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Fabrication and piezoelectric-pyroelectric properties of electrospun PVDF/ZnO composite fibers

Guo-Yi Li, Hong-Di Zhang®, Kun Guo, Xing-Sheng Ma and Yun-Ze Long®

Collaborative Innovation Center for Nanomaterials & Optoelectronic Devices, College of Physics, Qingdao University, Qingdao 266071, People’s Republic of China

E-mail: hongdi_zhang@163.com

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Abstract

Piezoelectric materials such as ZnO semiconductors and polyvinylidene fluoride (PVDF) have been extensively studied to produce flexible wearable devices, providing a viable method for energy collection. In this study, PVDF was mixed with ZnO nanoparticles to prepare PVDF/ZnO devices by electrospinning. The composite ZnO affects the diameter of electrospun fibers and the output performance of the devices. As ZnO was added, the diameter of the fibers decreases, but the output current of the devices increases. Moreover, compared with pristine PVDF, the bending output current and pyroelectric current of the devices were improved after mixed with ZnO. The results indicated that PVDF/ZnO composite was a promising flexible device that can provide power for small electronic devices.

1. Introduction

In recent years, with the rapid development of industry, the demand for fossil fuels is increasing. Due to the limited amount of fossil fuel energy and the increase of people’s awareness of current environmental energy conservation and protection, the development of alternative energy sources is urgently needed. At present, devices that can collect energy from the natural environment have been developed, for example, devices that use clean energy such as solar, wind, mechanical or thermal energy [1]. As new devices, they can be used to provide power to a variety of small electronic devices [2]. Piezoelectric materials such as ZnO [3–6], InN [7], GaN [8], CdS [9], and ZnS [10] can achieve energy collection by manufacturing devices, but the production conditions of devices made from such materials alone are relatively high, and such materials are brittle. It is difficult to integrate with flexible materials [11]. Another class of materials that can be used to harvest energy is piezoelectric polymers. Among them, PVDF have been widely concerned due to large piezoelectric coefficient, flexibility, chemical stability, and physical stability. They are used to prepare wearable devices and high sensitivity sensor [12, 13].

As we all know, PVDF is a four-crystalline phase polymer: α, β, γ, and δ phases [14]. Among them, α phase is the most abundant natural mode of PVDF, but only β phase has a piezoelectric property because of its polar crystalline-electroactive nature. In order to obtain the piezoelectric PVDF, the β-phase formation in PVDF is essential. Electrospinning is a method to directly and continuously produce PVDF nanofibers. [15, 16]. The forming of electrospun fibers is a very short process, involving chemistry, rheology, fluid mechanics, aerodynamics, classics and other disciplines [17, 18]. The typical electrospinning system includes a propulsion pump, a high voltage power supply, a special syringe, and a collector of aluminum foil as substrate. The positive electrode of the high voltage power supply is collected with the syringe containing spinning solution and the negative one linked to the collector. As the electrospinning process, the charged solution jets are extruded from the cone and continuous as spun fibers are formed under an electric field [19, 20]. Compared with spray deposition, electrospinning has the advantage that PVDF fibers can be prepared, and PVDF fibers are mostly in β phase [6]. However, the sample prepared by spray deposition is in the form of droplet and cannot form the fiber membrane structure.
There have been studies on the piezoelectric performance of PVDF and its composites. Mansouri et al. [21] studied the effect of zinc oxide nanoparticles on the morphology of polymer fibers and on the output power of the resulting synthesized devices. They found that well-formed nanofibers could be formed at low concentrations of PVDF and nano-zinc oxide particles. In the test of the prepared devices, it was found that the devices with uniform morphology and good tensile properties had higher output performance. Bafqi et al. [11] showed that adding ZnO nanoparticles to polymer solutions improved the crystalline structure of the polymer. Moreover, the addition of ZnO nanoparticles can significantly increase the output voltage of the device.

In this paper, ZnO nanoparticles were added into PVDF polymer precursor solution, and the fiber mats were synthesized by classical electrospinning. Periodic impact force was applied to the mats through various actions, and the influence of ZnO nanoparticle concentrations on device output performance was measured. Furthermore, the pyroelectric properties of PVDF/ZnO composite fibers were also reported here.

2. Experimental

The poly (vinylidene fluoride) (PVDF)/ZnO hybrid nanofibers were fabricated by electrospinning. N, N-Dimethylformamide (DMF, Merck Chem. Co.) and acetone (Merck Chem. Co.) were first mixed 1:1 by weight. Then 3, 5 and 10 wt% ZnO nanoparticles (Shanghai Hansi Chemical Industry Co. Ltd) with average particle size of about 30 nm were added and then sonicated for 3 h. Finally 22 wt % PVDF powder (Mₙ 550,000, Aladdin Co.) was dissolved in the resulting solution. The white homogeneous solution was used for electrospinning under the conditions of the electrospinning distance of 12 cm between the spinneret and aluminum foil collector, and electrospinning voltage (High voltage power supply module, Dongwen Tianjin) of 24 kV. A pristine PVDF solution was also fabricated with the same concentration and then electrospun under the same conditions. The collected PVDF/ZnO and pristine PVDF nanofiber membranes were stored in drying cabinet for further use.

To fabricate the device, firstly, a piece of rectangular sample with size of 3 cm × 3 cm was cut from the nanofiber membrane, and sandwiched with two aluminium foil as electrodes. Secondly, two copper foil tapes were pasted on the two aluminium foil electrodes, respectively, as top output electrodes. Finally, the device was covered with polysimethylsiloxane (PDMS) soft insulating film to complete the device (pristine PVDF and 5 wt% ZnO - PVDF devices).

The morphologies of the resultant nanofiber membranes were characterized by SEM (Hitachi, TM-1000). The internal structure of the fibers was analyzed by transmission electron microscopy (TEM). The composition and structure were measured by Labram Infinity spectrometer (Raman, Jobin Yvon S.A.) In order to provide pressure on the device, we used homemade pressure equipment, which could exert periodic impact force. In order to provide temperature, a flexible commercial polyimide heater served to quickly change the temperature of the device. Current-time (I-t) characteristic curves were measured using a source meter (Keithley 6487).

3. Results and discussion

Since the output performance of the device is related to the morphology of the synthetic fiber, we need to choose the device with good fiber morphology of uniform thickness and smooth surface). SEM images can be used to represent the morphology of samples. Figures 1(a), (b) are respectively the SEM images of the pristine PVDF electrospun fibers and the PVDF/ZnO electrospun fibers. Among them, the diameter of pristine PVDF electrospun fibers is about 1.2 μm−1.5 μm, the diameter of PVDF/ZnO electrospun fibers is about 0.8 μm − 1.0 μm., the thickness of the film is about 100 μm. When ZnO is mixed with PVDF, the diameter of electrospun fiber decreases. Because when ZnO is added to the solution, the conductivity of the solution increases, which has a significant effect on the diameter of the fiber. The solution with high conductivity has stronger charge-carrying capacity than the solution with low conductivity, which will make the jet of the solution with high conductivity subject to greater tensile force of electric field. When the conductivity of the solution is very low, the jet cannot be fully stretched. Increasing the conductivity of the solution can reduce the diameter of the fibers.

Figure 1(c) shows the TEM image of a single PVDF/ZnO electrospun fiber which indicates that ZnO nanoparticles are distributed inside the fiber. In addition, it can be found from the TEM image that ZnO nanoparticles do not exist as single particles in the electrospun fiber, because the surface activity of ZnO nanoparticles is strong and agglomeration phenomenon occurs between particles. But this agglomeration does not affect the piezoelectric properties of ZnO nanoparticles. Further, in order to confirm ZnO nanoparticles in the nanofibers, EDX energy spectrum analysis is required. EDX is a highly sensitive surface analysis technique that can determine the element composition of a substance. Figure 1(d) shows the energy spectrum analysis diagram of PVDF/ZnO composite fiber. It can be clearly seen that the elements are mainly fluorine, zinc and copper. Among them, fluorine is contained in PVDF, copper is contained in the copper mesh used for TEM
measurement, and zinc is contained in the doped ZnO. Therefore, the ZnO nanoparticles are wrapped in the PVDF fibers, which is consistent with the result of TEM measurement.

Raman spectroscopy has its own unique advantage for studying nanofibers because it can provide information on the molecular level of the fibers. Figure 2 shows the Raman spectra of ZnO nanoparticles, PVDF powder, PVDF fibers and PVDF/ZnO nanofibers. Figure 2(a) shows that the sharp narrow peak at 438 cm\(^{-1}\) is characteristic of mode for the hexagonal phase of ZnO. Figure 2(b) shows the characteristic peaks of the \(\alpha\) phase at 280 cm\(^{-1}\), 410 cm\(^{-1}\), 605 cm\(^{-1}\) and 795 cm\(^{-1}\). Figure 2(c) shows the characteristic peaks of the \(\beta\) phase occur at 265 cm\(^{-1}\), 443 cm\(^{-1}\), 527 cm\(^{-1}\) and 845 cm\(^{-1}\) for PVDF electrospun fibers, which indicates that electrospinning technology is an effective way to induce PVDF transformation from \(\alpha\) phase to \(\beta\) phase. Moreover, in the Raman spectra of PVDF/ZnO electrospun fibers (as shown in figure 2(d)), the peaks of

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**Figure 1.** (a) SEM images of pristine PVDF electrospun fibers, (b) PVDF/ZnO electrospun fibers, (c) TEM image of PVDF/ZnO electrospun fiber, (d) Energy spectrum analysis image.

**Figure 2.** Raman spectrums of (a) ZnO; (b) PVDF powder; (c) electrospun PVDF fibers; (d) PVDF/ZnO electrospun fibers.
characteristic peaks of PVDF phases at 310 cm$^{-1}$, 518 cm$^{-1}$ and 830 cm$^{-1}$ were significantly higher than those of pristine PVDF fibers, which indicate that adding ZnO nanoparticles can promote the transformation of PVDF from $\alpha$ phase to $\beta$ phase in the process of electrospinning. Therefore, ZnO nanoparticles can promote the piezoelectric property.

The output current can directly represent the performance of the device. So measuring the output current of the device is important to characterize the piezoelectric properties of the materials. During the test, we used the self-made pressure device to exert a constant force of 5 N on the device and maintain the impact of the device at a frequency of 0.4Hz. Figures 3(a)–(b) shows the schematic of the device structure and the diagram of piezoelectric test. It can be seen from figures 3(c)–(f), the output performance of the device was improved when ZnO nanoparticles were added. The peak output current of the pristine PVDF device was about 160 nA, and the effective value was about 110 nA. When combined with ZnO, the maximum output current of the device is 45 $\mu$A, and its RMS is about 30 $\mu$A. Increased output current per unit area device from 12 nA to 3.3 A. The peak output voltage of the pristine PVDF device was 1.7V, and the effective value was about 1.2V. When ZnO is mixed, the peak value of output voltage increases to 4.4V, and the effective value is 3.1V. The output voltage of the unit area device is increased from 0.133V to 0.344V. When ZnO nanoparticles were added, ZnO nanoparticles can act as nucleating agent and generate strong local interactions on the contact surface with PVDF, thus promoting the $\beta$ phase transformation in PVDF. During pressing, electron transfer from the bottom electrode to the top occurs to balance the induced charge. As the device moves from the pressed state to the straightened state, the mechanical strain gradually decreases and the electrical polarization gradually recovers, resulting in the reverse motion of the electron [22]. During this pressure test, the input power of the device to the device can be calculated by the following formula:

$$P_1 = \frac{FL}{15}$$

$F$ is the external force, $L$ is the compression amount when the device is subjected to external force (12.5 $\mu$m), $T$ is the acting time (0.25s), and $S$ is the device area. The input power of the device is $2.8 \times 10^{-5}$ W cm$^{-2}$. The output power of the device can be calculated from the electric power, namely $P_2 = 1.03 \times 10^{-5}$ W cm$^{-2}$. The working efficiency of the device can be calculated from the following formula:

$$\eta = \frac{P_1}{P_2}$$

That is, the working efficiency of the device is about 36.8%.
Table 1 shows the output currents of various ZnO nanostructured devices. It can be seen clearly that compared with the previously reported ZnO devices, the devices made of electrospun PVDF/ZnO in this study have obvious advantages.

The flexural and pyroelectric properties of PVDF/ZnO complex were also investigated and the same phenomenon was found, that is, the addition of ZnO nanoparticles promoted the output performance of the device during flexural and pyroelectric testing.

Figure 4 (a) is the schematic diagram of the bending test of the device. The results are shown in figures 4(b)–(e). The bending test frequency is 0.75Hz. The maximum output current of the device prepared by pristine PVDF was 4.5 nA when the device was bent, its effective value is 3 nA. After PVDF is compounded with ZnO, the maximum output current increased to 15 nA, and the effective value was 10 nA. The output current density of the device increased from 0.33 nA to 1.11 nA. During bending test, after mixing ZnO, the maximum output voltage of the device increased from 0.29 V to 0.71 V, and the effective value increased from 0.2 V to 0.5V. Output voltage per unit area device increased from 0.022 V to 0.056 V. At this point, the output power of the device is 0.56 nW cm\(^{-2}\). Under bending, most of the fibers in the device would be stretched lengthwise, which caused the fiber to generate a piezoelectric potential, accumulating an electric charge on top and bottom of the aluminium foil. Conversely, as the bending ended and the sample returned to its original state, the electrons on the aluminium foil moved in the opposite direction, producing an electric current and form a potential difference [23].

The change in thickness of nanofiber membrane is much greater by applying pressure directly than by bending. Therefore, when applying pressure directly on the device, the polarization change of the fiber in the

| Shape of the ZnO nanostructure | Area of NG (cm\(^2\)) | Working mode | output power | Reference |
|-------------------------------|-----------------------|--------------|--------------|-----------|
| ZnO nanoparticles             | 9                     | Mechanical impact | 10\(\mu\)W | present work |
| ZnO nanorods                  | 4                     | finger tapping  | 11.31\(\mu\)W | [8]       |
| ZnO nanoparticles             | 1                     | vibrational force | 32nW | [4]       |
| ZnO nanorods                  | 15                    | compression    | 78nW | [13]      |
device is much greater than that in bending. Therefore, the output current of directly exerting pressure on the device is greater than that of bending.

Figure 5(a) shows the schematic diagram of pyroelectric test and its test frequency is 0.2Hz. Figures 5(b)–(c) shows that the maximum pyroelectric output current of pristine PVDF is 1.2 nA (Its effective value is 0.8 nA), while the maximum output current after composite with ZnO is 3 nA (Its effective value is 2 nA). Output current per unit area increased from 0.089nA to 0.222 nA. The output voltage increased from 45 mV to 82 mV, the effective value increased from 31.8 mv to 58 mV, and the output voltage per unit area increased from 3.5 mV to 6.44 mV. When the device was heated, the temperature raised and the molecular thermal motion was very intense. The amplitude of the dipole oscillation in the fiber increased, thus reduced the spontaneous polarization strength inside the fiber, which resulted in the change of the bound charge on the material surface. The free charge on the aluminum electrode is then redistributed to compensate for the change in the bound charge, causing the thermal current to flow.

4. Conclusion

In conclusion, the PVDF/ZnO fiber composites was successfully prepared. The ZnO nanoparticles promoted the conversion of PVDF from $\alpha$ phase to $\beta$ phase in the process of electrospinning. In addition, through three different tests including pressing, bending and heating, the transverse comparison shows that the current change of the composite material is most sensitive to the pressing type, and the output current is also the largest. The piezoelectric-pyroelectric properties of electrospun composite fibers were improved with mixed ZnO nanoparticles.

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ORCID iDs

Hong-Di Zhang @ https://orcid.org/0000-0002-8240-8602

Yun-Ze Long @ https://orcid.org/0000-0003-3732-3324

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