Sensitivity enhancement of the tactile sensor based on hydrothermally grown ZnO nanorods modified by catalytic Au nanoparticles

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Keywords: flexible tactile sensor, piezoelectric, ZnO nanorods, Au nanoparticles

Abstract
Flexible piezoelectric tactile sensor with transverse planar electrodes based on hydrothermally grown ZnO nanorods (ZnO NRs) was presented by using polydimethylsiloxane (PDMS) as flexible substrate and packaging material. The effects of the content of gold nanoparticles (AuNPs) added into the precursor solution on the structural morphology of ZnO NRs and on the piezoelectric properties of the ZnO NRs tactile sensor were investigated. Tactile sensors show a linear piezoelectric response in the pressure range of 0–1 N, and the sensor for the precursor solution with AuNPs of 100 μl shows a high sensitivity of 1.42 V N⁻¹ due to the large aspect ratio of the ZnO NRs, indicating that a small amount of AuNPs addition can optimize the structural morphology of ZnO NRs and thus improve the piezoelectric response of the sensor. Meanwhile, the sensor is employed to monitor human information in real-time such as bending/stretching motion of finger and distinguish various objects.

1. Introduction

Tactile is one of the important ways for human beings to perceive the outer world through the multiple mechanoreceptors in different regions of the skin, which receive the external stimuli (e.g. pressing, tapping, slipping, and bending) and convert them to electronic signals [1, 2]. The ensemble information from these receptors is subsequently interpreted by the human brain as body positions, object sizes, shapes, texture, etc [2]. Flexible tactile sensors can mimic the sensing capabilities of human skin, and obtain the corresponding information from the external stimuli by interacting with the surrounding environment or objects [3, 4]. In recent years, flexible tactile sensors have attracted tremendous attention due to their superior perception ability to human skin in spatial resolution, response time, detection limit, etc [5–7], and their significant importance in various applications such as intelligent prosthesis, touch panels, artificial skins, human–machine interfaces, and wearable medical devices.

According to different physical transduction mechanisms, tactile sensors mainly include piezoresistive [8, 9], capacitive [10], piezoelectric [11, 12], and triboelectric [13] types, in which piezoelectric tactile sensor has gained more attention due to the advantage that it requires no power to generate the raw output signal, enabling the design of autonomous devices [14]. On the other hand, in human skin, touch sensing proceeds via mechanisms resembling piezoelectricity, i.e. via an electrical signal generated when a pressure is applied [15]. Furthermore, piezoelectric sensors can better mimic the skin fast adapting (FA) mechanoreceptors due to their fast response to dynamic load. Among piezoelectric materials, lead zirconate titanate (PZT)-based ceramics is the most typical one due to its high piezoelectric coefficient with $d_{33}$ up to 500 pC/N, high Curie temperature and low cost [16]. However, it is inadequate to satisfy the future requirements of wearable tactile sensors due to its lead-toxic and inflexibility.
Since the piezoelectric properties of ZnO nanorods (NRs) were reported and firstly used as piezoelectric nanogenerators (NGs) [17] and actual pressure sensitive devices [18], Tactile sensors based on ZnO NRs have attracted great interest from both industry and academia due to their higher sensitivity to small forces, good mechanical stretchability, inherent permanent dipole, high biocompatibility, low toxicity and low-cost fabrication [19]. So far, many efforts have been made to remarkably improve the sensitivity and broaden detection modes of the ZnO NRs-based tactile sensors, including normal force, shear force and bending strain, by optimizing synthesis process and morphological parameters [20], and by designing novel microstructures of sensors [21, 22]. Generally, to achieve higher piezoelectric performance, an effective control over their shape and crystallography for ZnO NRs should be desired, because the device performances depend on the morphological parameters of ZnO NRs [23]. Recently, it was reported that the gas sensors based on ZnO NRs modified by catalytic gold nanoparticles (AuNPs) exhibited a significant improvement in sensing performances to a variety of gases such as acetone [24] and methanol vapor [25], however, performance optimization of tactile sensors based on ZnO NRs modified by AuNPs has not still been reported. In addition, the currently reported ZnO NRs-based piezoelectric tactile sensors widely adopt the vertical sandwich structure which easily causes short circuit between the top and bottom electrodes. In this work, we propose a self-powered flexible tactile sensor with transverse planar electrodes that does not need an external power source for converting the applied pressure into a measurable voltage. The tactile sensors were fabricated on the polydimethylsiloxane (PDMS) substrates by using ZnO NRs as sensitive layers grown on the sputtered ZnO seed layers through a low temperature hydrothermal method. The whole device was packaged with PDMS, resulting in a one-piece flexible tactile sensor with an external force. The structural morphologies of ZnO NRs can be optimized by adding gold nanoparticles (AuNPs) into the aqueous precursor solution to improve the aspect ratio of ZnO NRs. The effects of the content of AuNPs on the morphology, structural, and optical properties of vertically aligned ZnO nanorods grown on PDMS substrates were analyzed. In particular, the piezoelectric response of the corresponding ZnO NRs tactile sensors was investigated.

2. Experiment

2.1. Piezoelectric tactile sensor fabrication

The fabricated tactile sensor with planar transverse electrodes was constructed by using the substrate, piezoelectric layer, and package shell. A PDMS film with a thickness of about 100 µm was used as the substrate due to its excellent flexibility, hydrophobicity, biological compatibility transparency and elasticity, which has extensive usage in flexible wearable electronic devices. The corresponding fabrication processes of the ZnO NRs tactile sensor are illustrated in figure 1. First, glass slides with 2.5 cm × 2.5 cm were cleaned ultrasonically in acetone, alcohol and deionized (DI) water for 15 min respectively, to remove the physically adsorbed contaminants, then dried on a hot plate. To easily strip the PDMS from the slide, the slide was soaked in soap water for about 30 min, and then dried at 60 °C. After that, the mixed solution with PDMS pre-polymer was spin-coated on the glass slide to form the PDMS film, and then the sample was solidified at 60 °C for 45 min and
vulcanized at 80°C for 5 min in an oven, respectively. A pure PDMS film with a specific thickness was obtained by ultrasonic stripping from the slide and acted as the substrate of the sensor (figure 1(a)). Next, an 80-nm thick ZnO seed layer (SL) was deposited on the PDMS substrate by using a radio frequency sputtering system (figure 1(b)). Then, The PDMS substrate with the ZnO seed layer was soaked in the precursor solution and placed in an autoclave reactor at 90°C for 3 h to grow the ZnO NRs by hydrothermal process (figure 1(c)). The precursor solution was prepared by mixing 0.125 M zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O) and 0.125 M hexamethylenetetramine (HMTA, C₆H₁₂N₄) in 35-ml deionized water and then stirring at room temperature for about 15 min. The precursor solutions with four different contents of AuNPs were obtained by adding the 40-nm sodium citrate-enwrapped AuNPs solution with the amount of 100 μl, 200 μl, 300 μl and 400 μl into the precursor solution, respectively. After hydrothermal synthesis, the sample was taken out from the solution after the autoclave had cooled to room temperature naturally, and then washed with DI water several times and dried at room temperature. Finally, a conductive copper foils were bonded on both sides of the ZnO NRs to form the left and right transverse electrode structure (figure 1(d)). After the wire-leading, the whole device was fully packaged by PDMS to provide mechanical support, moisture and dust resistance, and allow the sensor to be draped conformably over non-planar surfaces (figure 1(e)). The photograph of the ZnO NRs tactile sensor is shown in figure 1(f).

2.2. ZnO NRs performance test

The thicknesses of the ZnO SL and the PDMS substrate were measured by Profilometer (KLA Alpha-Step D-500) to be 80 nm and 100 μm, respectively. The morphologies of ZnO NRs were characterized by scanning electron microscopy (SEM) (ZEISS Merlin Compact). The crystallinities of ZnO NRs were analyzed by x-ray Diffraction (XRD) (Bruker D8). The x-ray source is a monochromatic CuKα radiation source (λ = 1.54178 Å). The optical properties of the ZnO NRs were investigated by room-temperature photoluminescence (PL) spectroscopy, where a 325-nm continuous He-Cd ultraviolet laser was used as an excitation source.

2.3. Piezoelectric responses test of tactile sensor

The piezoelectric responses of the ZnO NRs tactile sensors were characterized by the test system as shown in figure 2, which composed of a digital force gauge (Mark-10MS-200), charge amplifier, oscilloscope, DC power supply and data receiving computer terminal. Here, the charge amplifier is used to convert the charge signal generated by the ZnO NRs piezoelectric sensor into an output voltage. The tactile sensor was placed on the plate of a force gauge. When the sensor was pressed with a finger, the magnitude of pressing force was recorded by the force gauge. An oscilloscope along with the WaveForms software was used for acquiring and post-processing of the voltage response of the tactile sensor.

3. Results and discussion

3.1. ZnO NRs microstructure and defects

Figure 3 shows the cross-section SEM images of the aligned ZnO NRs synthesized on the seed-layer ZnO/PDMS substrates for the precursor solutions with different contents of AuNPs from 0 to 400 μL. SEM images revealed...
that the ZnO NRs were orderly arranged on the substrate regardless of the AuNPs content, well-oriented c axis with uneven surface, and uneven distribution of particle size. It can be analyzed from SEM images that the height distributions of ZnO NRs were shown in figures 3(b), (d), (f), (h), (j), respectively. The average height of AuNPs is

![Cross-sectioned SEM images and height distribution histograms of ZnO NRs for the precursor solutions with different contents of AuNPs.](image)

**Figure 3.** Cross-sectioned SEM images and height distribution histograms of ZnO NRs for the precursor solutions with different contents of AuNPs. (a), (b) no AuNPs, (c), (d) 100 μl AuNPs, (e), (f) 200 μl AuNPs, (g), (h) 300 μl AuNPs and (i), (j) 400 μl AuNPs.
only 815 nm for the precursor solution without adding AuNPs, while the average height of AuNPs increases to 1958 nm for the precursor solution with 100 μL AuNPs. However, when the amount of added AuNPs increases from 100 μL to 400 μL, the average height of ZnO NRs decreases from 1958 nm to 914 nm. This indicates that a small amount of AuNPs may promote the growth of ZnO NRs along c axis.

Figure 4 shows AFM images of the ZnO NRs with a scan area of 5 μm × 5 μm for the precursor solutions with different amounts of AuNPs. The average particle size and root-mean-square (RMS) surface roughness can be estimated from AFM images and summarized in Table 1. With the increase of the added AuNPs content, the average particle size and RMS surface roughness of the ZnO NRs are found to first increase and then decrease, exhibiting a maximal value, for the precursor solution with 300-μL AuNPs, which are 393.1 nm and 53.9 nm, respectively. For the precursor solution with 400-μL AuNPs, the reduction in the average particle size and RMS surface roughness of ZnO NRs are due to the inhibition of the growth of ZnO NRs caused by the excess AuNPs. The explanation can be further supported by the XRD analysis of the ZnO NRs. In addition, it's worth mentioning that the surfaces of ZnO NRs present an obvious wrinkle network structure regardless of whether the AuNPs are added in the precursor solution, which can be clearly observed in AFM images of the ZnO NRs for a large scan area (e.g. 15 μm × 15 μm) as shown in Figure 4(e). The wrinkle network structure arises from a crucial different in the thermal expansion coefficient between the ZnO SL and the PDMS substrate due to dynamic fluctuations of the temperature during sputtering deposition and hydrothermal growth processes. Fortunately, the ZnO NRs tactile sensor with the wrinkle network microstructure at the surface has an excellent perception to evaluate the surface roughness of detected objects.

Figure 5 shows the x-ray diffraction (XRD) patterns of the hydrothermally grown ZnO NRs for the precursor solutions with different contents of AuNPs. The strong and sharp diffraction peak near 2θ ~ 34.30° in the XRD patterns was clearly observed for all samples, which corresponds with the (002) plane of ZnO crystal, while the

| AuNPs content (μL) | Average height (nm) | Average diameter (nm) | RMS roughness (nm) | Aspect ratio |
|-------------------|---------------------|-----------------------|-------------------|-------------|
| 0                 | 815                 | 198.2                 | 25.6              | 4.1         |
| 100               | 1958                | 229.6                 | 39.7              | 8.5         |
| 200               | 1316                | 323.4                 | 40.3              | 4.1         |
| 300               | 952                 | 393.1                 | 53.9              | 2.4         |
| 400               | 914                 | 221.8                 | 34.3              | 4.1         |
The diffraction peaks corresponding with (101), (102), (103) and (202) planes are very weak, indicating that the aligned ZnO NRs were preferentially grown along the c-axis of the hexagonal wurtzite structure and perpendicular to the PDMS substrates. Whereas any diffraction peaks related to AuNPs are not observed. It is possible that the content of Au is so low that related peaks are covered by the peaks of ZnO or AuNPs are small enough to be wrapped in ZnO crystals. The average crystallite size of the ZnO NRs along the (002) peak is obtained by using Scherrer’s formula [26]:

\[
D = \frac{K\lambda}{\beta \cos \theta}
\]  

(1)

Where \( D \), \( \theta \), \( \lambda \), \( K \) and \( \beta \) represent the average crystallite size, Bragg diffraction angle, x-ray radiation wavelength, Scherrer constant \( (K = 0.89) \) and full width at half maximum (FWHM), respectively. Based on the (002) peak, the crystallite size of ZnO NRs can be calculated by using equation (2) for the precursor solution with different contents of AuNPs, as shown in table 2. The stress \( (\sigma) \) in the plane of the ZnO NRs film can be calculated using the following relations:

\[
\sigma = \left[ 2C_{13} - \frac{(C_{11} + C_{12})C_{33}^{NR}}{C_{13}} \right] \varepsilon_{zz}
\]  

(2)

The elastic constant \( (C_{33}^{NR}) \) of ZnO NRs can be expressed as:

\[
C_{33}^{NR} = \frac{0.99C_{33}}{(1 - \varepsilon_{zz})^2}
\]  

(3)

And:

\[
\varepsilon_{zz} = \frac{c - c_0}{c_0}
\]  

(4)

Where \( \varepsilon_{zz} \) is the strain in the lattice along the c-axis, and \( C_{ij} \) are elastic constants, for ZnO, \( C_{11}, C_{12}, C_{13} \) and \( C_{33} \) are 209.7 GPa, 121.1 GPa, 105.1 GPa and 210.9 Gpa, respectively [27], \( c \) and \( c_0 \) are the lattice constants of the ZnO NRs obtained from the XRD data and the standard lattice constant for unstrained ZnO (ICSD 01-074-0534: \( a_0 = 3.2495 \, \text{Å}, c_0 = 5.2069 \, \text{Å} \)), respectively. Table 2 summarizes the XRD peak position, FWHM value,
average crystallite size, and the stress $\sigma$ in the plane of the ZnO NRs film. It can be seen from table 2 that the half peak width corresponding to the (002) peak fluctuates with the increase of AuNPs content, in turn the values of 0.101°, 0.145°, 0.131°, 0.098° and 0.152°, and the corresponded crystallite sizes are 81.5 nm, 56.8 nm, 62.9 nm, 83.9 nm and 54.2 nm, respectively, which are significantly smaller than the particle sizes estimated from the AFM images of figure 4, indicating that a particle observed in AFM image may compose of multiple crystalline grains and hence the XRD-average crystallite size cannot be used for estimating the available particle size of the ZnO NRs film. In addition, according to the position of the (002) diffraction peak, the lattice parameter $c$ and stress $\sigma$ can be calculated for various AuNPs contents as also shown in table 2.

Structural and morphological changes of ZnO NRs with AuNPs content in the precursor solution can be explained as follows: when a small content (e. g. 100 $\mu$L of AuNPs) was added into the precursor solution, the grown rate of ZnO NRs along the c-axis direction was enhanced and so the lateral growth was restrained due to the catalysis effect of AuNPs, and thus resulting in a significant increase in the height of the ZnO NRs and a clear decrease in the crystallite size. Meanwhile, the stress in the plane of ZnO NRs film exhibits a compressive stress compared to the absent of AuNPs in the precursor solution (a tensile stress). The compressive stress is associated with interstitial oxygen, which was supported by PL spectrum of ZnO NRs, and has also been found in sputtered ZnO films by other workers [28]. With the content of AuNPs in the precursor solution was increased to 200 $\mu$L and 300 $\mu$L, the catalysis effect of the AuNPs is weakened, resulting in a slow growth in the c-axis direction and an enhancement in the lateral growth compared to the 100-$\mu$L AuNPs addition, so that the height of the ZnO NRs decreases and the crystallite size increases, while the compressive stress was weakened and even presents the tensile stress. However, as the content of AuNPs was increased to 400 $\mu$L, the catalytic effect of ZnO NRs may fail or even hinders the growth of ZnO NRs due to the aggregation of AuNPs, so both the height and crystallite size of ZnO NRs become smaller, and the stress is significantly released. Therefore, the longest height of ZnO NRs was obtained to be 1958 nm with the maximum aspect ratio of 8.1 for the 100-$\mu$L AuNPs addition.

Figure 6 shows the room-temperature photoluminescence (PL) spectra of the hydrothermally grown ZnO NRs on Si/ZnO/PDMS substrates under the photon excitation of 325 nm for different contents of AuNPs added in the precursor solution. Two emission bands were displayed in the UV and the visible regions, respectively. The UV emission is located at around 388 nm, which corresponded to the near-band-edge emission (NBE) of the ZnO wide band gap generated from the direct recombination of photo generated charge carriers [29], while the broad green emission between 450 and 700 nm centered at 560 nm is related to deep-level emission (DLE) of the ZnO band gap, which resulted from structural and intrinsic defects in ZnO NRs such as oxygen and zinc vacancies, as well as oxygen and zinc interstitials. The generated yellow emission near 560 nm is attributed to interstitial oxygen defects and Zn(OH)$_2$ groups which could leave a residue of the growth technique on the surface of the nanostructures during the hydrothermal synthesis of ZnO NRs [30].

The NBE peak intensity of the ZnO NRs from the free exciton recombination decreased with increasing the content of AuNPs in the precursor solution. Table 3 summarizes the NBE and DLE peak positions, FWHM of the NBE peak, and PL intensity ratio ($I_{NBE}/I_{DLE}$) of all samples, which were obtained by a double-peak Gaussian fitting method. the NBE and DLE peak positions of the ZnO NRs result in a red-shifted with the increase of the AuNPs content in the precursor solution. Normally, the intensity ratio of NBE peak to DLE peak ($I_{NBE}/I_{DLE}$) is
suitable for evaluating the concentration of structural defects in ZnO NRs \cite{31}. The highest $I_{\text{NBE}}/I_{\text{DLE}}$ is 1.83, which corresponds to the ZnO NRs grown in the precursor solution without adding AuNPs, and the $I_{\text{NBE}}/I_{\text{DLE}}$ decreases with the increase of AuNPs content. A possible cause is that the addition of AuNPs changes the nucleation process and growth orientation of ZnO crystal in hydrothermal chemical reaction, and thus results in an increase of the interstitial oxygen. However, the mechanism formation of interstitial oxygen is not clear and further investigated in detail in the future.

### 3.2. Voltage response of ZnO NRs sensors

Figure 7 shows the pressure response of the ZnO NRs tactile sensor for no AuNPs addition when the sensor is subjected to a transient pressure of 0.5 N generated by a finger press. The output voltage exhibits obvious switching behavior to the applied pressures. When the device is under a pressure, a negative voltage pulse signal appears instantly. However, there is no voltage generated when the pressure is retained. Afterwards, a positive voltage pulse signal is generated by the sensor instantly when the pressure is released. This phenomenon should be attributed to the incomplete releasing of ZnO NRs due to the rebounding of the PDMS material, resulting in a continued increase in the output voltage after the finger is lifted and detached from the top surface of the PDMS \cite{32}. During the process of pressing and releasing, the sensor is capable to convert the external force into electric signals. This switching behavior is in agreement with the working principle of piezoelectric energy harvesters and suggests that the ZnO NRs tactile sensor is suitable for detecting the dynamic strains other than the steady ones. Moreover, the electricity generated by the sensor has important application prospects for future self-powered devices.

The voltage response of the ZnO NRs tactile sensors for with and without AuNPs addition was investigated. Figure 8 shows the piezoelectric responses of the sensors for various contents of AuNPs added into the precursor solution under a tapping force of 0.5 N generated by human finger. The sensor for 100 $\mu$l AuNPs addition has the highest voltage peak of 797.9 mV, while the sensor for 300 $\mu$l AuNPs addition has the lowest voltage peak of

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**Table 3.** Summarized data from PL spectra of aligned ZnO NRs for different AuNPs contents.

| AuNPs content ($\mu$l) | NBE peak (nm) | DLE peak (nm) | FWHM (nm) | $I_{\text{NBE}}/I_{\text{DLE}}$ |
|------------------------|---------------|---------------|-----------|-------------------------------|
| 0                      | 386.25        | 561.65        | 29.59     | 1.83                          |
| 100                    | 387.84        | 566.93        | 25.28     | 0.44                          |
| 200                    | 388.97        | 568.93        | 25.43     | 0.32                          |
| 300                    | 389.24        | 569.25        | 27.29     | 0.36                          |
| 400                    | 395.13        | 570.59        | 22.12     | 0.27                          |
47.9 mV, which corresponds to the maximum and minimum aspect ratio of ZnO NRs, respectively. This is because the larger the aspect ratio, the larger the deformation of ZnO NRs generated by the same external pressure. It is worth noting that the voltage response of the sensor for 100 μl AuNPs addition is comparable to touch sensors fabricated using conventional silicon technology on non-flexible substrates \[33, 34\].

The voltage response of the ZnO NRs tactile sensors was also tested by applying variable force loads, ranging from 0.1 N to 1.0 N, figure 9 shows the voltage response of the sensors for the precursor solution with various contents of AuNPs under different tapping forces. The solid lines represent the linear fitting curves, which indicate that the sensors have good linearity between the load pressure and the output voltage within the measured range. The sensitivities calculated from the linear fitting curves are 534 mV N⁻¹, 1458 mV N⁻¹, 279 mV N⁻¹, 377 mV N⁻¹ and 382 mV N⁻¹ for the precursor solution with the AuNPs contents of 0 μl, 100 μl, 200 μl, 300 μl and 400 μl, respectively. Based on the above structural and morphology analyses of hydrothermally grown ZnO NRs, the high sensitivity of the sensor with 100 μl AuNPs addition is attributed to the large aspect ratio of ZnO NRs caused by the catalysis effect of AuNPs. However, excess AuNPs aggregates at the ZnO crystal boundary and produce a pinning effect on the domain wall and boundary, causing a deterioration in the crystallization of ZnO NRs and a decrease in the aspect ratio, and thus resulting in a reduce spontaneous polarization of ZnO NRs and exhibiting macroscopically reduced piezoelectric effect.

The impact of the frequency (strain rate) on the sensing performance is a key issue for practical applications. Figure 10 shows the output voltage signal generated by the ZnO NRs sensor for 100 μl AuNPs addition when the tapping frequency is changed from 4 to 7 Hz at fixed tapping force. It can be observed that the output voltage}

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**Figure 8.** Voltage response of the tactile sensors for various contents of AuNPs added into the precursor solution under a tapping force of 0.5 N generated by human finger press.

**Figure 9.** Piezoelectric voltage response of the tactile sensors for the precursor solution with different contents of Au NPs towards varying tapping forces.
generated by the piezoelectric effect of the sensor increases slightly with the tapping frequency. When the frequency increases from 4 to 7 Hz, the average peak-to-peak value of the output voltage ($V_{pp}$) increases from \(\approx 0.88\) to \(\approx 1.1\) V. According to the working principle of piezoelectric energy harvesters, the frequency-dependent sensing behavior could be explained by the fundamental piezoelectric theory. When the axial strain was induced in the ZnO NRs under an external force, the instant current in the external circuit ($i_{ex}$) would be generated to compensate for the piezopotential induced by the polarization charges. Suppose that the leakage current inside the device is ignored, $i_{ex}$ should be equal to the polarization charges generated by the piezoelectric effect per unit time ($q$), which can be expressed as

$$i_{ex} = q = d_{33} Y A S f$$

(5)

Where $d_{33}$, $Y$, $A$, $S$ and $f$ are the piezoelectric constant, Young’s modulus, the cross sectional area, the axial strain of the ZnO NRs and the tapping frequency, respectively. Our experimental result confirms that the output voltage generated by the sensors under the same strain (tapping force) increases linearly with the tapping frequency, which shows the agreement with the theoretical analysis.

3.3. Wearable application of ZnO NRs tactile sensor

Owing to the excellent flexibility, tailorability, hydrophobicity, biological compatibility, and elasticity of PDMS, the sensor can be easily designed into desirable size and integrated with wearable products. According to the excellent sensing performance of the ZnO NRs sensor for the 100 $\mu$l AuNPs addition, we further explore the practical application of detecting human movement such as bending/stretching motion of finger. In order to demonstrate the flexible and wearable potential to detect the human movements, the sensor is employed on the human finger joint to evaluate the sensing performance of bending/stretching of fingers as shown in inset of figure 11. Figure 11 exhibits the piezoelectric output voltage curves of the sensor under different bending states (small/large bending), respectively. The results reveal that the greater the bending angle of the finger, the greater the output voltage generated by the sensor. The sensor obtains a small output voltage of \(\approx 0.25\) V under small bending (the bending angle is about 25°), while the output voltage is \(\approx 0.52\) V under large bending (the bending angle is about 90°), as shown in the waveforms of the symbols 2 and 4 in figure 11, respectively. It can be explained that the ZnO NRs membrane experience more deformation under large bending state, resulting in higher output voltage. It is worth mentioning that the sensor integrates the functions of piezoelectric materials and the advantages of flexibility, biological compatibility, hydrophobicity, and wearing comfort, and so promoting the development of self-powered wearable smart devices.

Additionally, the high-performance sensor for the precursor solution with AuNPs of 100 $\mu$l can be used to distinguish various objects by sliding gently a finger attached the sensor on the surface of the object as shown in the inset of figure 12. Figure 12 shows the output voltage curves of the sensor when the finger slides gently left and right direction on the surface of desktop, glass dish and sponge thin board, respectively. The output voltage is only about 30 mV for the sliding action on the surface of the desktop, while the output voltage increases to 350 mV for the sliding action on the surface of the sponge thin board. This is because the surface of the sponge has a significantly higher roughness than that on the desktop, causing a larger friction force when the sliding action occurs due to the wrinkle network surface of the sensor (as shown in figure 4(e)), and thus resulting in a
higher output voltage. However, although the glass dish has a smoother surface than the desktop, the output voltage generated by sliding on the surface of the glass dish is about 280 mV, which is much higher than the output voltage generated by sliding on the surface of the desktop, and even close to that generated by sliding on the surface of the sponge. The result can be explained that despite the smooth surface of the glass dish, a significant adsorption force is produced in contact with the PDMS surface of the sensor, resulting in an obvious stretching behavior of ZnO NRs during the sliding movement. All in all, the sensor possesses the ability to distinguish various objects and monitor human movement.

4. Conclusions

In this work, a flexible tactile sensor with planar transverse electrodes was constructed by using a PDMS film as substrate, ZnO NRs as a piezoelectric layer, copper foil as the electrodes and PDMS as a package shell. ZnO NRs piezoelectric layers were prepared by a hydrothermal method on a flexible PDMS substrate with ZnO seed layer. The effects of the content of AuNPs in the precursor solution on the structural morphology of ZnO NRs and on the piezoelectric properties of the ZnO NRs tactile sensor were investigated by testing SEM, AFM, XRD and PL of ZnO NRs, and piezoelectric responses of the sensors, respectively. For the precursor solution added by AuNPs of 100 $\mu$l, the as-prepared sensor shows an excellent piezoelectric response with a high sensitivity of 1.42 V N$^{-1}$.
due to the large aspect ratio of ZnO NRs. Meanwhile, the sensor could be employed to distinguish various objects and detect human movements such as bending/stretching motion of finger. Therefore, the proposed tactile sensor can be adapted for constructing self-powered piezoelectric sensor and can be well utilized to monitor human information in real-time.

Acknowledgments

This work was supported in part by the National Natural Science Foundation of China (No. 61871195), the Natural Science Foundation of Guangdong Province (Nos. 2021A151011872, 2016A030313474).

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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