conductivity, large aspect ratio, and good mechanical properties. Furthermore, the conductive CB particles, which are abundant materials, have a large surface area, desirable conductivity, and cost advantage. Additionally, the 3D porous structure has excellent elasticity and can increase the penetration of conductive fillers into the framework walls, thereby reducing the distance between conductive materials under compressive strain. Therefore, conductive composites with 3D porous structures are widely used due to their excellent viscoelasticity and good porosity, which can generate significant and stable resistance signals in a wide pressure range. The research results demonstrated that the flexible piezoresistive pressure sensor had good performance when the weight ratio of CB/MWCNTs was 1:1 and the interdigital electrode line width and spacing were 60 μm. Under those conditions, the sensor achieved high sensitivity (3.57 kPa⁻¹, ~21 kPa), a wide detection range (0–275 kPa), a fast response time (96 ms), and excellent stability (about 3000 cycles) and repeatability. This is attributed to the interaction of the porous structure and synergistic conductive network. Benefiting from these comprehensive sensing properties, the sensor can accurately sense heavy grabbing, mouse clicks, and finger and wrist bending. Thus, our research contributes to the development of cost-effective piezoresistive pressure sensors with promising applications in human motion detection and smart wearable devices.

2. EXPERIMENTS

2.1. Materials and Chemicals. The following materials and chemicals were used in the pressure sensor’s fabrication process. CB (about 30 USD for 200 g) of the model XF115 was purchased from XFNANO, Nanjing, China, with a diameter of about 23 nm. The carboxy-functionalized MWCNT (about 36 USD for 30 g) powder was purchased from Kaisa (Guangdong) New Materials Co., Ltd., with an average diameter of 3–15 nm and a length of 15–30 μm. PDMS (about 67 USD for 500 g) was purchased from Shanghai Deji Trading Co., Ltd. Nickel foam (width: 200 mm, length: 300 mm, thickness: 1.7 mm; about 4 USD) was supplied by Guangshengjia New Materials Co., Ltd. Isopropyl alcohol (IPA; about 6 USD for 500 mL) was purchased from Tianjin Tianli Chemical Reagent Co., Ltd. All materials and reagents are non-toxic and harmless. Additionally, all the materials and chemicals were used as received directly from the suppliers without any further treatment.

2.2. Preparation of the Porous PDMS Sponge. First, the purchased nickel foam was cut to the desired size. The nickel foam was sequentially and thoroughly cleaned with acetone, 95% ethanol, and deionized water in an ultrasonic bath for 5 min. Next, the PDMS precursor mixture was formulated (base elastomer/curing agent weight ratio = 10:1). The PDMS precursor mixture was sonicated for 30 min. Then, the cleaned nickel foam was immersed in the PDMS precursor mixture, after which it was degassed in a vacuum oven for 2 h to facilitate the infiltration. Subsequently, the PDMS@Ni foam was placed on a clean filter paper and flipped every 15 min to prevent the accumulation of PDMS at one side of the Ni foam, eventually allowing the PDMS to uniformly penetrate the Ni foam. Next, the treated PDMS@Ni foam was cured in an oven at 80 °C for 2 h. Finally, the cured PDMS@Ni foam was immersed in a FeCl₃ solution at room temperature for several hours to etch away the nickel scaffolds, and the porous PDMS foam was obtained.

2.3. Preparation of the CB/MWCNTs/PDMS Composite Film. First, the conductive fillers of CB and MWCNTs with weight ratios of 3:1, 2:1, 1:1 (0.1125 g:0.1125 g), 1:2, and 1:3 were weighed and dissolved in 40 mL of isopropanol.
Second, the mixture was sonicated for 1 h to obtain a homogeneous dispersion of the CB/MWCNTs. Then, the porous PDMS foam was immersed in the homogeneous dispersion of the CB/MWCNTs and sonicated for 1 h. Finally, the CB/MWCNTs/PDMS nanocomposites were obtained by drying the CB/MWCNTs/PDMS in an oven at 60 °C for 1 h. The whole fabrication process (ultrasonic and drying) was simple and environmentally friendly.

2.4. Pressure Sensor’s Fabrication Process. To further study its performance, a flexible piezoresistive pressure sensor based on CB/MWCNTs with a porous structure was prepared by assembling a CB/MWCNTs/PDMS composite film on a pair of PI interdigitated electrodes and encapsulated by a polyethylene terephthalate film. A schematic of the thin and flexible proposed sensor’s preparation procedure is shown in Figure 1.

2.5. Pressure Sensor Measurement. In this work, a series of tests were conducted to analyze the performance of flexible piezoresistive pressure sensors. The microstructure and morphology of the CB/MWCNTs/PDMS composites were characterized by using scanning electron microscopy (SEM, SU8010, Hitachi) with an accelerating voltage of 3 kV. Resistance measurements were performed using a digital push-pull gauge (DS2-50 N), a digital multimeter (K2400), and a linear stepper motor (LinMot-Talk) to record the resistance variation and the real-time continuous measurement of loading/unloading pressure sensing. Cyclic stability was measured via a digital multimeter (K2400) combined with a linear stepper motor (LinMot-Talk). An electrochemical workstation (PARSTAT PMC 1000) was employed to investigate the response time and the current (I)−voltage (V) characteristics. Finally, a series of practical application tests were carried out. For example, the sensors were mounted on wrists, knuckles, index fingertips, thumb fingertips, etc., to demonstrate the piezoresistive pressure sensors’ ability to respond to important human physiological signals.

3. RESULTS AND DISCUSSION

3.1. Microstructure and Morphology. The piezoresistive mechanisms are greatly related to the microstructures and dispersion state of nanocarbon materials. The SEM images of the composites obtained at different weight ratios (CB/MWCNTs) are shown in Figure 2. The CB and MWCNTs are intertwined and contacted with each other in the composites, forming an intricate and well-distributed conductive network. The CB is located at the end of the MWCNTs and can be observed in Figure 2. This indicates that CB bridges the gap between MWCNTs and MWCNTs, forming an MWCNT-CB-MWCNT conductive path, which enhances the compactness of the nanocomposite’s conductive network, leading to increased conductivity. Additionally, a “grape cluster-like” structure of the CB/MWCNT composite film can be observed. In the “grape cluster-like” structure, CB resembles “grape berries”, while MWCNTs are comparable to “grape stems”. Additionally, MWCNTs act as conductive bridges between adjacent CBs, providing remote conductive paths that cannot be provided by CB, thereby improving the construction efficiency of internal conductive paths; while CB is equivalent to providing a short conductive path. Meanwhile, CB can also act as a conductive bridge to connect uniformly dispersed CNTs. The “grape cluster-like” structure of the CB/MWCNTs
is crucial for the stability of the conductive network, which confirms the occurrence of “synergies”.

3.2. Pressure Sensor’s Working Mechanism. Figure 3a shows the schematic diagram of the CB/MWCNTs porous structure-based flexible piezoresistive pressure sensor’s working principle. Figure 3b demonstrates the distribution of CB and MWCNTs filled in the porous structure. The CB/MWCNT composite conductive layer’s resistance can be calculated as $R = R_1 + R_2 + R_3$, where $R_1$ represents the intrinsic resistance of CB, $R_2$ is the intrinsic resistance of MWCNTs, and $R_3$ represents the contact resistance between the mixed conductive materials. $R_1$ and $R_2$ were constant, while $R_3$ varied with applied pressure. When the pressure was applied to the sensor, the pores inside the sensor were compressed. As the sensor was gradually compressed, the randomly arranged CBs and MWCNTs in the pores became closer to each other, even becoming in contact, leading to an increase in the conductive path (Figure 3b). These increased conductive paths led to a decrease in the resistance between the two electrodes (i.e., the negative piezoresistive effect). Therefore, $R_3$ decreased, resulting in a decrease in $R$. On the contrary, when the pressure was released, the structure gradually recovered and the contact between the CB and MWCNTs gradually decreased due to its superior mechanical properties, resulting in a gradual increase in resistance. Therefore, $R_3$ increased, which caused $R$ to increase.

3.3. Simulation Analysis. In this paper, we carried out a series of simulation analyses to predict the sensor’s sensing behavior. Additionally, we provided guidance for further fabrication of sensors with excellent performance. In this simulation, three models were established to simulate stress distribution, which were rectangular, circular, and conical (Figure 4). Since the characteristics of mixed conductive fillers were not clear, and their mixing ratio was different, the characteristics were different. Therefore, the characteristics of mixed conductive fillers were simulated by Digimat software in this paper. In Digimat simulation software, we inputted the conductive material used in this paper, set material mixing and proportion, crossover, and collision to get the characteristics of the mixed material. Subsequently, we inputted the characteristic of the mixed material into COMSOL for simulation. The physical field was set to the solid mechanics and current module, setting the fixed constraints and the pressure (0–6 N) applied to the sensor. The piezoelectric coupling matrix of the material was set in the current module, and finally, the mesh was set to extremely fine. Before fitting: After completing the above settings, clicked Calculate to get the simulation results. After fitting: According to the above settings, the simulation results can be obtained through calculation. The calculation formula of resistance in this simulation is $R = \rho L/S$. $\rho$ is the resistivity. The resistivity $\rho$ of the model was obtained by simulating the piezoelectric coupling matrix of the material, $L$ is the length. $S$ is the cross-sectional area. The cross-sectional area $S$ was obtained by integrating the model. Thus, the resistance of the model before and after the stress was obtained, and then obtained the rate of resistance changed. During the simulation, the lower boundary of the model was fixed and different pressures were applied to the upper boundary.

Figure 4b shows that when pressure is applied to the composite film, the porous structure deforms, which leads to contact between the filled CB and MWCNTs inside the structure, resulting in the change of the electrical conductivity inside the structure. The finite element analysis results demonstrate that the strain distribution of composite films had different shapes under loading, the film structure was different, and the maximum deformation position distribution was also different. The analysis determined that the optimal shape was rectangular (Figure 4c1). After determining the film’s shape, the line width and spacing parameters of the rectangular interdigital electrode were designed. After adjusting the size parameters and optimizing the relationship between the pressure and the strain, the interdigital electrodes’ optimal line width and spacing were determined to be 60 $\mu$m (Figure 4c2). Figure 4c3 shows that the sensor that was prepared when the weight ratio of CB/MWCNTs was 1:1 had the highest sensitivity when the line width and spacing were constant. Therefore, the sensor that was prepared when the weight ratio of CB/MWCNTs was 1:1 and having the rectangular interdigital electrodes’ line width and spacing of 60 $\mu$m is the optimal one.

3.4. Sensing Performance. 3.4.1. $I$−$V$ Characteristics and Sensitivity Analysis. The current−voltage ($I$−$V$) characteristic curves of the proposed piezoresistive sensors
under different applied pressures are presented in Figure 5a. In the voltage range of $-5$ to $5$ V, all $I-V$ characteristic curves exhibit a good linear relationship, demonstrating the typical “ohmic” behavior of pressure sensors, which shows a stable response. With the increase of applied pressure, there was a corresponding increase in the slope of the $I-V$ curve, indicating that the corresponding resistance of the sensor decreases. The piezoresistive-sensing behavior of the CB/MWCNTs composite film relies on the resistance variation caused by the compressive deformation.

Pressure sensitivity is a key parameter for evaluating pressure sensor performance. It can be defined as follows:

$$S = \frac{\delta(\Delta R/R_0)}{\Delta p} = \frac{\delta((R_0 - R)/R_0)}{\Delta p}$$

where $\Delta R$ represents the resistance change due to applied pressure; $R_0$ represents the initial resistance of the sensor; $R$ is the real-time resistance; and $P$ represents the pressure applied to the sensor. According to eq 1, the sensor’s sensitivity can be obtained by analyzing and calculating the experimental data.

Figure 4. (a1 and a2) Force condition of the pressure sensor: (a1) Initial state. (a2) After loading. (b1 and b2) Force condition of the internal structure: (b1) Initial state. (b2) After loading. The local plot shows the distribution of the conductive filler. (c1–c3) Sensor’s relative resistance change ($\Delta R/R_0$) in response to applied pressure: (c1) Interdigital electrode’s shape. (c2) Interdigital electrode’s line width and spacing. (c3) Weight ratio of mixed conductive fillers.
According to the applied pressure, the calculated results of the sensor’s sensitivity can be divided into two stages, as shown in Figure 5. The main reasons for the different stages are based on the evolution of the 3D porous structure and the synergistic conductive network of CB/MWCNTs. When pressure is applied, the structure is compressed, resulting in a decrease in the distance between the two electrodes and a consequent change in the contact between CB and MWCNTs, which consequently results in a change in the conduction path.

To determine the optimal shape of the interdigital electrode, the optimal line width and spacing of the interdigital electrode, and the optimal weight ratio of the conductive mixed filler, we compared and analyzed the influence of each parameter on the sensor’s piezoresistive performance. Figure 5b shows that the rectangular interdigital electrode sensor has significantly higher sensitivity and wider detection range compared to the sensors with conical and circular interdigital electrodes. Figure 5c indicates that when the line width and spacing of the interdigital electrodes are 60 μm, the sensor’s relative resistance manifestly changes. In this case, the sensor’s sensitivity was the highest and the detection range was the widest. Additionally, when the weight ratio of CB/MWCNTs was constant, the line width and spacing of the interdigital electrodes had different effects on the sensor’s sensitivity and detection range.

Figure 5d reveals that when m CB/m MWCNTs = 1:1, the pressure sensor had the highest sensitivity and a more obvious relative resistance variation. In this paper, the total amount of CB and CNTs is fixed, and only the weight ratio is changed. CNTs have higher electrical conductivity and a larger aspect ratio than CB. CNTs with large aspect ratios are entangled with each other to form a conductive network. The CB particles are relatively loose, and the conductive network is formed by the point-to-point contact of the CB nanoparticles. During the loading process, the intertwined CNT network is relatively stable. With the addition of CB, the entanglement phenomenon is gradually reduced, and a relatively fragile CNTs-CB contact point is formed, which leads to an increase in the sensitivity of the device. When the weight ratio of CB over CNTs is greater than 1:1, there are relatively more CB particles and relatively few CNTs. Although a more fragile CNTs-CB contact point is formed, the contact between the two will be relatively reduced, and fewer conductive paths will be formed, resulting in a decrease in the sensitivity of the device. Therefore, the 1:1 weight ratio of CB over CNTs leads to the best sensitivity of the pressure sensor. Moreover, the weight ratio of CB/MWCNTs only had a large effect on the sensor’s sensitivity but has little effect on its detection range. The experimental results are consistent with the simulation results of COMSOL Multiphysics.

The recovery of pressure sensors is also an important performance for evaluating the pressure sensor performance. The loading/unloading curves of the proposed piezoresistive sensor under large pressure are shown in Figure 5b–d. It can be clearly seen in Figure 5 that the sensitivity test curves under different parameters are in good agreement with each other, indicating that the pressure sensor has good recovery performance with good consistency and little lag. The results show that our proposed pressure sensor can be recovered to the initial state even under large pressure.
3.4.2. Repeatability and Durability Analysis. Good mechanical properties are very important for the practical application of pressure sensors. Figure 6a reports the stress−strain curves of the composite films when the weight ratio of CB to CNTs is 1:1. It can be found from the figure that when the strength is 0.86 MPa and the deformation is 139%, the composite film (CB/MWCNTs = 1:1) is torn. According to the experimental results, the modulus of the composite film is calculated by solving the slope of the elastic deformation curve. The modulus of the composite film (CB/MWCNTs = 1:1) is 0.59 MPa.

Reliability and stability under long-term loading/unloading conditions are some of the main parameters that assess the piezoresistive pressure sensors’ performance. To verify that the proposed sensor can possess these characteristics, we further studied its stability under dynamic cyclic pressure and repeated a series of dynamic loading/unloading experiments.

At a certain weight ratio \(m_{CB}/m_{MWCNTs} = 1:1\), the sensor’s relative resistance changes \(\Delta R/R_0\) were recorded under different dynamic period pressures, as shown in Figure 6b. These results demonstrate that the relative resistance change increases with increasing pressure. Additionally, we can conclude that for a single pressure, good stability and repeatability can be achieved. As shown in Figure 6c, the relative resistance change \(\Delta R/R_0\) of the pressure sensor was recorded under different weight ratios (CB/MWCNTs) at a pressure of 3 N. Under a certain pressure, when \(m_{CB}/m_{MWCNTs} = 1:1\), the relative resistance changed, and the sensor response.

Figure 6. (a) Stress−strain test curves of mixed conductive fillers. (b) Measurements of repeated loading/unloading experiments at different pressures. (c) Measurement results of repeated loading/unloading experiments at different weight ratios (CB/MWCNTs).

Figure 7. (a) Pressure sensor’s response time upon applying a certain pressure. (b) Durability of pressure transducers under cyclic pressure loads.

Table 1. Comparison between Our Work and Previous Sensors

| ref | main raw materials | fabrication process | sensitivity (kPa\(^{-1}\)) | range (kPa) | cost | process | time |
|-----|-------------------|---------------------|---------------------------|-------------|------|---------|------|
| this work | CB/MWCNTs | foam template method; ultrasonic bath | 3.57 (~21 kPa) | 275 | * | * | * |
| 26 | PANI/PDMS | cyclic voltammetry; foam template method | 0.641 | 60 | * | ** | * |
| 30 | PPy/PVA-co-PE | polymerization; replication imprinting; solvent evaporation | 1.24 (<150 Pa) | 6.53 | ** | *** | * |
| 31 | CNFNs | electrospinning; pre-oxidation; thermal treatment | 1.41 (~0.25 kPa) | 4.5 | * | *** | ** |
| 32 | CB/MWCNTs | solution mixing; solvent evaporation; spin-coating; photolithography; wet etching | 3.2 (~1 kPa) | 10 | * | *** | * |
| 33 | AgNPs/CNTs | sonication (ice bath); spraying; dipping; coating; | 0.02 (~1.67 kPa) | 33.3 | * | *** | * |
| 34 | CB/PU sponges | ultrasonic method; alternate dipping | 0.068 (<2.3 kPa) | 16.4 | * | ** | * |
| 35 | SWNT/tissue paper | coating; heat treatment; electron beam evaporation; | 2.2 (35–100 Pa) | 11.7 | * | *** | * |
| 36 | carbon ink/paper | soak-drying | 5.54 (0.5–5 kPa) | 60 | * | * | * |
| 39 | hydrogel | situ polymerization | 0.05 (~3.27 kPa) | 7 | * | ** | * |

*The number of “*” means the grade. One “*” represents the lowest grade.*
was most manifest. In summary, the sensor can accurately distinguish different pressures and weight ratios (CB/MWCNTs). Simultaneously, when $n_{CB}/n_{MWCNTs} = 1:1$, the sensor was the most sensitive, which is consistent with the results of the above sensitivity analysis (Figure 5).

Additionally, the response and recovery times of the pressure sensor under a certain pressure were studied. Sensor response time represents the sensor’s agility in responding to applied pressure. These results, as shown in Figure 7a, demonstrate that the pressure sensor’s response and recovery times were about 96 and 198 ms, respectively. The long-term durability of pressure sensors is critical for practical applications. Figure 7b shows the results of the pressure sensor repeating thousands of dynamic loading/unloading cycles at a certain pressure. These results demonstrate that the samples returned to the initial state immediately after releasing the pressure. Moreover, they indicate that the piezoresistive pressure sensor maintains good stability and durability under a certain pressure. Even at about 3000 loading/unloading cycles, the performance did not alter. Additionally, the piezoresistive pressure sensors’ resistive response under compression cyclic force loading was consistent. We found that the structure of the sensor remained intact and the function was still excellent, indicating the sensors’ long lifetime and reliability. Stability and repeatability are essential for maintaining the sensors’ functionality in flexible applications, such as flexible wearable products and electronic skin sensing.

The performance of the pressure sensor prepared in this work is compared with that of the previously reported work, and the results are shown in Table 1. The results show that our fabricated flexible piezoresistive pressure sensor based on CB/MWCNTs has the advantages of low cost and high performance.

### 3.5. Applications of the Pressure Sensor

Due to their low cost, simple preparation, high sensitivity, large sensing range, fast response, and good durability, CB/MWCNT flexible piezoresistive pressure sensors have broad application prospects in wearable devices. As shown in Figure 8a, the piezoresistive pressure sensor was taped to the beaker to detect the human hand operation of grasping and releasing it. Due to its good sensitivity, the sensor’s relative resistance change increased immediately upon grasping the cup and decreased upon releasing it. Moreover, it is clear from Figure 8a that the signals could be differentiated by the amplitude and frequencies of the corresponding pressure feedback. This proves that the pressure sensor has a good response to different movements. Additionally, the sensor’s high sensitivity and fast response make it suitable for mouse-clicking applications. The pressure sensor exhibited synchronized and stable responses to successive clicks, including quick click and slow click (Figure 8b,c), which demonstrates the sensor’s ability to recognize mouse operations within extremely short time intervals. The prepared sensor was fixed on the wrist by medical tape to detect wrist motion (Figure 8d). The flexible piezoresistive pressure sensor can be bent with the movement of the wrist and recorded the change of its relative resistance in real time when the wrist was periodically bent to different angles. Similarly, when the wrist was released to its initial state, the resistance also returned to its initial value. Therefore, the obtained results (Figure 8d) show that the pressure sensor can detect the real-time response of the wrist to different stimuli causing movements at different angles. Moreover, the prepared sensor was fixed on the knuckle with medical tape to monitor the finger’s movement (Figure 8e). The experiment demonstrated that the flexible sensor can bend with the finger’s movement. Upon periodically bending the finger at an angle,
the real-time resistance change was recorded and further released to the initial state. The corresponding relative resistance changes provide good recognizability of the bent and unbent states of the finger. Therefore, the obtained results show that the sensor can detect finger movements. Figure 8f shows the resistance change during clenched fist-release, demonstrating that small force changes can be detected. As demonstrated, the signals can be distinguished by the corresponding pressure feedback, thus confirming that the pressure sensor has a good response to different movements. The results indicate that the proposed pressure sensor is promising when it comes to simulating human touching, grasping, and manipulating objects during human–computer interaction or in robot-assisted surgical systems. Undoubtedly, the sensor has a broad application prospect in wearable devices.

4. CONCLUSIONS

In summary, we developed a simple, environment-friendly, low-cost method of fabricating high-performance flexible piezoresistive pressure sensors based on CB/MWCNTs nanocomposites. The sensor demonstrated a huge pressure sensing range (up to 275 kPa), a high sensitivity of 3.57 kPa \(^{-1}\) (∼21 kPa), fast response time (96 ms), rapid recovery time (198 ms), and good durability over about 3000 loading/unloading cycles. These excellent properties are a result of the interaction between the 3D porous structure and the synergistic conductive network of CB/MWCNTs. Additionally, the sensor has promising practical applications in monitoring and identifying human activities, including grasping heavy objects and bending fingers. Due to its low cost, green environmental protection, easy fabrication, and excellent performance, this sensor was proved to be an excellent candidate for a wide variety of practical applications. We believe that this work provides a good strategy for fabricating high-performance CB/MWCNTs piezoresistive sensors with a wide range response and high sensitivity for human motion monitoring.

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Notes

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