Effect of electrode material on piezoelectric output of PVDF sensor with electrospun nanofiber web

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Abstract

The electrospun PVDF (Polyvinylidene Fluoride) nanofiber web is commonly agreed on a kind of new sensitive materials for the sensor testing the dynamic pressure and energy harvesting, and has the characteristics of fast response and high sensitivity of pressure. As a result of the nanofiber web, it must be packaged to collect piezoelectric charge and bear strong mechanical behavior before industrial practice. The packaging of PVDF nanofiber web is usually sandwiched by incorporating a pair of flexible electrode. However, the effects of the surface and mechanical properties of electrodes such as morphology, roughness and compressibility have not been well investigated yet. This work will introduce three common types of packaging electrode materials (adhesive copper foil tape, indium tin oxide (ITO) thin film, adhesive conductive cloth.) in previously published literatures, compares the piezoelectric output of their sensor prototypes under a periodic impact, and discusses the effect of surface morphology, electrical resistance, and compressibility. The results showed that it has higher output of PVDF piezoelectric sensor packaged by electrode materials with the smooth surface and low mechanical compressibility. This result provides a guideline for designing the textile electrode material for the PVDF nanofiber web. Copyright © 2018 VBRI Press.

Key words: PVDF, electrospinning, nano-fiber web, piezoelectric, electrode.

Introduction

Earlier research demonstrated the feasibility of the electrospun PVDF (Polyvinylidene Fluoride) and its copolymer web as a material for sensors and actuators, which have the characteristics of fast response, high sensitivity and wide range of pressure, etc. [**1-4**]. These works mainly focused on the preparation processes of PVDF nanofiber web [**5-7**] as well as their effect on the piezoelectric properties, and few discussed the influence of the web size[**8**].

However, the process conditions during fabrication of the sensor and actuator devices greatly determine their performance. The PVDF nanofiber web is a sheet of nano-level fiber ensembles produced by electrospinning technology, and generally has weak tensile and shear strength. To fabricate sensor and actuator devices on the base of electrospun PVDF nanoweb, the web is indispensably sandwiched between two pieces of electrodes as well as protective or insulate layers. The assembled piezoelectric devices produced high outputs and were applied to mechanical generators and sensors. As the electrode materials, sometimes, the out layers sandwiched between PVDF nanoweb work as both the electrode and the protective matrix. The position of electrodes on the PVDF sample has been observed to have a great influence on the piezoelectric response of devices[**9**].

To evaluate the piezoelectric properties of PVDF nanofiber web, different electrode materials in previous studies have been adopted to fabricate device prototype. PVDF web is sandwiched between two pieces of very thin aluminum electrodes [**10-11; 7;12-13;9**], and the conductive silver is used to glue the connection lead wires of electrodes. And also, the electrospun PVDF-GO membrane[**14**], the conductive adhesive copper foil[**15**], the plastic film coated with indium tin oxide (ITO) [**2**] was used as the electrodes. Zeng et al. set four PVDF/NaNbO3 nanofiber nonwoven fabrics sandwiched between two electrically conducting knitted fabric electrodes, which consistently produces a peak open-circuit voltage of 3.4 V and a peak current of 4.4 μA in a cyclic compression test[**16**]. Mandal et al used the circular conductive adhesive carbon tape as bottom electrode and the nickel-copper plated polyester fabric as a top electrode[**6**]. Previous reports showed that the measured output voltage of electrospun PVDF nanofibers under periodic bending stress were highly affected by the actual contact areas between the interdigitated silver (nanoparticles or nanowires) electrodes and the PVDF nanofibers [**17**]. Higher resistance materials used as electrodes will show a decrease in piezoelectric output voltage[**18**].

On the other hand, the sputtered metal membrane on the nanofiber web was used as the electrodes [**19**]. Son et al[**17**] prepared the electrodes with Ag NPs or Ag NWs by spray-deposition using an air-brush of a spray gun, and observed that the electrical contacts for generating the piezoelectric responses are affected by different surface roughness of the printed electrodes controlled by the morphology of silver nanostructures. However, these studies focused on the piezoelectric effect of electrospinning PVDF fiber web with respect to the electrospinning technological parameters.

To fabricate piezoelectric device with conventional thin PVDF deposit membrane, some electrode material, such as the sputtered gold membrane [**20-21**], the attached copper foil[**22**] and the copper grating wires[**23**], the screen-printing Ag paste[**24**], PEDOT:PSS ink[**25**], the attached jet-printed interdigitated silver (nanoparticles or nanowires) on flexible polyethylene terephthalate (PET) films [**17**], the inkjet-printed silver ink (with a measured bulk resistivity of 150 μΩ.cm) [**26**], on both top and bottom layers, were put forward to make piezoelectric sensor. For the attached electrodes, the contact interface between PVDF and electrode is glued by the conductive silver adhesive. Wang et al [**2**] compared two kinds of thin film protection material, i.e. polyimide (PI) and polythylene terephthalate (PET), as well as two kinds of insulate binder, i.e. one-component and two-component epoxy resin binder. Their experimental results showed that the packaging materials and the insulate binder significantly affect the stimulus-response delay.

These reported piezoelectric devices on the basis of PVDF nano-fiber web were constructed by assembling different electrodes together, for example graphene films, ITO/PET films, evaporated metallic films, etc. However, little attention was paid to the effect of electrode material on the piezoelectric response of PVDF sensor. The imporosity and reduced mechanical flexibility of these devices make them unsuitable for application in wearable devices because human and animal skin needs breathability. Due to the poor fatigue resistance of metal foils and a mismatch of Young's modulus and Poisson's ratio of the coating and the PVDF web, metal foil electrodes or metal coated thin film electrodes showed a very short utility life under repeated mechanical deformation. To demonstrate the feasibility of textile electrodes in fabricating piezoelectric device with PVDF nanofiber web, this work will assemble the devices with three typical kinds of electrode, and investigates their piezoelectric responses to periodic force loading.

Preparation process of PVDF prototype

To make the device prototype, a patch of electrospun PVDF nanofiber web with a thickness of 47±10μm was firstly cut by a size of 3x3cm, and then its surface was attached by a pair of electrode materials with size of 2x2 cm. There is no adhesive binder between the PVDF nanofiber web and each of two electrodes. The silver-plated wires are used as the lead of the electrode, and then it can be connected with a signal acquisition device, as showed in **Fig. 1**. The prototype has good insulate effect due to the greater web area than the upper and lower electrode area. Finally, the common thin polyester woven fabric with high yarn density is used to protect and hold together the packaging electrodes and the PVDF nanofiber web. Note, more attention is paid to the fitness of the woven fabric to the nanofiber web and the surface smoothness of the surface of the electrode in the packaging process.

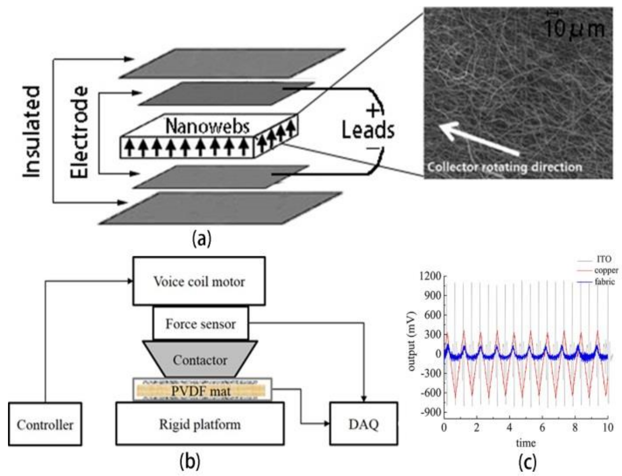

Fig. 1. Packaging structure of the PVDF nanofibers web as sensor prototype.

To compare the influence of electrode material on the piezoelectric devices with the PVDF nanofiber web, this study used three different materials as the electrodes, i.e. adhesive copper foil tape, ITO/PET film and adhesive conductive cloth, respectively. Although each of three device prototypes has different electrode materials, they have the same size, assembled structure and packaging technology. **Fig. 2** shows the prototypes of three devices made of the same size and thickness of the PVDF nanofiber web.

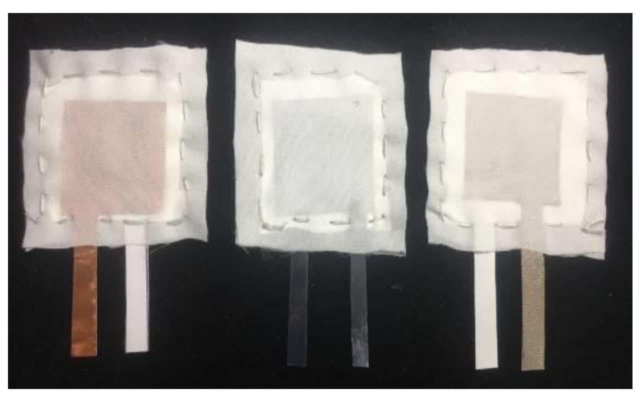

Fig. 2 Three PVDF sensor prototypes produced by different material electrodes (A -adhesive copper foil tape, B - ITO thin plate, C - adhesive conductive cloth).

Of three electrode material, the adhesive copper foil is a kind of flexible metal tape and coated by a layer of sticky paste, the ITO film is the PET film coated ITO, and adhesive conductive fabric is a kind of the conductive fabric with adhesive binder. The conductive fabric is made of 45% of the metal fibers and 55 of the cotton fibers. Their specifications are listed in **Table 1**.

Table 1. Main parameters of three kinds of electrodes.

electrode / index	copper foil tape	ITO thin film	conductive cloth
Composites	copper foil + conductive adhesive	transparent sheet	Conductive fabric+ conductive adhesive
Surface resistance（Ω/cm^2）	300~500	90~150	800~1000
thickness (mm)	0.15	0.25	0.22
Compressibility	ITO< Copper foil<conductive cloth		

Piezoelectric testing

To evaluate the piezoelectric responses of the fabricated devices, the customized cyclic compression tester, which is illustrated in **Fig. 1**, was used to measure the output voltage of samples. The piezoelectric sensor was placed on a hard plastic platform. The double-faced adhesive tape was used to adhesive the device and the plastic platform, and to reduce electrical noise. The controller managed the movement of the load cell. When PVDF device is pressed by a contactor, the nanofiber mat and the electrodes together are compressed and deformed, and this deformation determines the amplitude of the piezoelectric response. The stainless steel contactor with flat circle tip of 20mm^2 moves up and down with a frequency of 4.0Hz and the maximum contact force of 80N. In testing, the contactor initially contacted with the insulated top surface of the device at a low force of 0.001N. The output voltage was recorded by data acquisition card (Advantech, PCI-9111). The load cell (Omega-0.5-50, Transducer Techniques Inc., CA, USA) detected the force on the piezoelectric device surface when the contactor pressed.

With respect to each kind of three electrode materials (adhesive copper foil tape, ITO thin film, adhesive conductive cloth), five prototypes are fabricated. Each of prototypes has three repeated testing under the maximum compression force of 10N、20N、40N、60N、80N, respectively. According to the tested piezoelectric responses, the response intensity, sensitivity, linearity, and response hysteresis are calculated.

Results and discussions

The typical piezoelectric outputs of the prototypes with three different electrode materials are shown in **Fig. 3.** Observably, each of prototypes has strong piezoelectric responses to the cyclic mechanical activation, but the response nearly keeps the same frequency to that of

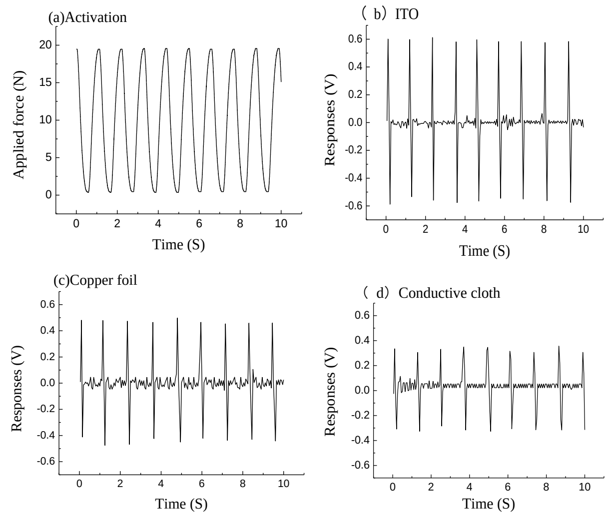

Fig. 3. Piezoelectric responses of different sensor prototypes to periodic compression forces.

dynamic compression force. Relatively, the sensor prototype by ITO electrode has the highest responses to the cyclic compression, and that by conductive cloth has the smallest piezoelectric peaks. In addition, the piezoelectric response of the sensor with ITO film is more stable under the same dynamic pressure.

To compare the difference of piezoelectric responses between three electrode materials, the averaging positive voltage amplitudes were calculated, and the results are showed in **Fig. 4**. Apparently, the sensor prototype with ITO thin film has the biggest piezoelectric response, 600mv, and that with the conductive cloth the smallest, 300mv.

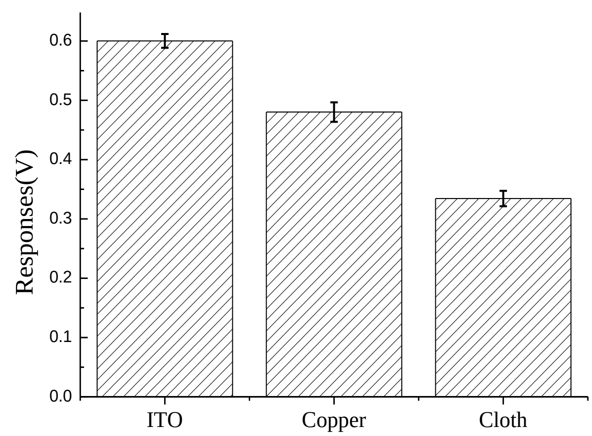

Fig. 4. The average responses of five sensor prototypes under the dynamic pressure loading (20N，1Hz).

In fact, previous studies have reported that the surface roughness of electrode for PVDF membrane affects the recorded responses of the packaged sensor[**17**], and the electrode material with high conductivity has the strongest piezoelectric output[**18**]. According to the properties of three kinds of electrodes listed in **Table 1**, observably, the ITO thin film has the smallest surface resistance, and the next is the copper foil tape. And also,

Fig. 5 shows the SEM surface morphology of each of three electrodes, and apparently, the ITO thin film has a nano-level smooth surface, which means the small contact resistance between the ITO thin plate electrode and the electrode. Relatively, the surface of conductive fabric is rough, and the size of the texture elements is 200 µm or so, which is much larger than the size of PVDF nanofibrous web. In this sense, the ITO thin film has the highest charge collection capability among three tested electrode materials.

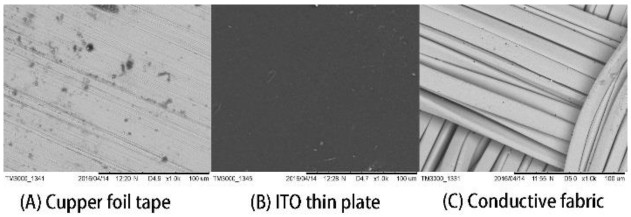

Fig. 5. SEM image of three kinds of electrodes

The ratio of actual contact areas can be determined by the capacitances of the piezoelectric sensors because the capacitances are directly proportional to contact areas. the piezoelectric responses can be remarkably improved with increasing the actual contact areas even though the piezoelectric sensors have the same size and piezoelectric properties.

To further find the difference among sensors packaged by three typical electrode materials, the maximum piezoelectric responses to various maximum compression forces are showed in **Fig. 6**. For each of three kinds of electrodes, the piezoelectric peak outputs linearly change with an increasing maximum compression force, and they have high positive correlation. They are fitted by a simple linear equation with zero intercept, and the results are showed in **Fig. 6**. The response sensitivity of PVDF nanofiber web to cyclic compression force is the ratio of the output voltage change to the magnitude of the input amplitude, i.e. the slope of the fitted line. It can be seen that the sensor with ITO thin film has the best sensitivity, 0.026V/N, and then sequentially the copper foil tape and the conductive cloth, 0.013 V/N and 0.010 V/N, respectively.

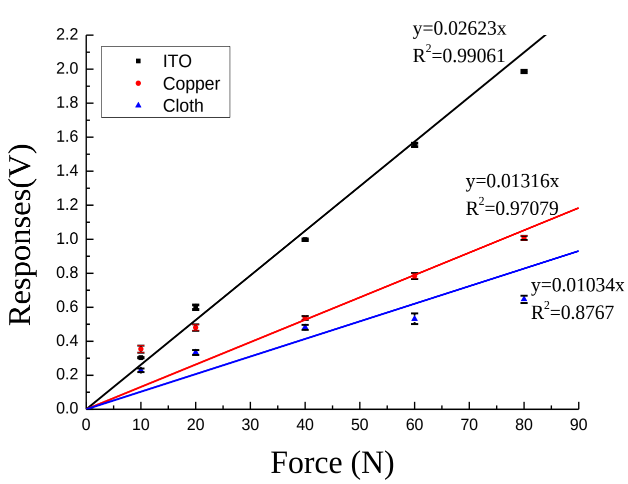

Fig. 6. Results of dynamic experiment under excitation (the frequency is 1HZ).

To note, the linearity between the loading force magnitude and the piezoelectric output is different among three kinds of electrode materials. The fitted goodness coefficient, i.e. R value, shows this difference. A greater fitted goodness coefficient signifies a stronger linear relationship. Therefore, the sensor with ITO thin film has the highest linearity, and relatively the prototype with the adhesive conductive cloth has low linearity.

These difference may be attributed to the mechanical properties of the electrode material and the contact deformation between the electrode and the PVDF web.

Response hysteresis is the main dynamic property of the sensor. The smaller the response hysteresis is, the faster the sensor will response to the stimulus input. To obtain the response hysteresis, the third peak after the dynamic compression was chosen as the starting point, and the piezoelectric response profiles were shifted to build the same reference time, as shown in **Fig. 7**.

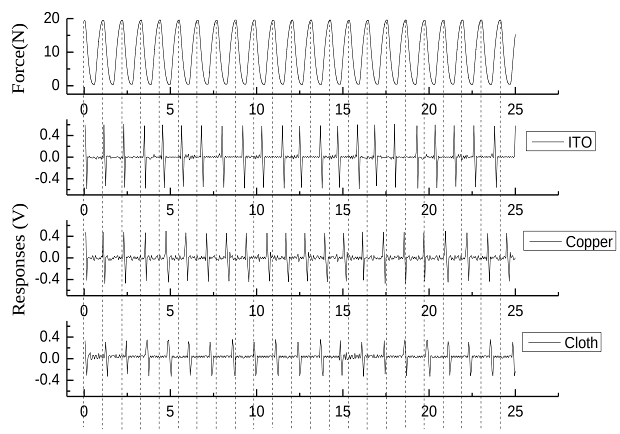

Fig. 7. Responses time of different sensor prototypes to periodic pressures.

The response hysteresis of three kinds of samples was expressed as the total response time over the cyclic compression activation, and the results are shown in **Fig. 8.** The cyclic compression frequency is 1.0 Hz. From the **Fig. 8,** the prototype with the ITO film generates 20 response peaks for about 21.5 seconds, while those with the conductive copper foil and conductive cloth, respectively, need 22.25 seconds and 23.6 seconds.

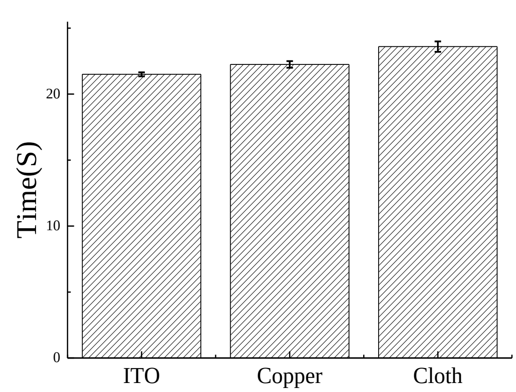

Fig. 8. The average and variance of response time of five sensor prototypes.

The reason is analyzed from the physical properties of the electrode material. The ITO film has the smallest compressibility, so the ITO film electrode quickly response to the excitation force, and then activate the PVDF nanofiber web. The adhesive copper foil tape is the electrode materials with the thinnest thickness, therefore, the electrode made of copper foil adhesive tape will closely conform to the fiber web. The ITO thin film has the largest compressibility, i.e. the excitation force is totally loaded into the PVDF nanofibers web by the electrode of ITO thin film.

Conclusion

This paper compared the piezoelectric responses of PVDF nanofiber web sensor prototypes sandwiched with three different types of packaging electrode materials, and demonstrated their effect on the piezoelectric performance of the packaged prototype device.

Their piezoelectric responses under the same cyclic compression showed that the PVDF sensor sandwiched by ITO thin film can get bigger and more steady uniform response than that of conductive cloth as well as the copper foil tape as electrodes. At the same time, the sensor made of ITO thin film has higher sensitivity and linearity and less response hysteresis.

The difference of piezoelectric responses among prototypes packaged by three kinds of electrodes are attributed to the surface roughness and the compressibility of the electrode materials. This study demonstrated the feasibility of conductive cloth as the packaging electrode material, however, it is need to study further the effect of cloth surface and lateral compression properties on the collected the piezoelectric responses.

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