A DIRECT-WRITE PIEZOELECTRIC PVDF NANOGENERATOR

Chieh Chang*, Yiin-Kuen Fuh, and Liwei Lin
Berkeley Sensor and Actuator Center, Department of Mechanical Engineering, University of California, Berkeley, California, USA

ABSTRACT
In this paper, we have successfully demonstrated the capability of a direct-write piezoelectric poly(vinylidene fluoride) (PVDF) nanogenerator using near-field electrospinning (NFES). Repeated and consistent output voltage up to 8.5 mV has been generated under an external strain of 0.092% from a single electrospun PVDF nanofiber, of which the output power is approximately 7.2 pW. We believe this technology can open up unprecedented possibilities in the field of NEMS/MEMS to convert mechanical strain into electricity for energy harvesting or strain sensing applications.

KEYWORDS
Piezoelectric, nanogenerator, electrospinning, PVDF, nanofiber, energy harvesting, direct write

INTRODUCTION
Over the past decades, intensive research efforts have been carried out in developing energy harvesting system for portable and wireless applications. In particular, piezoelectric generator offers the most robust and simple solutions for mechanical energy harvesting. The main advantage of piezoelectric generator is its scalability. This is why the recent reports of energy harvesting from the environment using ZnO nanowire arrays have attracted great interests by scaling down the power source to nanoscale [1-3]. PVDF is a highly non-reactive, flexible, inexpensive, and leading polymer with good piezoelectric property [4]. However, it must first be stretched and poled in a strong electrical field for its piezoelectricity. In this work, we present a direct-write technology to produce and place piezoelectric PVDF nanofibers at the same time with the in-situ poling and mechanical stretching process simultaneously as the foundation for nanogenerators.

PVDF exists in α, β, and γ crystalline phases depending on the chain conformations. Among them, β phase is primarily responsible for its piezoelectric properties because the piezoelectric activity is based upon dipole orientation within crystalline phase of PVDF. As shown in Figure 1, the non-polar α phase has random orientation of dipole moments while the polar β phase has all the dipole moments pointing to the same direction. Figure 2 shows the schematic of electrospinning with in-situ poling process. The strong electric field and stretching force during electrospinning process force dipole moments in the crystal to face in nearly the same direction. Therefore electrospinning of PVDF from its solution promotes the transformation from its non-polar α phase to the polar β phase [5].

![Figure 1: The unit cell of α and β phase crystalline within PVDF. The β phase is responsible for the piezoelectricity.](image1.png)

![Figure 2: Schematic of the electrospinning and in-situ poling process.](image2.png)

SYSTEM DESIGN AND FABRICATION
We have electrospun PVDF nanofibers from different solutions using NFES [6,7]. In our experiment, PVDF is dissolved in both dimethyl sulfoxide (DMSO) and dimethylformamide (DMF) solutions with concentration ranging from 5-20 wt%. The PVDF solutions with concentration less than 10 wt% are too thin while those with concentration higher than 20 wt% are too viscous, making NFES and conventional electrospinning from these solutions impossible. PVDF solutions with concentration ranging from 12.5-15 wt% would possess the optimal visco-elasticity for the electrospinning process. Since DMSO and DMF are not volatile solvents, the addition of acetone in the solvents is required to adjust the evaporation rate of the polymer solution, which is a crucial factor in the electrospinning process. In our experiment conditions, we find that the solvent-to-acetone weight ratio of 8:2 is suitable for NFES. Too many acetones in the solvent
would cause the polymer droplet to dry out rapidly during electrospinning and terminate the process. Furthermore, because of the low electrical conductivity of the DMSO, DMF, and PVDF, we add tetrabutylammonium chloride (TBAC) to improve the electrical conductivity of PVDF solution so that ionic charges are increased to induce more electrical force to stretch the polymer jet. Detailed experimental conditions and operating parameters are listed in Table 1.

Table 1: Experimental conditions and operating parameters.

<table>
<thead>
<tr>
<th>Parameters and conditions</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVDF concentration</td>
<td>12.5~15 wt%</td>
</tr>
<tr>
<td>Solvent (DMF:Acetone) weight ratio</td>
<td>8:2</td>
</tr>
<tr>
<td>Additive (TBAC) concentration</td>
<td>3 wt%</td>
</tr>
<tr>
<td>Applied voltage</td>
<td>1~1.2 kV</td>
</tr>
<tr>
<td>Needle-to-collector distance</td>
<td>1 mm</td>
</tr>
</tbody>
</table>

SEM pictures of electrospun PVDF nanofibers are shown in Figure 3 with diameter ranging from 500 nm to 4 μm. The important fact is that we adopted NFES process to avoid the typical random distribution of nanofibers by conventional electrospinning as shown in Figure 3(a) where the polarities of PVDF nanofibers mostly cancel out each other such that the electrical output is close to zero.

Figure 3: (a) Spiraling and random pattern of electrospun PVDF nanofibers. (b) A single electrospun PVDF nanofiber with diameter of 500nm.

Figure 4(a) and (b) show the fabrication process of the nanogenerator. First, two aluminum electrodes are put on the plastic substrate with a spacing of 500 μm to 1 mm. The aluminum electrodes serve as the collector for NFES process and output leads for piezoelectricity measurement. Secondly, we directly write PVDF nanofiber across two grounded aluminum electrodes using the NFES process. Finally, silver pastes are applied at the two ends of PVDF nanofiber so that the bonding between nanofiber and electrodes are reinforced and the contact resistance is reduced. Figure 4(c) shows actual device with a single PVDF nanofiber. The PVDF nanofiber has a diameter of 700 nm and is suspended across two aluminum electrodes that are 700 μm apart as shown in Figure 4(d).

Figure 5 shows the experimental setup for measuring the piezoelectric responses. The uniaxial stress is applied along nanofiber length by the four-point bending method. Simulation result of the potential distribution of uniaxial stretched PVDF nanofiber is plotted in Figure 5 as well. The piezoelectric constant, $g_{33}$, of PVDF is negative such that stretching PVDF nanofibers along the poling axis (i.e. the electrospinning direction) will generate a voltage with opposite polarity as the poling voltage. Experimentally, we stretch the PVDF nanofiber and measure the output voltage (potential differences) between the two electrodes using forward connection where positive probe connects to positive voltage and negative probe to negative voltage. A positive output voltage should be recorded in forward connection in order to verify that the output voltage is coming from piezoelectric responses. A foil strain gauge is glued on the surface of the control substrate to measure the longitudinal strains.

![Figure 5](image5.png)  
**Figure 5**: Experimental setup for measuring the piezoelectric response of PVDF nanogenerator.

**EXPERIMENTAL RESULT AND DISCUSSION**

The relationship between output voltage of a single PVDF nanofiber and applied strain is plotted in Figure 6. The magnitude of output voltage increases with the applied strain. Theoretically, an external stress, $\sigma$, creates an electric field, $E$, on the piezoelectric material and the magnitude of the electrical field is proportional to the piezoelectric voltage coefficient, $g_{33}$, as [8]:
\[ E = g_{33} \sigma \]  \hspace{1cm} (1)

One may simplify the problem as \( E=V/L \) and \( \sigma=\varepsilon Y \), where \( L \) is length of the material, and \( Y \) is the Young’s modulus of the material. The output voltage, \( V \), can be expressed as

\[ V=g_{33}\varepsilon Y L \]  \hspace{1cm} (2)

The experimental results are in accordance with the theory as observed. Furthermore, we can see the piezoelectric output enhancement in Figure 6 by incorporating carbon nanotubes (CNTs) with PVDF solution in the NFES process. We believe several reasons contribute to this observation. (1) CNTs increase the electrical conductivity of PVDF solution as shown in Figure 7, thus leading to a greater Coulombic force during the electrospinning and in-situ poling process to induce more \( \beta \) crystalline phase. (2) The as-electrospun PVDF-CNT composite nanofiber has a higher Young’s modulus, which increases the output voltage from equation (2).

Figure 6: Experimental results showing the relationship between output voltage and applied strain for PVDF nanofiber and PVDF-CNT composite nanofiber.

Figure 8(a) and (b) show the dynamic response of the output voltage of PVDF nanofiber and PVDF-CNT composite nanofiber respectively. We apply 0.076% strain on both samples to generate 1.5 mV and 6.2 mV across a 10 M\( \Omega \) load resistor respectively. It is noted that the PVDF-CNT nanofiber generate a sharper peak of output voltage. We try to explain this by modeling our nanogenerator as a resistor and a capacitor (including the contribution from the system). The equivalent circuit is shown in the inset in Figure 8(a) where \( R_i \) is the internal resistance of nanofiber, \( C \) is the capacitance of the system, and \( R_L \) is the load resistance. When we apply a strain on the PVDF nanofiber, piezoelectric charges will be generated at two ends of the nanofiber, building up a potential difference according to the capacitance of the system. The piezoelectric charges will then diminish due to the RC discharging process with a time constant,

\[ \tau=(R_i+R_L)C \]  \hspace{1cm} (3)

The output voltage lifetime, which is defined as full width at half maximum (FWHM) of the output voltage, for PVDF nanofiber and PVDF-CNT composite nanofiber are 0.436 sec and 0.372 sec respectively. The PVDF-CNT composite nanofiber shows a shorter output voltage lifetime than PVDF nanofiber because CNTs form several conduction paths throughout the nanofiber [9] and, as a result, the internal resistance of nanofiber is reduced to yield a smaller time constant.

Figure 7: I-V measurement of PVDF solution and PVDF-CNT solution.

Figure 8: Dynamic response when stretching (a) PVDF nanofiber and (b) PVDF-CNT composite nanofiber. The inset in (a) shows the equivalent circuit of PVDF nanogenerator.

The continuous piezoelectric response is recorded in a forward connection when an external strain is repeatedly applied as shown in Figure 9. The output voltage is measured across a 10 M\( \Omega \) load resistor. We can observe positive peaks of the output voltage when stretching the PVDF nanofiber and negative peaks when releasing the strain (i.e. stop the stretching). The negative peaks are due to discharging process of the capacitance of the system. The magnitude and frequency of output voltage are
consistent with those of the applied strain, verifying the piezoelectric activities of the PVDF-CNT composite nanofiber. The output power of our nanogenerator is evaluated by the equation,

$$ P = \frac{V^2}{R_L} \quad (4) $$

where $V$ is the output voltage across a 10MΩ load resistor under an external strain of 0.092%. From Figure 6, the average output voltage is 8.5 mV and therefore the output power would be ~7.2 pW from a single PVDF-CNT composite nanofiber.

CONCLUSION
In this work, piezoelectric PVDF nanofiber and PVDF-CNT composite nanofiber are directly written and polarized simultaneously onto the plastic substrate as nanogenerator using NFES. For the first time, the piezoelectric response of PVDF nanofiber is recorded due to the direct-write capability of NFES. Repeated and consistent output voltage up to 8.5 mV has been generated under an external strain of 0.092% from a single PVDF-CNT composite nanofiber, of which the output power would be ~7.2 pW. The principle and the nanogenerator demonstrated could be the basis for new self-powered nanodevices that harvest electricity from the environment for applications such as implantable biomedical devices, wireless sensors, and portable electronics.

ACKNOWLEDGMENTS
The authors would like to acknowledge Prof. Haw Yang in the Department of Chemistry, UC Berkeley and UC Berkeley Microfabrication Laboratory for the experiment facilities, and Dr. Taku Hirasawa, Dr. Jong-Yoon Ha, Kevin Limkarilassiri for useful discussions and helps. This project is partially supported by the MF3 center under the DARPA MEMS/NEMS Fundamental Program.

REFERENCES

CONTACT
* Chieh Chang, email: chieh@berkeley.edu