Sea Urchin-like Microstructures Pressure Sensors with Ultra-sensitivity and Super Working Range

Xiu Wang

Chongqing University

Lu-Qi Tao

Chongqing University

Min Yuan

Chongqing University

Ze-Ping Wang

Chongqing University

Jiabing Yu

Chongqing University <https://orcid.org/0000-0001-7206-6592>

Ding Xie

Chongqing University

Feng Luo

Chongqing University

Xian-Ping Chen (✉ xianpingchen@cqu.edu.cn)

Chongqing University

Ching-Ping Wong

Georgia Institute of Technology

Research Article

Keywords: pressure sensors, Sensitivity, sea urchin-like

Posted Date: September 18th, 2020

DOI: <https://doi.org/10.21203/rs.3.rs-75243/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Version of Record: A version of this preprint was published at Nature Communications on March 19th, 2021. See the published version at <https://doi.org/10.1038/s41467-021-21958-y>.

Sea urchin-like microstructures pressure sensors with ultra-sensitivity and super working range

Xiuman Wang¹, Lu-qi Tao², Min Yuan¹, Zeping Wang¹, Jiabing Yu¹, Dingli Xie¹, Feng Luo¹, Xianping Chen^{*1,2} & ChingPing Wong^{*3}

¹Key Laboratory of Optoelectronic Technology & Systems, Education Ministry of China, Chongqing University and College of Optoelectronic Engineering, Chongqing University, Chongqing 400044, China

²State Key Laboratory of Power Transmission Equipment & System Security and New Technology and School of Electrical Engineering, Chongqing University, Chongqing 400044, China.

³School of Materials Science and Engineering, Georgia Institute of Technology

***Corresponding author:** xianpingchen@cqu.edu.cn cp.wong@mse.gatech.edu

Abstract

Sensitivity and pressure range are two significant parameters of pressure sensors. The existing pressure sensors are difficult to achieve both high sensitivity and a wide pressure range. In this regard, we proposed a new pressure sensor with a ternary nanocomposite Fe₂O₃/C@SnO₂. Notably, the sea urchin-like Fe₂O₃ structure promoted signal transduction and protected Fe₂O₃ needles from mechanical breaking; while, acetylene carbon black improved the conductivity of Fe₂O₃. Moreover, one part of SnO₂ nanoparticles adhered to the surface of Fe₂O₃ needles and formed Fe₂O₃/SnO₂ heterostructures whereas its other part of nanoparticles dispersed into the carbon layer and formed SnO₂@C structures. Collectively, the synergy of the three structures (Fe₂O₃/C, Fe₂O₃/SnO₂ and SnO₂@C) improved the limited pressure response range of a single structure. The experimental results demonstrated that the Fe₂O₃/C@SnO₂ pressure sensor exhibits high sensitivity (680 kPa⁻¹), fast response (10 ms), broad range (up to 150 kPa), and good reproducibility (over 3500 cycles under a pressure of 110 kPa). This implies that the new pressure sensor has wide application prospects especially in wearable electronic devices and health monitoring.

Introduction

In the past few years, pressure sensors are considered promising candidates for use in wearable devices, electronic skins, and human-machine interfaces due to their low cost, flexibility, simple fabrication process, high integration potential, among others¹⁻⁴. In particular, pressure sensors are classified into four main types namely: capacitive⁵⁻⁷, piezoresistive⁸⁻¹⁰, piezoelectric¹¹⁻¹³, and triboelectric sensors¹⁴⁻¹⁶. Furthermore, piezoresistive pressure sensors have multiple benefits, including low energy consumption, easy signal collection, simple device assembly, and high sensitivity. Recently, different microstructure or nanostructure geometries such as (interlocked microstructures¹⁷, hollow-sphere microstructure¹⁸, micro-pyramid array¹⁹, and porous structure²⁰) has been explored to improve the sensitivity of piezoresistive pressure sensors. Among them, the tapering geometry or spine structure confers a clever design that not only promotes signal transduction for high sensitivity, but also protects the bristle from mechanical breaking^{21,22}. Similar structural has been employed in mechanical sensors and yielded enhanced sensing performance. For example, Yin et al. noted that ZnO sea urchin-shaped microparticles with a low-temperature solution process exhibited a high sensitivity of 121 kPa⁻¹(pressure range 0 - 10 Pa)²³. Lee et al. achieved a sensitivity of 2.46 kPa⁻¹ (pressure range 0 – 1 kPa) with a piezoresistive pressure sensor based on sea-urchin shaped metal nanoparticles²⁴. In another work by Shi et al. studied the urchin-like hollow carbon spheres, and the sensitivity reached 260.3 kPa⁻¹ at 1 Pa²⁵. Based on the above background, the piezoresistive pressure sensors have high sensitivity only under a small pressure range. Additionally, without

any additives, that is, relying only on its own structure and performance, it is difficult for the sensing material to achieve high sensitivity and wide pressure working range at the same time. Of note, the low conductivity of a single metal oxide semiconductor limits the pressure response range of the piezoresistive pressure sensors.

There are two widely researched metal oxide including Fe_2O_3 and SnO_2 , because of their low-cost, environmental friendliness, and natural abundance. Studies have reported that coupling metal oxide and carbon compounds to form metal oxide/C nanocomposite, may improve photocatalytic ²⁶ and electrochemical performances ²⁷. Despite metal oxide/C nanocomposite processing large specific surface area and strong conductivity, they have rarely been employed in fabricating flexible pressure sensors.

In this work, we proposed a nanostructure design of materials with ultra-sensitivity for an ultra-broad-range pressure sensor. Particularly, this strategy involves the use of acetylene black carbon as a carrier due to its strong conductivity and high specific surface. The acetylene black carbon encloses particles Fe_2O_3 , thereby forming $\text{Fe}_2\text{O}_3/\text{C}$ structure. Furthermore, one part of SnO_2 nanoparticles were dispersed into the carbon layer and formed $\text{SnO}_2@\text{C}$ structures, whereas its other part of nanoparticle adhered to the surface of Fe_2O_3 needles and formed $\text{Fe}_2\text{O}_3/\text{SnO}_2$ heterostructures. Carbon improves the conductivity of a single metal oxide. Collectively, the synergy of the three structures ($\text{Fe}_2\text{O}_3/\text{C}$, $\text{Fe}_2\text{O}_3/\text{SnO}_2$ and $\text{SnO}_2@\text{C}$) improved the limited pressure response range of a single structure. Notably, the $\text{Fe}_2\text{O}_3/\text{C}@\text{SnO}_2$ (3:1:4) pressure sensor exhibited high sensitivity (680 kPa^{-1}), fast response (10 ms), broad range (up to 150 kPa) and good reproducibility (over 3500 cycles under a pressure of 110 kPa).

Results and discussion

Structural Characterization

Fig. 1 Schematic illustration of the fabrication pressure sensor

Fig. 2. **a** The XRD patterns of acetylene carbon black, Fe_2O_3 , SnO_2 , $\text{Fe}_2\text{O}_3/\text{C}$ (3:1) and $\text{Fe}_2\text{O}_3/\text{C}@ \text{SnO}_2$ (3:1:4). SEM images of **b** Fe_2O_3 , **c** $\text{Fe}_2\text{O}_3/\text{C}$ (3:1), and **d** $\text{Fe}_2\text{O}_3/\text{C}@ \text{SnO}_2$ (3:1:4), TEM images of **e** Fe_2O_3 , **f** $\text{Fe}_2\text{O}_3/\text{C}$ (3:1), and **g** $\text{Fe}_2\text{O}_3/\text{C}@ \text{SnO}_2$ (3:1:4), elemental mapping of **h** $\text{Fe}_2\text{O}_3/\text{C}$ (3:1), and **i** $\text{Fe}_2\text{O}_3/\text{C}@ \text{SnO}_2$ (3:1:4).

The fabrication process used in this study is illustrated in Fig. 1. First, conductive materials were synthesized using hydrothermal method. Then, a clean melamine sponge was soaked in the sample solution. Finally, after the electrode connection, a pressure sensor with a melamine sponge substrate was obtained.

The phase structure of acetylene carbon black, Fe_2O_3 , SnO_2 , $\text{Fe}_2\text{O}_3/\text{C}$ (the mass ratio of $\text{Fe}_2\text{O}_3/\text{C}$ 3:1), and $\text{Fe}_2\text{O}_3/\text{C}@\text{SnO}_2$ (the mass ratio of $\text{Fe}_2\text{O}_3/\text{C}@\text{SnO}_2$ 3:1:4) was characterized using X-ray diffraction (XRD), as depicted in Fig. 2a. The acetylene carbon black indicated a broad peak at $20^\circ \sim 30^\circ$, corresponding to its (002) crystal plane. The XRD pattern with (012), (104), (110), (113), (024), (116), and (125) was regarded as the formation of Fe_2O_3 (JCPDS 33-0664). The pristine SnO_2 nanoparticles exhibited a tetragonal structure (JCPDS 41-1445). Remarkably, the diffraction peaks of acetylene carbon black and Fe_2O_3 was observed in $\text{Fe}_2\text{O}_3/\text{C}$. Besides, as the carbon mass increased, the carbon peaks became stronger (Fig. S1a, Supporting information). The XRD pattern of the $\text{Fe}_2\text{O}_3/\text{C}@\text{SnO}_2$ revealed sharp peaks, whereas all the diffraction peaks corresponded well with single acetylene carbon black, Fe_2O_3 and SnO_2 , and thus, indicating the $\text{Fe}_2\text{O}_3/\text{C}@\text{SnO}_2$ nanocomposite with high purity. Notably, the peak of SnO_2 was stronger in $\text{Fe}_2\text{O}_3/\text{C}@\text{SnO}_2$ (3:1:8) nanocomposites, thus suggesting a higher content of SnO_2 in this composite (Fig. S1b).

The microstructures of the Fe_2O_3 , $\text{Fe}_2\text{O}_3/\text{C}$ (3:1), and $\text{Fe}_2\text{O}_3/\text{C}@\text{SnO}_2$ (3:1:4) were characterized using scanning electron microscopy (SEM), transmission electron microscopy (TEM), elemental mapping, and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), which are shown in Fig. 2b-i. The

images of Fe_2O_3 reflected a typical sea urchin-like structure, with a diameter of about 3 μm , as indicated in Fig. 2b. The microstructure of $\text{Fe}_2\text{O}_3/\text{C}$ nanocomposite is shown in Fig. 2c and Fig. 2f. In addition, a carbon material was embedded in the gap between adjacent Fe_2O_3 needles, thus forming $\text{Fe}_2\text{O}_3/\text{C}$ structure. The SEM images of resulting $\text{Fe}_2\text{O}_3/\text{C}@\text{SnO}_2$ (3:1:4), in which SnO_2 nanoparticles are visible is elucidated in Fig. 2g. Besides, one part of SnO_2 nanoparticles were well tightly attached to Fe_2O_3 needles, which indicates the formation of a heterojunction between the Fe_2O_3 and SnO_2 . Fig. S2i illustrates the interfacial structure of the $\text{Fe}_2\text{O}_3/\text{C}@\text{SnO}_2$ (3:1:4), that was examined using a high-resolution TEM (HRTEM) technique. The SnO_2 nanoparticles grew on the (104) surface of the Fe_2O_3 , along the direction of (110) SnO_2 , and thereby forming (104) Fe_2O_3 / (110) SnO_2 heterojunction. On the other hand, the other part of SnO_2 nanoparticles penetrated the carbon layer, forming $\text{SnO}_2@\text{C}$ (Fig. 2g). It was noted that $\text{Fe}_2\text{O}_3/\text{C}@\text{SnO}_2$ contains three structures composing of $\text{Fe}_2\text{O}_3/\text{C}$, $\text{SnO}_2@\text{C}$, and $\text{Fe}_2\text{O}_3/\text{SnO}_2$ heterojunction. Besides, as the mass of carbon and SnO_2 increases, the carbon layer and SnO_2 nanoparticles are more elucidated in the SEM images, as viewed in Fig. S2a-f, which was consistent with the XRD experimental results. The microstructure and compositional distribution of nanocrystals were further investigated using STEM and EDX mapping. The tin signal for SnO_2 , the iron signals for Fe_2O_3 , and carbon signals overlapped completely across the entire sample, which implied that Fe_2O_3 , carbon, and SnO_2 were uniformly combined (Fig. 2h and Fig. 2i).

Fig. 3 **a**. The XPS of Fe₂O₃, Fe₂O₃/C (the mass ratio of 3:1), Fe₂O₃/C@SnO₂ (the mass ratio of 3:1:4), **b** high-resolution curves of **c** Fe, Sn, and **d** C.

Furthermore, to explore the composition of the Fe₂O₃/C and Fe₂O₃/C@SnO₂ nanostructure, the XPS technique was used. The full spectrum characteristic peaks composed of Fe 2p, C 1s, O 1s, and Sn 3d states, as displayed in Fig. 3a. The peaks at 712.2 and 725.6 eV were ascribed to the Fe 2p_{3/2} and Fe 2p_{1/2}, while the peak at 715.9 eV was attributed to Sn 3p_{3/2}²⁸. The Fe₂O₃/C@SnO₂ sample shows the Sn 3d_{3/2} and Sn 3d_{5/2} around 493.3 and 484.9 eV, with a spin-orbit splitting of 8.4 eV, which agree with the previously reported energy values for SnO₂²⁹.

Sensing properties of the $\text{Fe}_2\text{O}_3/\text{C}@\text{SnO}_2$ pressure sensor

Fig. 4. **a** The sensitivity of Fe_2O_3 , $\text{Fe}_2\text{O}_3/\text{C}$ with the mass of ratio of (3:1), and $\text{Fe}_2\text{O}_3/\text{C}@\text{SnO}_2$ with the mass of ratio of 3:1:4 based sensors. **b** Response time of $\text{Fe}_2\text{O}_3/\text{C}@\text{SnO}_2$ (3:1:4) pressure sensor. **c** Detection of weak pressure: current curve of the proposed $\text{Fe}_2\text{O}_3/\text{C}@\text{SnO}_2$ (3:1:4) pressure sensor pressed by paper and rice grain. **d** The current response due to increased pressures under loading and unloading. **e** Stability performance of the $\text{Fe}_2\text{O}_3/\text{C}@\text{SnO}_2$ (3:1:4) pressure sensor with loading-unloading of more than 3500 cycles.

To measure the piezoresistive characteristics of is pressure sensor, we set up a custom-made system composed of a universal testing machine and a digital source meter. The formula for calculating sensitivity was based on $S = (\Delta I / I_{\text{unloading}}) / \Delta p$, where $\Delta I = I_{\text{loading}} - I_{\text{unloading}}$, which refers to relative current change, while Δp refers to the change of pressure. The measurement results are depicted in Fig. 4a, Fig. S3, and Table. S1. The sensitivity of Fe₂O₃/C@SnO₂ pressure sensor was higher than that of Fe₂O₃, Fe₂O₃/C, and SnO₂@C pressure sensors. The sensitivity of Fe₂O₃/C@SnO₂ (3:1:4) sensors is $S_1 \sim 680 \text{ kPa}^{-1}$ when the pressure is below 10 kPa, is $S_2 \sim 98 \text{ kPa}^{-1}$ within the pressure range of 10 – 50 kPa, and is $S_3 \sim 35 \text{ kPa}^{-1}$ within the pressure range of 50 – 150 kPa. It is apparently higher than that of ZnO sea urchin-like, carbon sea urchin-like, Ag/Au sea urchin-like, and other pressure sensors, as shown in Table S2. Although the sea urchin-like Fe₂O₃ structure promoted signal transduction and protected Fe₂O₃ needles against mechanical breakage, the sensitivity of the sensor (3 kPa^{-1}) was still lower, because Fe₂O₃ has poor conductivity. Also, the change in current was still smaller even under the effect of larger pressure. Fig. S3a and Table. S1 shows the current response of the pressure sensors under the different mass ratio of Fe₂O₃ and carbon, which indicates that the mass ratio of (3:1) has the highest sensitivity (203 kPa^{-1}) compared to the other lower ratios (2:1, 1:1 and 1:2) and also the large one (4:1), let alone the pure carbon. A major reason for the high sensitivity of the Fe₂O₃/C pressure sensor can be explained as follows. On one hand, the microfibers of sponge are composed of nanocomposites so that the contact area is increased and thus leading to an increase of current, as viewed in Fig. S6. On the other hand, when adding carbon

into the Fe_2O_3 system, the $\text{Fe}_2\text{O}_3/\text{C}$ nanocomposite exhibits a larger current variation compared to that of pure carbon. Under the constant mass of Fe_2O_3 , followed with increased amounts of carbon, the sensitivity of the $\text{Fe}_2\text{O}_3/\text{C}$ pressure sensor increases due to the increase of the conductive path. However, the excess addition of carbon to the sensor may significantly increase conductivity (when the mass ratio of carbon and Fe_2O_3 exceeds 1:3) and thus making it become a good conductor, but in return affecting its further increase of corresponding conductive pathways. Here, we noted that the addition of carbon greatly improves the sensitivity of the sensor in the pressure range (within 50 kPa), but does not obviously improve the sensitivity in the pressure range (over 50 kPa), as displayed in Fig. S3a.

To improve the sensitivity of the pressure sensor under the high-pressure range (over 50 kPa), $\text{Fe}_2\text{O}_3/\text{C}$ (3:1) was further combined with SnO_2 . The addition of SnO_2 nanoparticles not only improves the sensitivity of the sensor in the low-pressure range (within 50 kPa) but also improves its sensitivity in the pressure range (over 50 kPa) (Fig. S3b and Table S1). Furthermore, when the two semiconductors were brought in contact and subjected to high-temperature calcination, the band alignment occurred driven by the equilibration of the Fermi level as shown in Fig. S4^{30,31}. Consequently, an n-n type heterostructure was formed between Fe_2O_3 and SnO_2 , which promotes the transfer of electrons from Fe_2O_3 to SnO_2 , thus enhancing the conductivity of the pressure sensor. Besides, Fig. S2i show that the SnO_2 nanoparticles grew on the (104) surface of the Fe_2O_3 , along the direction of (110) SnO_2 , and thereby forming (104) _{Fe_2O_3} /(110) _{SnO_2} heterojunction. Collectively, the synergy of the three structures ($\text{Fe}_2\text{O}_3/\text{C}$,

$\text{Fe}_2\text{O}_3/\text{SnO}_2$ and $\text{SnO}_2@\text{C}$) improved the limited pressure response range of a single structure. Of note, the content of SnO_2 in $\text{Fe}_2\text{O}_3/\text{C}@\text{SnO}_2$ exhibited a significant role in sensing the performance of the pressure sensor as elucidated in Fig. S3b. In addition, when more SnO_2 ($\text{Fe}_2\text{O}_3/\text{C}@\text{SnO}_2(3:1:8)$) was added in the synthesis, the polymerization of SnO_2 nanoparticles occurred due to their high surface energy, and subsequently leading to a non-uniformed distribution of SnO_2 nanoparticles in $\text{Fe}_2\text{O}_3/\text{C}@\text{SnO}_2$. Conversely, when less SnO_2 ($\text{Fe}_2\text{O}_3/\text{C}@\text{SnO}_2(3:1:1)$) was added in the synthesis, less “accumulation layer” was formed on SnO_2 . It affected the conductivity of the pressure sensor. Therefore, the obtained $\text{Fe}_2\text{O}_3/\text{C}@\text{SnO}_2(3:1:8)$ and $\text{Fe}_2\text{O}_3/\text{C}@\text{SnO}_2(3:1:1)$ deemed lower sensitivity compared with $\text{Fe}_2\text{O}_3/\text{C}@\text{SnO}_2(3:1:4)$. Besides, $\text{Fe}_2\text{O}_3/\text{C}@\text{Sb}_2\text{O}_3(3:1:4)$ was synthesized and characterized to verify whether the ternary structure has a certain universality in improving the sensitivity and expanding the pressure working range of the piezoresistive pressure sensor. The sensitivity of $\text{Fe}_2\text{O}_3/\text{C}@\text{Sb}_2\text{O}_3(3:1:4)$ sensors is $S_1 \sim 303 \text{ kPa}^{-1}$ when the pressure is below 10 kPa, is $S_2 \sim 41 \text{ kPa}^{-1}$ within the pressure range of 10 – 50 kPa, and is $S_3 \sim 13 \text{ kPa}^{-1}$ within the pressure range of 50 – 150 kPa as shown in Fig. S5. The experimental result showed that the ternary structure has a certain universality in improving the sensitivity and expanding the pressure working range of the piezoresistive pressure sensor.

Besides, we further assessed the low limit detection of the $\text{Fe}_2\text{O}_3/\text{C}@\text{SnO}_2(3:1:4)$ pressure sensor as outlined in Fig. 4c. To evaluate the low limit detection of the sensor, a weight of 4.2 g glass slide was placed on the pressure sensor. Thereafter, a paper (~

0.52 pa, $m = 0.0107$ g, $S = 1 \times 2$ cm²) and rice ($m = 0.0116$) were put on the glass slide. The glass slide served two purposes including (1) completing the contact between the electrode and the sensor, and (2) making the current more stable. Moreover, the response time of the Fe₂O₃/C@SnO₂ (3:1:4) pressure sensor is depicted in Fig. 4b. Compressing the sponge pressure sensor by 0.02 mm at a speed of 500 mm/min, the response time and recovery time of the Fe₂O₃/C@SnO₂ (3:1:4) pressure sensor was 10 and 22 ms, respectively. Hence, the hysteresis of the recovery time of this pressure sensor may be mainly attributed to the sponge substrate. To evaluate the stability of the pressure sensor under the different pressures, the Fe₂O₃/C@SnO₂ (3:1:4) pressure sensor was set under various pressure values of 3, 8, 14 and 22 kPa as illustrated in Fig. 4d. The findings revealed that the current gradually increases with increasing pressure. Therefore, suggesting that Fe₂O₃/C@SnO₂ (3:1:4) pressure sensor can clearly distinguish the pressure of different levels. Furthermore, repeated compression/release test over 3500 cycles with a peak pressure of 110 kPa was performed (Fig. 4e). The insets revealed the 5 cycles of the current response at the inception (left) and termination (right) of the stability test, whereas, the sensor indicated a stable signal without offset during the cycles test, and thereby reflecting that the performance of the sensor is still stable under long cycles and high pressure. The SEM images of sponge in the original state and compression/release over 3500 cycles state are displayed in Fig. S2g-h. Compared with the original state, the micromorphology of Fe₂O₃ exhibited no change when the sensor was repeatedly compressed/released under the high pressure. However, only a small part of the Fe₂O₃ needles was detached from the sea urchin-

shaped microspheres. In this work, the good stability of the sensor could be attributed to two reasons namely (1) the tapering geometry of Fe_2O_3 protects the bristle from mechanical breaking^{21,22}, and (2) there is a lot of space between the Fe_2O_3 needle, which can allow carbon and SnO_2 nanoparticles to easily absorb onto the interval gap, and hence protecting the integrity of the Fe_2O_3 needle structure.

Extremely high-pressure resolution

Fig. 5. Detection of micro pressure under loading pressures of **a** 1.5 kPa, **b** 10 kPa, and **c** 50 kPa. **d** Experimental set-up of a car with a $\text{Fe}_2\text{O}_3/\text{C}@\text{SnO}_2$ (3:1:4) pressure sensor attached under a front tire. **e** Current signals corresponding to an unloaded, loaded, and unloaded 4 kg carton of milk on the driving seat of the car. **f** Current signals corresponding to a 73 kg male passenger getting into and out of the car.

The key feature of the $\text{Fe}_2\text{O}_3/\text{C}@\text{SnO}_2$ (3:1:4) pressure sensor is high sensitivity in a wide pressure range. In this respect, to evaluate the sensitivity of this sensor under high pressure, it was tested as follows. Specifically, the pressure sensor was subject to different pressure values at 1.5, 10 and 50 kPa, as illustrated in Fig. 5a-c. First, the sensor was compressed to the set pressure value, followed by consecutive addition of

three coins, each weighing about 3.19 g, which is equivalent to a pressure of 86 Pa. Each pressure increment caused a step increase of current, and the current signal is stable. In another experiment, a pressure sensor with a volume of $V = 19 \times 19 \times 4 \text{ mm}^3$ was placed under the front wheel of a car (the weight of the car is 1670 kg) as shown in Fig. 5d. Thereafter, a carton of milk weighing 4 kg put on the driving seat of the car and then taken away as indicated in Fig. 5e. Consequently, the changes in current were successfully detected. Likewise, when the male passenger with a weight of 73 kg gets into or out of the car, the current changed significantly (Fig. 5f). The circled vibrations in Fig. 5f demonstrated that the sensor can accurately capture the movement of the male passenger getting on or off the car. It shows that the sensor still has high sensitivity under the high pressure.

Wearable device demonstration

Fig. 6. **a** The current response caused by the arterial pulse waves with the sensor attached to the wrist. **b** The recorded current signal versus time pronouncing. Finally, **c** the signal variations of relative current corresponding to different occlusion, **d** human palm, **e** finger motion, and **f** walking.

Due to the high sensitivity, faster response, and broad pressure regime of the sensor ($\text{Fe}_2\text{O}_3/\text{C}@ \text{SnO}_2$ (3:1:4)), it can thus be applied in many fields. For instance, it can be used to detect voice, wrist pulse, and human motion activities. Fig. 6a shows the real-time wrist pulse detecting using the $\text{Fe}_2\text{O}_3/\text{C}@ \text{SnO}_2$ (3:1:4) pressure sensor. The testing curves revealed strong characteristic peaks of the human sphygmie waveforms, and the pulse rate at about 73 times/min, which is the normal level. Notably, based on the excellent performance of the $\text{Fe}_2\text{O}_3/\text{C}@ \text{SnO}_2$ (3:1:4) pressure sensor, it can be used for monitoring human health. Subsequently, this pressure sensor was attached to the human throat to monitor and distinguish subtle differences during the muscle motions near the throat, when the words “one”, “two” and “three” were spoken as shown in Fig. 6b. Interestingly, this technique can be applied to deaf and mute people who are unable to speak. It is well-known that their vocal cords can vibrate, and thus vibration produced can be transformed into the required sound ⁷. Moreover, the pressure sensor was mounted on the cheek to monitor the occlusion movement of humans as displayed in Fig. 6c. Upon occlusion, the current changed significantly, which once again proves the excellent performance of the sensor. Also, the pressure sensor was attached to the arm to detect the radial muscle contraction, which occurs when making a fist as viewed in Fig. 6d. When the tester made a fist, the current signal increased as well as the compression of the sensor. Therefore, this result illustrates its valuable potential application in physical training and curing muscle damage. The response of the sensor for continuously bending six different motions of the finger is elucidated in Fig. 6e. Consequently, it was noted that the sensor showed different responsive current signals

to different motions of the finger. In particular, the current signal exhibited a slight increase when the finger bent in small-scale (motion-I, motion-II, and motion-III), whereas larger-scale bending led to the sharp increase of current value (motion-IV, motion-V, and motion-VI). The large-scale movements resulted in a strong compression of the sensor and thus forming more conductive pathways. These findings demonstrated that the pressure sensor can precisely distinguish different-scale motions of the finger. In addition, Fig. 6f shows the pressure sensor mounted on foot using tape to monitor walking states. The response signals of walking motion were stable and repetitive. This suggests that it can be applied for gait recognition and motion monitoring. Conclusively, these outcomes enumerate that the $\text{Fe}_2\text{O}_3/\text{C}@\text{SnO}_2$ pressure sensor holds broad application prospects in the fields of medical health and wearable electronic devices.

Conclusion

In summary, we present a sea urchin-shaped microstructure $\text{Fe}_2\text{O}_3/\text{C}@\text{SnO}_2$, which was synthesized using a simple and environmentally friendly hydrothermal method. We also provide a pressure sensor with high sensitivity and a large working range based on a simple dip-coating process method. Notably, the $\text{Fe}_2\text{O}_3/\text{C}@\text{SnO}_2$ pressure sensor exhibits high sensitivity (680 kPa^{-1}), fast response (10 ms), broad range (up to 150 kPa), and good reproducibility (over 3500 cycles under a pressure of 110 kPa). Interestingly, multiple human physiological activities (such as pulse, pronouncing, joint bending, and walking, among others) could be monitored using the $\text{Fe}_2\text{O}_3/\text{C}@\text{SnO}_2$ pressure sensor. Lastly, based on the above excellent performance of the device, it has significant implications especially in wearable electronics, health

monitoring, and measuring pressure distribution.

Experimental

Synthesis of Fe₂O₃

The detailed processing method for the synthesis of Fe₂O₃ used in this study can be found in one of the authors' previous works ³². In particular, the Fe₂O₃ was synthesized through a hydrothermal process, where 0.405 g FeCl₃·6H₂O and 0.205 g Na₂SO₄ were first dissolved in distilled water (30 mL) and stirred for 10 min. Afterward, the mixture was heated at 120 °C for 6 h in a Teflon-lined stainless-steel autoclave. Lastly, after cooling, filtering, drying, and thermal annealing at 400 °C for 3 h under air, Fe₂O₃ was obtained.

Preparation of Fe₂O₃/C composites

Besides adding different masses of carbon, the same process was used for the synthesis of Fe₂O₃/C composites.

Synthesis of Fe₂O₃/C/SnO₂ composites

First, Fe₂O₃/C composite (0.145 g), Na₂SnO₃ (0.145 g, 0.036 g, 0.290 g) and urea (1.16 g, 0.290 g, 2.320 g) was dissolved in ethanol/H₂O solution and kept V_{ethanol}:V_{H₂O}=2:3. Subsequently, after stirring for 15 min, the mixture was heated at 180 °C for 6h in a Teflon-lined stainless-steel autoclave. Next, after cooling naturally in air, the Fe₂O₃/C@SnO₂ composites were washed several times with distilled water and absolute ethanol. Finally, the Fe₂O₃/C@SnO₂ composites were dried at 60 °C for 12 h.

Preparation of conductive sponges and electrode

Melamine sponge was cut into a cuboid with a length of 19 mm, width (19 mm),

and height (4 mm). Then it was the melamine sponge was washed several times with ethanol and dried at 45°C. Thereafter, Fe₂O₃/C@SnO₂ (SnO₂@C, Fe₂O₃/C, Fe₂O₃, SnO₂, and C) and Polyvinylidene fluoride (PVDF) binder were dissolved in N-methyl pyrrolidone (NMP) in a weight ratio of 10:1 and mixed to form a slurry. Next, the melamine sponge strip was immersed in slurry until full and dried at 45°C in a vacuum. The copper wire was soldered on the copper tape with a size of 19 mm×19 mm while the sponge was sandwiched between two copper tape.

Characterization of structures and performance of the sensors

The crystal structures of the samples were explored using X-ray diffraction (XRD, PANalytical X'Pert Powder), whereas, the morphology was characterized using scanning electron microscopy (SEM; Quattro S), high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), elemental mapping and transmission electron microscopy (TEM; Talos F200S). The binding energy of products was investigated using X-ray photoelectron spectroscopy (XPS; ESCALAB250Xi). Moreover, the loading of pressure was examined using a universal testing machine (ETM-5038, Shenzhen Wance Testing Machine Co., Ltd.), while the electrical signals of the pressure sensors were recorded at the same time using a Keithley 2450 digital meter at a constant voltage of 0.1 V. Finally, to assess the response time of the pressure sensor, a Keithley DAQ6510 multimeter was used.

Reference

1. Shin, M. K., Oh, J., Lima, M., Kozlov, M. E., Kim, S. J., & Baughman, R. H. Elastomeric conductive composites based on carbon nanotube forests. *Advanced Materials*, 22(24), 2663-2667 (2010).
2. Jian, M., et al. Flexible and highly sensitive pressure sensors based on bionic hierarchical structures. *Advanced Functional Materials*, 27(9), 160666(2017).
3. Zhou, Z., Li, Y., Cheng, J., Chen, S., & Li, L. Supersensitive all-fabric pressure sensors using printed textile electrode arrays for human motion monitoring and human-machine interaction. *Journal of Materials Chemistry C*, 6(48), 13120–13127 (2018).
4. Schwartz, G. et al. Flexible polymer transistors with high pressure sensitivity for application in electronic skin and health monitoring. *Nature Communications*, 4, 1859 (2013).
5. Bai, N., Wang, L., Wang, Q., Deng, J., & Guo, C. F. Graded intrafillable architecture-based iontronic pressure sensor with ultra-broad-range high sensitivity. *Nature Communications*, 11(1), 209 (2020).
6. Cho, S. H. et al. Micropatterned pyramidal ionic gels for sensing broad-range pressures with high sensitivity. *Acs Applied Materials & Interfaces*, 9(11), 10128-10135 (2017).
7. Mannsfeld, S. C. et al. Highly sensitive flexible pressure sensors with microstructured rubber dielectric layers. *Nature Materials*, 9(10), 859-864 (2010).
8. Pang, Y. et al. A flexible highly sensitive and wearable pressure and strain sensors with graphene porous network structure. *Acs Applied Materials & Interfaces*, 22374-22381(2016).
9. Maheshwari, V., & Saraf, R. High-resolution thin-film device to sense texture by touch. *Science*, 312(5779), 1501-1504(2006).
10. Lou, Z., Chen, S., Wang, L., Jiang, K., & Shen, G. An ultra-sensitive and rapid response speed graphene pressure sensor for electronic skin and health monitoring. *Nano Energy*, 7-14(2016).
11. Sun, J. et al. Piezo-phototronic effect improved performance of n -Zno nano-arrays/p -Cu₂O film based pressure sensor synthesized on flexible cu foil. *Nano Energy*, 32, 96-104(2016).
12. Wen, zhuo. et al. Taxel-addressable matrix of vertical-nanowire piezotronic transistors for active and adaptive tactile imaging. *Science*, 340(6135):952-957(2013).
13. Sumin. et al. Transparent and stretchable interactive human machine interface based on patterned graphene heterostructures. *Advanced Functional Materials*, 25,375(2015).
14. Khan, U. et al. Graphene tribotronics: graphene tribotronics for electronic skin and touch screen applications. *Advanced Materials*, 29, 1603544(2017).
15. Wang, X., et al. Self-powered high-resolution and pressure-sensitive triboelectric sensor matrix for real-time tactile mapping. *Advanced Materials*, 28(15), 2896-2903(2016).

16. Su, Y., Chen, J., Wu, Z., & Jiang, Y. Low temperature dependence of triboelectric effect for energy harvesting and self-powered active sensing. *Applied Physics Letters*, 106(1), 3788(2015).
17. Pang, C. et al. A flexible and highly sensitive strain-gauge sensor using reversible interlocking of nanofibres. *Nature Materials*, 11(9), 795-801(2012).
18. Pan, L. et al. An ultra-sensitive resistive pressure sensor based on hollow-sphere microstructure induced elasticity in conducting polymer film. *Nature Communications*, 5,3002(2014).
19. Choong, C. L. et al. Highly stretchable resistive pressure sensors using a conductive elastomeric composite on a micropyramid array. *Advanced Materials*, 26(21), 3451–3458(2014).
20. Chen X. P. et al. A dual-functional graphene-based self-alarm health-monitoring e-skin. *Advanced Functional Materials*, 29(51) (2019).
21. H.E. Dechant, F. Rammerstorfer, & F. Barth. Arthropod touch reception: stimulus transformation and finite element model of spider tactile hairs., 187(10), 851-851(2001).
22. Barth, F. G. Spider mechanoreceptors. *Current Opinion in Neurobiology*, 14(4), 415-422 (2004).
23. Yin, B., Liu, X., Gao, H., Fu, T., & Yao, J. Bioinspired and bristled microparticles for ultrasensitive pressure and strain sensors. *Nature Communications*, 9(1),5161(2018).
24. Lee, D. et al. Highly sensitive, transparent, and durable pressure sensors based on sea-urchin shaped metal nanoparticles. *Advanced Materials*. 28, 9364-9369(2016).
25. Shi, L. et al. Quantum effect-based flexible and transparent pressure sensors with ultrahigh sensitivity and sensing density. *Nature Communications*, 11(1),3529(2020).
26. Xiang, Q., Yu, J., & Jaroniec, M. Synergetic effect of MoS₂ and graphene as cocatalysts for enhanced photocatalytic H₂ production activity of TiO₂ nanoparticles. *Journal of the American Chemical Society*, 134(15), 6575-6578(2012).
27. Lin, J. et al. Graphene nanoribbon and nanostructured SnO₂ composite anodes for lithium ion batteries. *Acs Nano*, 7(7), 6001-6 (2013).
28. Wang, B. B. et al. Fabrication and gas sensing properties of hollow core-shell SnO₂/α-Fe₂O₃. heterogeneous structures. *Journal of Alloys & Compounds*, 587, 82-89(2014).
29. Tian, Q., Li, L., Chen, J., Yang, L., & Hirano, S. I. Facile fabrication of robust TiO₂@SnO₂@C hollow nanobelts for outstanding lithium storage. *Journal of Power Sources*, 376(1), 1-10 (2018).
30. Zhou. X. et al. Ordered porous metal oxide semiconductors for gas sensing. *Chinese Chemical Letters*, 29, 405 (2018).
31. Zhao, T. et al. Hierarchical branched mesoporous TiO₂–SnO₂ nanocomposites with well-defined n–n heterojunctions for highly efficient ethanol sensing. *Advanced Science*, 6,02008(2019).

32. Wang, X. M. et al. Excellent cyclic performance of $\text{Fe}_2\text{O}_3@\text{C}/\text{SnO}_2$ controlled by $\text{Fe}_2\text{O}_3@\text{C}$ and SnO_2/C hybrid structures for lithium-ion batteries. *Journal of Physics & Chemistry of Solids*, 132,130-137(2019).

Acknowledgements

This research was supported in part by the National Key Research and Development Program under Grant 2018YFB2100100, in part by the Pre-Research Project for 13th Five-Year Plan under Grant 614041404, in part by the China Postdoctoral Science Foundation under Grant 2019M663433, in part by the National Natural Science Foundation of China under Grant 61901064, in part by the Fundamental Research Funds for Central Universities under Grant 2019CDXYDQ0009, Grant 2019CDXYGD0028, Grant 106112017CDJQJ128836, Grant 2019CDQYDQ024, and Grant 2019CDJGFGD007, in part by the Key Science and Technology Program of Chongqing under Grant CSTC2017SHMS-ZDYFX0028, and in part by the Technology Innovation and Application Project of Chongqing under Grant CSTC2018JSZX-CYZD0587.

Competing interests

The authors declare no competing interests.

Supplementary information

Supplementary data associated with this paper about the experiment section and related details can be found in the online vision.

Figures

Figure 1

Schematic illustration of the fabrication pressure sensor

Figure 2

a The XRD patterns of acetylene carbon black, Fe₂O₃, SnO₂, Fe₂O₃/C (3:1) and Fe₂O₃/C@SnO₂ (3:1:4). SEM images of b Fe₂O₃, c Fe₂O₃/C (3:1), and d Fe₂O₃/C@SnO₂ (3:1:4), TEM images of e Fe₂O₃, f Fe₂O₃/C (3:1), and g Fe₂O₃/C@SnO₂ (3:1:4), elemental mapping of h Fe₂O₃/C (3:1), and i Fe₂O₃/C@SnO₂(3:1:4).

Figure 3

a. The XPS of Fe₂O₃, Fe₂O₃/C (the mass ratio of 3:1), Fe₂O₃/C@SnO₂ (the mass ratio of 3:1:4), b high-resolution curves of c Fe, Sn, and d C.

Sensing properties of the $\text{Fe}_2\text{O}_3/\text{C}@\text{SnO}_2$ pressure sensor

Figure 4

a The sensitivity of Fe_2O_3 , $\text{Fe}_2\text{O}_3/\text{C}$ with the mass of ratio of (3:1), and $\text{Fe}_2\text{O}_3/\text{C}@\text{SnO}_2$ with the mass of ratio of 3:1:4 based sensors. b Response time of $\text{Fe}_2\text{O}_3/\text{C}@\text{SnO}_2$ (3:1:4) pressure sensor. c Detection of weak pressure: current curve of the proposed $\text{Fe}_2\text{O}_3/\text{C}@\text{SnO}_2$ (3:1:4) pressure sensor pressed by paper and rice grain. d The current response due to increased pressures under loading and unloading. e

Stability performance of the Fe2O3/C@SnO2 (3:1:4) pressure sensor with loading/unloading of more than 3500 cycles.

Figure 5

Detection of micro pressure under loading pressures of a 1.5 kPa, b 10 kPa, and c 50 kPa. d Experimental set-up of a car with a Fe₂O₃/C@SnO₂ (3:1:4) pressure sensor attached under a front tire. e Current signals corresponding to an unloaded, loaded, and unloaded 4 kg carton of milk on the driving seat of the car. f Current signals corresponding to a 73 kg male passenger getting into and out of the car.

Figure 6

a The current response caused by the arterial pulse waves with the sensor attached to the wrist. b The recorded current signal versus time pronouncing. Finally, c the signal variations of relative current corresponding to different occlusion, d human palm, e finger motion, and f walking.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [Supportinginformation.docx](#)