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Proceeding Paper

Effects of Catalysts on the Structure and Piezoelectric Properties of PVDF/ZnO Nanowires for the Robotic Tactile Sensor †

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Abstract: Polyvinylidene fluoride (PVDF)-coated ZnO nanorod piezoelectric sensors were prepared on silicone-based polymer polydimethylsiloxane (PDMS) substrates using a hydrothermal method. The effects of catalysts (sodium hydroxide, ammonium hydroxide, and hexamethylenetetramine) on the lattice microstructure and piezoelectric properties of ZnO nanorods were analyzed. The piezoelectric properties of polyvinylidene fluoride-coated ZnO nanorods' tactile sensors with different catalysts were measured under different forces. ZnO nanorods with hexamethylenetetramine have a high c-axis (002)-preferred orientation hexagonal wurtzite crystal structure with a maximum length of 5800 nm and an aspect ratio of 72.5. The Polyvinylidene fluoride/ZnO nanorod sensor with hexamethylenetetramine showed an excellent linear response to external pressure in the range of 0.1~1.2 N, and the best sensitivity is 61.1 mV/N.

Keywords: ZnO; PVDF; nanorods; piezoelectric

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1. Introduction

In recent years, there has been extensive research on tactile sensors for applications involving human skin, leading to their widespread adoption across various fields such as smart skin, wearable devices, the Internet of Things (IoT), and smart industries. Tactile sensors are categorized based on their physical mechanisms into piezoelectric, piezoresistive, capacitive, and photoelectric types. Among these, piezoelectric sensors have attracted considerable attention due to their numerous advantages, including high sensitivity, rapid response speed, low power consumption, and independence from external power sources [1–4]. The piezoelectric materials such as ZnO, $PbZr_xTi_{1-x}O_3$ (PZT), and polyvinylidene fluoride have been studied by many researchers and applied to tactile sensors due to their high piezoelectric and sensitivity properties [5–8]. However, PZT has limited applications because it contains lead. Polyvinylidene fluoride has good flexibility, high sensitivity, and softness properties, which are appropriate for wearable tactile sensors [9,10]. In addition, ZnO nanorods have gained widespread research interest due to their high sensitivity, good flexibility, and high piezoelectric coefficient [11,12].

Therefore, we combined ZnO nanorods and polyvinylidene fluoride for tactile sensor applications. The tactile sensors were prepared utilizing the high aspect ratio, large surface area, and excellent piezoelectric properties of ZnO nanorods and the high responsiveness and sensitivity of polyvinylidene fluoride to effectively convert the mechanical force into electrical signals. In this study, ZnO nanorods were synthesized on the flexible substrates using the hydrothermal method. The hydrothermal method is appropriate for preparing

ZnO nanostructures on polymer plastic substrates due to its simplicity, low cost, and low growth temperature. However, the crystal structure and morphology of ZnO nanorods are affected by processing parameters such as catalysts, solution concentration, temperature, and duration, which must be optimized. The crystal structure and morphology of ZnO nanorods can be improved by optimizing the conditions.

To further clarify the relationship between the microstructure and piezoelectric properties of ZnO nanorods and improve their piezoelectric properties, the effects of various catalysts (sodium hydroxide, ammonium hydroxide, hexamethylenetetramine) on the crystal structure and morphology of ZnO nanorods were analyzed. In this research, polyvinylidene fluoride was coated on the ZnO nanorod to form a polyvinylidene fluoride/ZnO nanorod tactile sensor. The effects of catalysts on the crystallization properties of the ZnO nanorods were studied, and the piezoelectric-sensing characteristics of polyvinylidene fluoride/ZnO nanorod tactile sensors with different catalysts were also investigated.

2. Materials and Methods

ZnO thin films were prepared as a seed layer on the polymer polydimethylsiloxane (PDMS) substrates using the sol–gel method. A homogeneous mixture of $Zn(C_2H_3O_2)_2{\cdot}2H_2O$ and $C_3H_8O_2$ was prepared at a concentration of 0.5 M and stirred at 60 °C for 3 h. The seed layer was then deposited onto the PDMS substrate using spin-coating at 3000 rpm for 30 s and was annealed at 600 °C for 2 min. ZnO nanorods were synthesized using the hydrothermal method using a zinc acetate solution (10 mM) mixed with sodium hydroxide (NaOH), ammonium hydroxide (NH_4OH), or hexamethylenetetramine ($C_6H_{12}N_4$) at 90 °C for 6 h. Subsequently, polyvinylidene fluoride films were deposited onto the ZnO nanorods using sol–gel and spin coating methods. PVDF powder was dissolved in N,N-dimethylformamide (DMF) solvent, and the solution was spin-coated onto the substrate surface. The polyvinylidene fluoride/ZnO nanorods were annealed at 90 °C for 1 h to remove the solvent and solidify the PVDF film. The copper electrodes adhered to both sides of the polyvinylidene fluoride film through conductive silver gel to form electrodes of the tactile sensor. Finally, the PDMS thin film with good flexibility was spin-coated on the PVDF thin film to complete the tactile sensor structure, as shown in Figure 1. The pressure was transferred to the piezoelectric layer using the PDMS thin film, protecting the sensor from damage by the external environment.

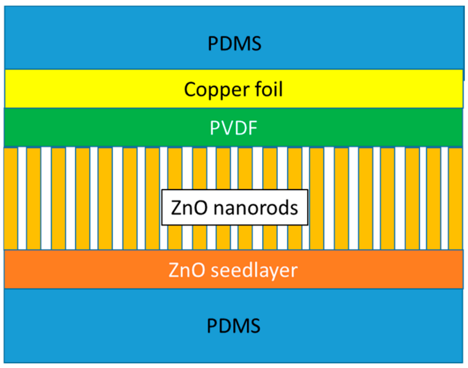

Figure 1. Structure of polyvinylidene fluoride/ZnO nanorod tactile sensor.

The lattice structure of ZnO nanorods was measured using an X-ray diffractometer (Rigaku Dmax 2200 X, Rigaku Corporation, Tokyo, Japan). The X-ray source is CuKα radiation (λ = 1.5418 Å), and the measurement angle range is 20–60°. The surface microstructure of ZnO nanorods was measured using a field emission scanning electron microscope (FE-SEM JEOL JSM-6700F, JEOL Ltd., Tokyo, Japan). The piezoelectric properties of PVDF/ZnO nanorod tactile sensors were measured using a charge amplifier to convert the pressure-generated charge signal into an output voltage. The experiment involved placing a polyvinylidene fluoride/ZnO nanorod tactile sensor on the measuring plate of a digital force gauge. When pressure was applied to the sensor with a finger, the force exerted was recorded using the digital force gauge. Simultaneously, the output voltage waveform of the tactile sensor was measured using a digital oscilloscope and was subsequently subjected to post-processing.

3. Results and Discussion

Figure 2 shows the X-ray diffraction crystallinity comparison of ZnO nanorods prepared with different catalysts (sodium hydroxide, ammonium hydroxide, and hexamethylenetetramine). All XRD patterns showed a hexagonal wurtzite structure and a strong c-axis orientation along the (002) plane (JCPDS card number 36-1451). ZnO nanorods with hexamethylenetetramine have the highest (002) diffraction peak intensity and exhibit excellent crystallinity compared with other samples. The catalyst impacted the crystallinity and structural properties of the ZnO nanorods. Hexamethylenetetramine promoted favorable nucleation and growth conditions for ZnO crystallization than sodium hydroxide and ammonium hydroxide catalysts.

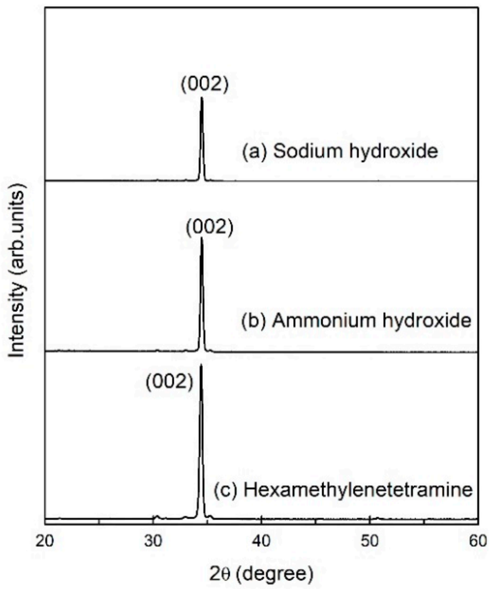

Figure 2. X-ray diffraction pattern of ZnO nanorods with catalysts of (**a**) sodium hydroxide, (**b**) ammonium hydroxide, and (**c**) hexamethylenetetramine.

Figure 3a–c shows the plane SEM images of the ZnO nanorods with sodium hydroxide, ammonium hydroxide, and hexamethylenetetramine, and Figure 3d presents the cross-sectional SEM image of ZnO nanorod with hexamethylenetetramine. The parameters of the average diameter, aspect ratio, and length of the ZnO nanorods are presented in Table 1. The average diameters of ZnO nanorods with sodium hydroxide, ammonium hydroxide, and hexamethylenetetramine catalysts are 40, 60, and 80 nm, respectively. The average lengths for sodium hydroxide, ammonium hydroxide, and hexamethylenetetramine were 1250, 3800, and 5500 nm, respectively. The average diameter, length, and aspect ratio of the ZnO nanorods with hexamethylenetetramine were the largest. This is because when hexamethylenetetramine was added to the aqueous solution, it was cleaved to form amines and provide OH groups to nucleate ZnO on the surface of the ZnO seed layer. Moreover, the amine cleavage rate of hexamethylenetetramine was slowed, and the pH value of the aqueous solution changed little, resulting in a low concentration of metal ion complexes [13]. Therefore, the nucleation reaction of ZnO was carried out at low supersaturation, which facilitated heterogeneous growth and made ZnO crystals easily grow into nanorods [14]. When sodium hydroxide and ammonium hydroxide catalysts were added to aqueous solutions, the pH of the solution changed significantly, resulting in high concentrations of metal complexes. ZnO enabled uniform nucleation, resulting in smaller diameters and lengths of nanorods [15].

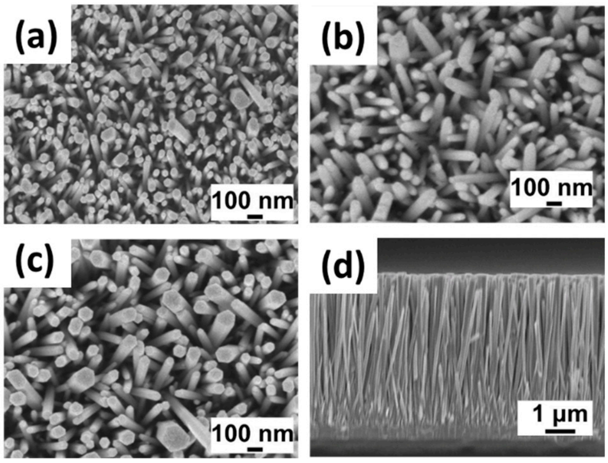

Figure 3. Plane SEM images of ZnO nanorods with the catalysts of (**a**) sodium hydroxide, (**b**) ammonium hydroxide, and (**c**) hexamethylenetetramine, and the cross-sectional SEM images of ZnO nanorods with hexamethylenetetramine (**d**).

Table 1. Structure parameters of ZnO nanorods with different catalysts.

Catalysts	Length (nm)	Diameters (nm)	Aspect Ratio
Sodium hydroxide	1250	40	31.3
Ammonium hydroxide	3800	60	63.3
Hexamethylenetetramine	5800	80	72.5

To measure the piezoelectric response of the nanorod tactile sensor, the charge signal generated by the sensor was converted into an output voltage using a charge amplifier, which was then captured and processed using a digital oscilloscope. Figure 4a–c shows the piezoelectric voltage of the PVDF/ZnO nanorod sensor with sodium hydroxide, ammonium hydroxide, and hexamethylenetetramine. The piezoelectric voltage peaks of the ZnO nanorod tactile sensors with sodium hydroxide, ammonium hydroxide, and hexamethylenetetramine were measured at 10, 35, and 53 mV, respectively, under a force of 1 N. The polyvinylidene fluoride/ZnO nanorod tactile sensor with hexamethylenetetramine showed a maximum voltage peak amplitude of 61 mV, as shown in Figure 4d, as the enhanced radial stress of ZnO nanorods with hexamethylenetetramine had the largest aspect ratio of 72.5 under the same pressure, resulting in enhanced piezoelectric displacement on the Z-axis of the nanorods [16]. In addition, when the piezoelectric polymer polyvinylidene fluoride film was coated on the ZnO nanorods, the voltage peak of the tactile sensor also increased. This was attributed to the fact that polyvinylidene fluoride is a piezoelectric material that can generate electrical charges in response to mechanical stress or pressure and increase the sensitivity of tactile sensors. ZnO nanorods enhanced the piezoelectric output of polyvinylidene fluoride films. This phenomenon has been reported in prior research, which the piezoelectric enhancement output of the polyvinylidene fluoride/ZnO nanorod structure was attributed to the synergistic effect of both polyvinylidene fluoride and ZnO nanorods [17–19]. The combination of ZnO nanorods and polyvinylidene fluoride film enhanced the overall responsiveness and performance of the tactile sensor when pressure is applied to the sensor [20].

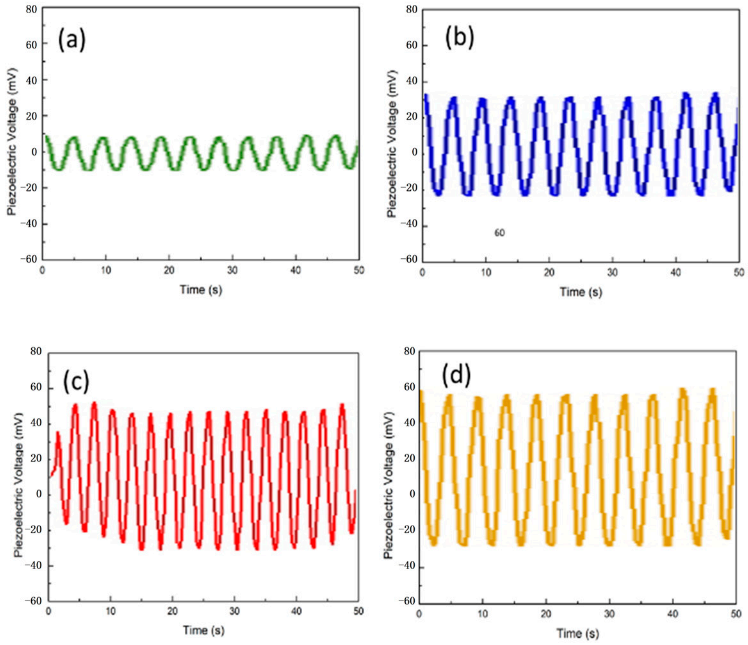

Figure 4. Comparison of piezoelectric sensing voltages of the ZnO nanorods tactile sensors with (**a**) sodium hydroxide, (**b**) ammonium hydroxide, (**c**) hexamethylenetetramine, which (**d**) is the polyvinylidene fluoride/ZnO nanorods with hexamethylenetetramine.

Figure 5 illustrates the influence of various catalysts on the voltage response of the polyvinylidene fluoride/ZnO nanorod tactile sensors across a range of external forces from 0.1 to 1.1 N. The corresponding voltage peak amplitudes in the dynamic piezoelectric response waveform of the tactile sensor are extracted upon the application of different forces. The voltage response of all tactile sensors exhibits a linear increase with rising pressure. The output voltages and sensitivities of the polyvinylidene fluoride/ZnO nanorods tactile sensors with different catalysts are shown in Table 2. The sensitivities of polyvinylidene fluoride/ZnO nanorod tactile sensors with sodium hydroxide, ammonium hydroxide, and hexamethylenetetramine are 31.8, 39.6, and 61.1 mV/N respectively. The polyvinylidene fluoride/ZnO nanorod tactile sensor with hexamethylenetetramine achieves a high sensitivity of 61.1 mV/N. Compared with sodium hydroxide, the sensitivity of ZnO nanorods with hexamethylenetetramine increased by about 2-fold. This was attributed to the significant aspect ratio c-axis orientation of ZnO nanorods with hexamethylenetetramine.

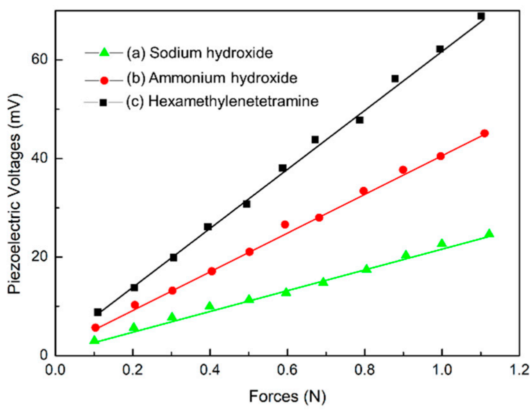

Figure 5. Piezoelectric sensing voltage of the polyvinylidene fluoride/ZnO nanorods tactile sensors with different catalysts under different pressures.

Table 2. Comparison of piezoelectric sensing voltage and sensitivity of the polyvinylidene fluoride/ZnO nanorods tactile sensors.

Catalysts	Piezoelectric Sensing Voltages (mV)	Sensitivity (mV/N)
Sodium hydroxide	22	31.8
Ammonium hydroxide	40	39.6
Hexamethylenetetramine	61	61.1

4. Conclusions

The polyvinylidene fluoride/ZnO nanorod piezoelectric tactile sensors were prepared on PDMS substrates using the hydrothermal method to study the effects of catalysts (Sodium hydroxide, Ammonium hydroxide, and Hexamethylenetetramine) on the lattice structure and surface microstructure of ZnO nanorods. The largest diameter, length, and aspect ratio of the ZnO nanorods were obtained using hexamethylenetetramine. The polyvinylidene fluoride/ZnO nanorod's tactile sensor with hexamethylenetetramine showed a maximum voltage peak of 61 mV and sensitivity of 61.1 mV/N, which was attributed to the high aspect ratio of the ZnO nanorod and the coating of polyvinylidene fluoride. The prepared polyvinylidene fluoride/ZnO nanorod piezoelectric tactile sensor has great potential for applications in robot tactile sensing and wearable devices.

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References

1. Kumar, V.S.; Krishnamoorthi, C. Development of electrical transduction based wearable tactile sensors for human vital signs monitor: Fundamentals, methodologies and applications. *Sens. Actuators A Phys.* **2021**, *321*, 112582–112623. [CrossRef]
2. Tang, Z.J.; Wang, Z.; Lu, J.Q.; Ma, N.Q. Design of robot finger based on flexible tactile sensor. *Int. J. Adv. Robot. Syst.* **2019**, *16*, 1–10. [CrossRef]
3. Lepora, N.F.; Church, A.; de Kerckhove, C.; Hadsell, R.; Lloyd, J. From pixels to percepts: Highly robust edge perception and contour following using deep learning and an optical biomimetic tactile sensor. *IEEE Robot. Autom. Lett.* **2019**, *4*, 2101–2107. [CrossRef]
4. Wu, C.X.; Kim, T.W.; Park, J.H.; Koo, B.; Sung, S.Y.; Shao, J.J.; Zhang, C.; Wang, Z.L. Self-powered tactile sensor with learning and memory. *ACS Nano* **2020**, *14*, 1390–1398. [CrossRef] [PubMed]
5. Zhu, L.; Xiang, Y.; Liu, Y.; Geng, K.; Yao, R.; Li, B. Comparison of piezoelectric responses of flexible tactile sensors based on hydrothermally-grown ZnO nanorods on ZnO seed layers with different thicknesses. *Sens. Actuators A Phys.* **2022**, *341*, 113552. [CrossRef]
6. Misra, M.; Srivastava, A.K.; Kadam, A.N.; Salunkhe, T.T.; Kumar, V.; Nikalje, A.P.G. Substantial enhancement of optoelectronics and piezoelectric properties of novel hollow ZnO nanorods towards efficient flexible touch and bending sensor. *Colloids Surf. A Physicochem. Eng.* **2024**, *685*, 133232. [CrossRef]
7. Hari, M.A.; Karumuthil, S.C.; Rajan, L. Optimization of PVDF nanocomposite based flexible piezoelectric tactile sensors: A comparative investigation. *Sens. Actuators A Phys.* **2023**, *353*, 114215.
8. He, H.; Fu, Y.; Zang, W.; Wang, Q.; Xing, L.; Zhang, Y.; Xue, X. A flexible self-powered T-ZnO/PVDF/fabric electronic-skin with multi-functions of tactile-perception, atmosphere-detection and self-clean. *Nano Energy* **2017**, *31*, 37–48. [CrossRef]

9. Yang, J.; Chen, Q.S.; Xu, F.; Jiang, H.X.; Liu, W.L.; Zhang, X.Q.; Jiang, Z.X.; Zhu, G.D. Epitaxy enhancement of piezoelectric properties in P(VDF-TrFE) copolymer films and applications in sensing and energy harvesting. *Adv. Electron. Mater.* **2020**, *6*, 1–13. [CrossRef]
10. Siponkoski, T.; Nelo, M.; Palosaari, J.; Per¨antie, J.; Sobocinski, M.; Juuti, J.; Jantunen, H. Electromechanical properties of PZT/P(VDF-TrFE) composite ink printed on a flexible organic substrate. *Compos. B Eng.* **2015**, *80*, 217–222. [CrossRef]
11. Tan, Y.S.; Yang, K.; Wang, B.; Li, H.; Wang, L.; Wang, C.X. High-performance textile piezoelectric pressure sensor with novel structural hierarchy based on ZnO nanorods array for wearable application. *Nano Res.* **2021**, *14*, 3969–3976. [CrossRef]
12. Yang, T.; Pan, H.; Tian, G.; Zhang, B.; Xiong, D.; Gao, Y.; Yan, C.; Chu, X.; Chen, N.; Zhong, S.; et al. Hierarchically structured PVDF/ZnO core-shell nanofibers for self-powered physiological monitoring electronics. *Nano Energy* **2020**, *72*, 104706–104711. [CrossRef]
13. Govender, K.; Boyle, D.S.; Kenway, P.B.; O'Brien, P. Understanding the factors that govern the deposition and morphology of thin films of ZnO from aqueous solution. *J. Mater. Chem.* **2004**, *14*, 2575–2591. [CrossRef]
14. Greene, L.E.; Law, M.; Goldberger, J.; Kim, F.; Johnson, J.C.; Zhang, Y.; Saykally, R.J.; Yang, P. Low-temperature wafer-scale production of ZnO nanorods arrays. *Angew. Chem. Int.* **2003**, *42*, 3031–3034. [CrossRef] [PubMed]
15. Vayssieres, L.; Keis, K.; Hagfeldt, A.; Lindquist, S. Three-dimensional array of highly oriented crystalline ZnO microtubes. *Chem. Mater.* **2001**, *13*, 4395–4398. [CrossRef]
16. Deng, W.; Jin, L.; Zhang, B.; Chen, Y.; Mao, L.; Zhang, H.; Yang, W. A flexible fieldlimited ordered ZnO nanorod-based self-powered tactile sensor array for electronic skin. *Nanoscale* **2016**, *8*, 16302–16306. [CrossRef] [PubMed]
17. Bhunia, R.; Das, S.; Dalui, S.; Hussain, S.; Paul, R.; Bhar, R.; Pal, A.K. Flexible nano-ZnO/polyvinylidene difluoride piezoelectric composite films as energy harvester. *Appl. Phys. A Mater.* **2016**, *122*, 637. [CrossRef]
18. Lee, M.; Chen, C.Y.; Wang, S.; Cha, S.N.; Park, Y.J.; Kim, J.M.; Chou, L.J.; Wang, Z.L. A Hybrid Piezoelectric Structure for Wearable Nanogenerators. *Adv. Mater.* **2012**, *24*, 1759–1764. [CrossRef] [PubMed]
19. Ramadoss, A.; Saravanakumar, B.; Lee, S.W.; Kim, Y.S.; Kim, S.J.; Wang, Z.L. Piezoelectric-Driven Self-Charging Supercapacitor Power Cell. *ACS Nano* **2015**, *9*, 4337–4345. [CrossRef] [PubMed]
20. Fraleoni-Morgera, A.; Cesini, I.; Kumar, P.; Oddo, C.M. Hydrothermally grown ZnO nanorods as promising materials for low cost electronic skin. *ChemNanoMat* **2020**, *6*, 15–31. [CrossRef]