LARGE ARRAY ELECTROSPUN PVDF NANOGENERATORS ON A FLEXIBLE SUBSTRATE

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ABSTRACT

This paper presents PVDF (Polyvinylidene fluoride) based electrospun nanofibers as nanogenerators in series and/or in parallel to amplify harvested energy due to mechanical strain on a flexible substrate. A chemically resistive flexible polymer substrate has been used with patterned comb-shape gold electrodes by means of a conventional lithography process. A total of 500 parallel nanofibers have been fabricated and connected to amplify current outputs under repeated mechanical straining tests. Peak current of 35nA has been collected with a 0.2mV of peak voltage.

KEYWORDS

PVDF, nanogenerator, nanofiber, energy harvester, flexible substrate

INTRODUCTION

Various approaches in scavenging energy from the environments have been pursued as energy crisis rises globally. There are many forms of energy harvesters ranging from human scale [1] to large scale such as ocean waves and waterfalls [2]. Among various methodologies, energy harvesting devices based on one-dimensional nanostructures have achieved great progresses recently toward potential practical applications. Most common yet important principle is piezoelectric based method. For example, nanogenerators using large amounts (1400~1500 nanowires/mm^2) of ZnO nanowires have been shown to generate decent values of energy outputs in which LED light is powered and up to 1V of voltage is generated [3-5]. However, these nanowires have short structural length (a few μm) which could limit their energy harvesting capacity. Furthermore, high processing temperature and difficulty in controlling the orientation of individual wires could complicate their manufacturing process and cost. Polymer based piezoelectric materials could be the alternative approach. For example, single PVDF nanogenerators have been demonstrated by using near-field electrospinning [6] with good control over the deposition location and theoretically infinite length for possible applications such as electric clothing [7, 8]. This work advanced the current state-of-the-art technologies in which parallel connections of multiple nanofibers are used to enhance the current outputs. The prototype device is fabricated on a flexible substrate through conventional lithography process such that direct integration with surfaces of arbitrary shape could be feasible.

WORKING PRINCIPLE

Piezoelectric materials have been widely studied in the micro to nano scale as energy harvesters for their inexpensive price and higher piezoelectric constants. Among the piezoelectric polymers, PVDF has been widely used for its good piezoelectric constant, superior mechanical properties and biocompatibility [9-10]. Specifically, PVDF powders can be easily dissolved in solvents and electrospun on various substrates.

Figure 1 shows the working principle of the prototype device. A total of 10 pairs of comb-shape, gold electrodes have been designed by using 100μm-wide gaps as the working distance and 1mm-wide gaps as the separation distance. A total of 50 parallel nanofibers have been electrospun on top of the electrodes such that there are 500 active working contacts to collect charges generated from these PVDF nanofibers. Under axial strain by bending the bottom plastic substrate, aligned dipoles can generate electrical potentials. Since the connections are in parallel, output currents will be amplified.

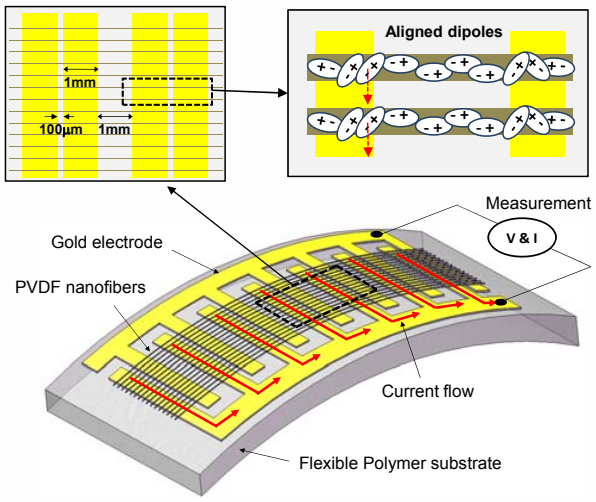

Figure 1. Working principle of the large array energy harvesting device by electrospun nanofibers. A total of 50 parallel nanofibers and 10 electrode pairs have been designed in the device on top of a flexible substrate.

DEVICE FABRICATION

Device fabrication process is based on conventional lithography and the near-field electrospinning process as shown in figure 2.

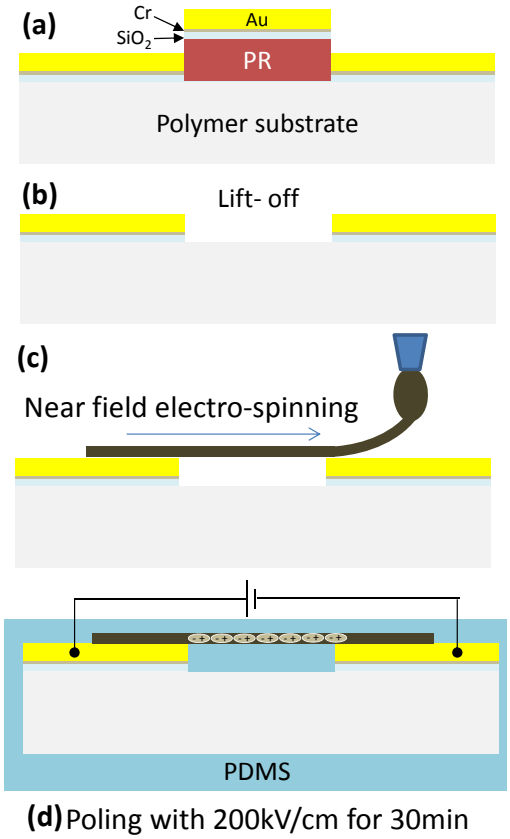

Figure 2. Device fabrication starts with chemically inert flexible polymer substrate (Thermanox™). (a) Silicon dioxide (15nm), Chromium (10nm) and Gold (150nm) are deposited and (b) patterned with e-beam evaporation in sequence and a lift-off process. (c) PVDF nanofibers are deposited using near-field electrospinning. (d) PDMS shielding and poling at 200kV/cm for 30mins.

Firstly, the flexible substrate (Thermanox®) is treated with IPA cleaning and nitrogen dry several times prior to the lithography process. G-line photo resist is spun on the polymer substrate followed by pattering the photo resist. A 15nm-thick silicon dioxide layer is deposited by the e-beam evaporation to enhance electrical insulation and promote adhesion. Afterwards, 10nm-thick chromium is evaporated followed by the deposition of 150nm-thick gold layer. After that, the lift-off process defines the electrode area and near-field electrospinning is performed to deposit PVDF nanofibers. These nanofibers are deposited under a computer-controlled x-y stage with continuous loops such that the deposition direction of nanofibers on top of the electrodes is always unchanged. A high potential is applied afterwards as part of the poling process to further assist aligning dipoles in PVDF nanofibers. The breakdown voltage of air (~60kV/cm) is too low for the poling process for PVDF, a 2mm-thick PDMS (Breakdown voltage: ~250kV/cm) layer is applied to cover the electrodes and cured at 70°C for 30minutes. Electrical poling of 200kV/cm for 30mins [11] on a 70°C hot plate is applied to further enhance the piezoelectricity of PDVF nanofibers in the lateral direction as higher temperature helps the active movement of diploes.

Figure 3 shows optical images of fabricated device with electrospun nanofibers on top of the plastic substrate before PDMS is applied. The typical diameters of these nanofibers are around 1-2μm. The magnified optical photos on the right-side of the figure illustrate working gaps of about 100μm across these well-aligned nanofibers. The diameter of these nanofibers can be controlled via applied voltage and mixture ratio of the polymer solutions. Generally, smaller applied voltage results in thinner diameter of nanofibers.

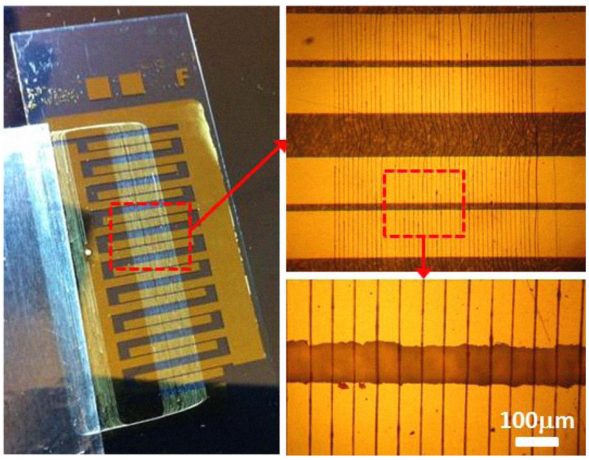

Figure 3. Optical images of fabricated device with well-aligned nanofibers. The working gap between two electrodes is 100μm. Nanofibers have been deposited by electrospinning continuously without stopping controlled by a x-y stage and the deposition direction for nanofibers was maintained.

Figure 4 shows the COMSOL® simulation results for the electrical poling process. The simulation focuses on the electrostatic fields in the 100μm and 1mm gaps during the electrical poling process. Results show the electrical potential streamlines when one electrode is grounded and the neighboring electrode is applied at 2kV. It is expected that stronger electrical field occurred in the 100μm gap (about 2×10^7V/m) as compared with the 1mm gap (2×10^6V/m). The typical electrical poling for PVDF should be higher than 2×10^7V/m while it won't cause electrical breakdown between the gaps. Some of the local concentration effects as shown in the simulation could enhance the local electrical field to be higher than the average values. Therefore, it is expected that some of the local areas in the 100μm gap had gone through successful electrical poling process while the area in the 1mm gap

probably didn't have enough electrical poling to have meaningful piezoelectric properties.

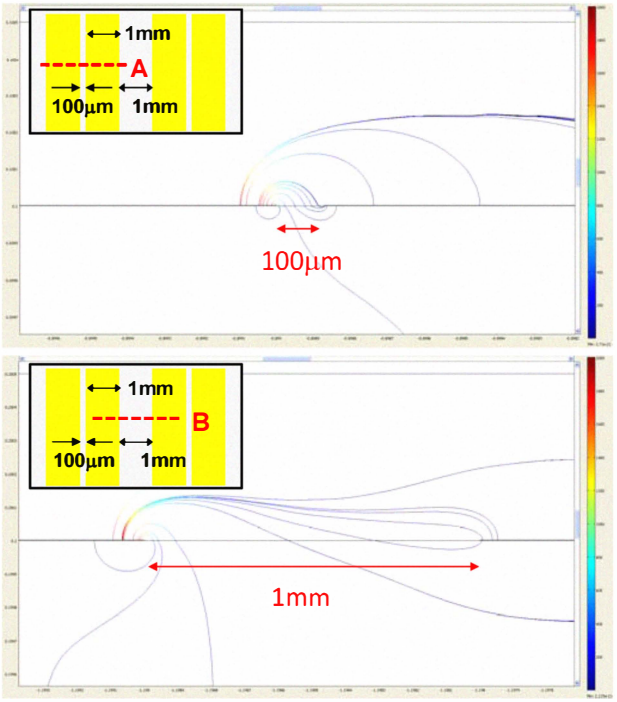

Figure 4. Electrostatic potential streamlines between the 100µm and 1mm gaps of two electrodes have been simulated to estimate the electric poling effects under voltage difference of 2kVolts. Strong electrostatic filed is expected in the 100µm gap (cross section A) as compared with the 1mm gap (cross section B) for good poling results. It is also noted that local strong electrostatic fields have been observed in the simulation due to geometric effects.

EXPERIMENTAL RESULTS

The fabricated devices have been characterized under repeated external strains by using a DC motor at 1Hz to control the deformation magnitude of the plastic substrate. As the dipoles in nanofibers are aligned in parallel along the longitudinal direction of the nanofibers, d_{33} mode has the strongest piezoelectric effect. The estimated strain from the bending of the substrate from the motor is 0.06±0.02%. Current and voltage generated from the device have been measured inside a Faraday cage to block out external noises. Figure 5 shows the current measurement results for the forward and reverse connections. This test is important to validate results were coming from the piezoelectric responses instead of artificial effects. If the signal is coming from the noise or other forms instead of than piezoelectric responses, the shape of the response should remain same even if the polarity of the contacts has been changed. Since the induced piezoelectric response has its own polarity pending on the electrical poling direction, the electrical measurements should have reversed responses when the polarity of the contacts was reversed. The bottom plots show magnified pattern of one single bending and release process. The peak current in forward direction measurement was about 35nA while the reverse connection shows about 2nA. The observed reduced response after polarity change is not clearly understood. One reason could be inherent current flowing inside the measurement equipment. If that is the case, the real current generated from the device is average of two responses in which inherent current should be subtracted from forward direction data and should be added to the reverse direction data. More rigorous test is being performed to understand the reason. The voltage measurement result is plotted in Figure 6. Similar to the current measurement, the forward and reverse direction measurement was conducted and the shape of response was flipped as expected. Bottom plots in Figure 6 show voltage measurement of single bending and release. The peak voltage was about 0.2mV in both forward and reverse connections. A significant decrease in voltage measurement was not observed as voltage measurement is not effected by current flow but by potential difference.

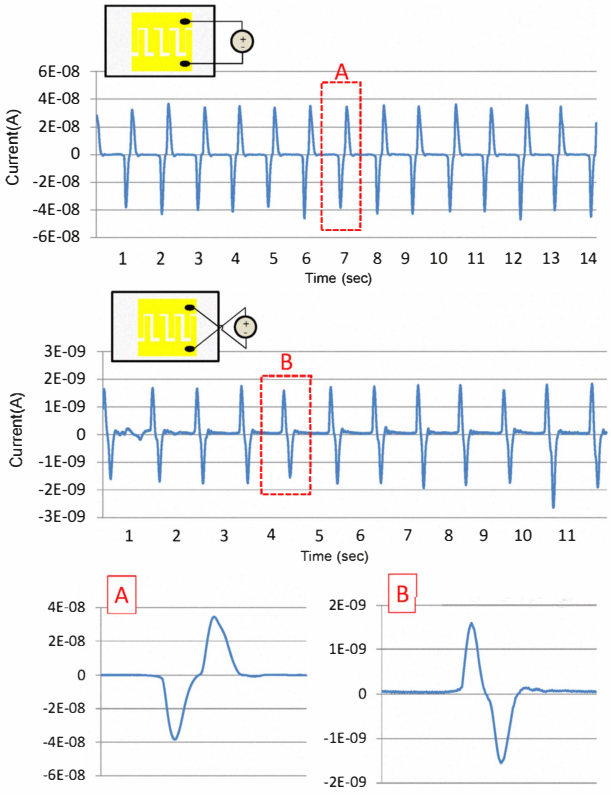

Figure 5. Current generated from device is monitored under repeated application of strains. The response shape is flipped when the measurement polarity is switched. Peak current is measured about 35nA in the forward connection and 2nA in reverse connection. Small current flowing inside the measurement device may have resulted in the unsymmetrical response.

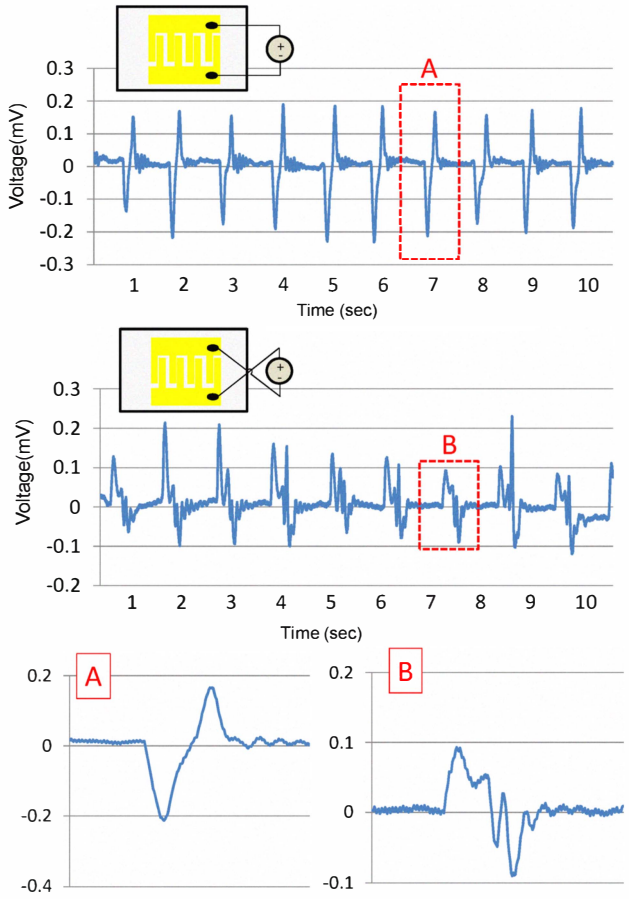

Figure 6. Voltage generated from the device is measured in both forward and reverse connections. The response shape is flipped when the measurement polarity is switched. Peak voltage is about 0.2mV and no significant reduction of signal is monitored in the reverse connection measurement. The output is small under the parallel connection of nanogenerators.

It is noted that both current and voltage outputs of these PVDF nanogenerators are about at least one order of magnitude less than the previous report on a single PVDF nanofiber [6]. Possible explanations are: (1) the *in-situ* poling process could be more effective to induce stronger piezoelectric effects as compared with the post poling process in this work; (2) partial reverse energy generation effects from the opposite neighboring electrodes which generate counter voltages and currents in the current work; and (3) encapsulation of the nanofiber in the current work could increase the loss of charges to the package material. These will be further investigated.

CONCLUSION

Piezoelectric energy harvesters based on electrospun nanofibers with current amplifying design have been demonstrated on flexible substrate. A total of 500 active parallel connecting points have been made between the gold electrodes and PVDF nanofibers. Under a repeated maximum strain of 0.05%, a peak current of 35nA and peak voltage of 0.2mV have been measured. Switching the measurement polarity resulted in flipped responses of the nanogenerators which validates the piezoelectric responses. As such, power generation from these PVDF energy harvesters can be further enhanced by various electrodes designs to boost either current or voltage.

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