

ULTRA-SENSITIVE AND STRETCHABLE STRAIN SENSOR BASED ON PIEZOELECTRIC POLYMERIC NANOFIBERS

M. Asadnia^{1,2,*}, A.G.P. Kottapalli^{1,2}, J.M. Miao¹ and M.S. Triantafyllou^{2,3}

¹School of Mechanical and Aerospace Engineering, Nanyang Technological University,
SINGAPORE

²Center for Environmental Sensing and Modeling (CENSAM), Singapore-MIT Alliance for
Research and Technology (SMART), SINGAPORE

³School of Mechanical Engineering, Massachusetts Institute of Technology, USA

ABSTRACT

There have been increasing demands for stretchable and highly sensitive sensors for use in structural health monitoring, human motion capturing, sport performance monitoring and rehabilitation. Such high performance myoelectric sensors are also remarkably important in developing artificial limbs where a combination of robotic actuators and sensory systems are required to provide lifelike, affordable, functional and easy to use devices that can interact with the human body. Here, we present a highly stretchable, self-powered and ultra-sensitive strain sensor based on piezoelectric PVDF nanofibers. We demonstrate the performance of the proposed device in response to an oscillatory load at very low frequency (0.5Hz). We also examined the applicability of our strain sensor on human's motion recognition by fabricating a glove with two sensors mounted on the middle and index fingers.

INTRODUCTION

There is an immense need for building myoelectric limbs that could help amputees to regain independence in their everyday lives. Myoelectric sensors are required to provide signals for control of artificial limbs. In the recent years, there has been a considerable research progress towards developing stretchable strain sensors using materials such as carbon nanomaterial or silver nanowires [1]. Although devices employing these materials show superior performance, lack of stretchability and high power consumption pose a major disadvantage for use in real-time applications. The proposed PVDF nanofiber strain sensor demonstrates a higher sensitivity and excellent stretchability while not requiring power supply to operate.

In the past, piezoresistive and piezoelectric materials such as PZT and PVDF in the form of bulk and thin films have been extensively used for developing various MEMS sensors [1-4]. During the last decade, (PVDF) nanofiber has gained remarkable interest in many applications such as energy harvesting [5], tissue engineering [6] and sensors [7]. PVDF exhibits impressive, mechanical and electrical characteristics such as piezoelectricity (highest

among the synthetic polymers), nonlinear optical properties and flexibility [8]. In the past, various methods were developed to fabricate PVDF nanofibers such as conventional far field electrospinning (CFFES) [9], modified far field electrospinning (FFES) [10] and near field electrospinning (NFES) [11, 12]. The main difference between these methods is the distance between needle and collector, which is higher for FFES (around 100mm) as compared to that of the NFES (1mm). Having a small emitting distance for fibers in NFES method allows us to provide well aligned fibers in desired forms [7]. Figure 1 shows a schematic view of far field electrospinning process. After the jet of fibers is dispensed from the needle to the collector, they bend in a complex shape and form a chaotic path (see figure 2). In order to determine the molecular and crystalline structure of the PVDF after electrospinning process, various characterization methods such as X-ray Diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Raman spectra can be used which are explained in [8].

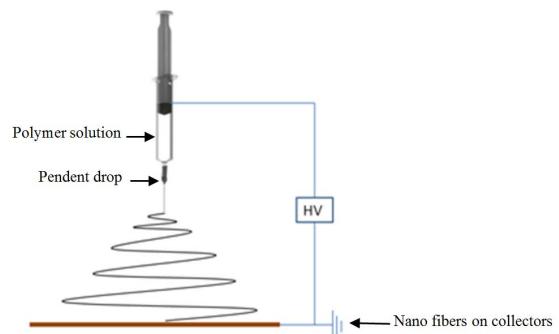


Figure 1. Schematic view of the far field electrospinning process

PVDF ELECTROSPUN NANOFIBER

PVDF is a semicrystalline polymer with a structure consisting of linear chains with sequence hydrogen and fluoride along with carbon backbone with a simple chemical formula (CH_2-CF_2). The

chemical structure of PVDF falls between structure of Polytetrafluoroethylene (PTFE) which is (CF_2-CF_2) and Ethylene (CH_2-CH_2). While having close structure to Ethylene provides a great flexibility for PVDF, the crystalline similarity with PTFE gives stereochemical constraint to PVDF [13]. Due to this structural characteristic, PVDF forms in different crystal structures depending on sample preparation conditions. In nature, PVDF appears in different phases which are known as α , β , γ and δ . Each of these phases is transferable to the others under certain external conditions. In general, α -phase is the most available phase in nature which typically obtained when the PVDF is cooled and solidified from melt. While the α -phase is known as a non-polar structure which does not show piezoelectricity, β -phase is understood as the only PVDF ferroelectric crystalline structure (polar) with strong piezoelectric effect [5]. In general, high mechanical (approximately 50%) and electrical stretches (to align the dipoles) are required to predominantly convert the PVDF from α -phase to that of with β -phase [13]. In the past various methods have been proposed to increase the ratio of the β -phase in the materials. For instance, annealing the sample at high pressure and high temperature or adding strongly polar hexamethylphosphorictriamide (HMPTA) in the solution [14]. It is also reported that adding carbon nanotubes in the PVDF solution can increase the Young's modulus of the material and enhance the growth of the β -phase structure and provide PVDF composites fiber with improved piezoelectric properties [11].

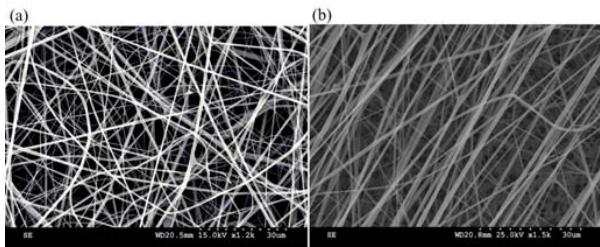


Figure 2. Electrospun nanofiber collected by (a) stationary collector which forms a chaotic fibers (b) rotatory collector (500 rpm) which forms aligned nanofibers.

Developing PVDF with β -phase requires careful optimization of electrospinning process and solution preparation. In order to observe the material phase after each step of optimization, we performed XRD. Figure 3 shows the XRD patterns of the PVDF nanofibers which are observed with a Siemens D5000 X-ray diffractometer with $Cu K\alpha$ radiation ($\lambda=1.54 \text{ \AA}$). The tests are conducted in reflection mode at an ambient temperature with two theta (degree) varying between 10° and 50° . Figure 3 reveals a strong peak at 20.2° for the nanofibers which shows the β -phase is the dominate structure in

the material. α -phase absorption bands, such as, 18.3° and 41.1° are not evident in the XRD pattern which indicates the existence of a very small portion of α -phase [15].

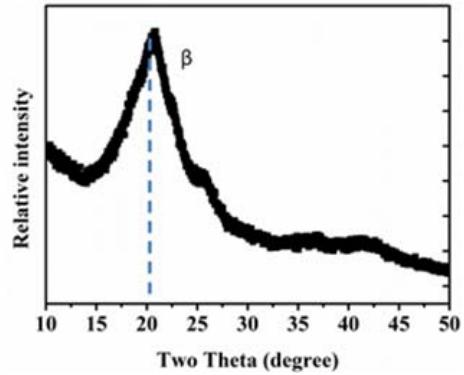


Figure 3. XRD patterns recorded for PVDF nanofibers of diameter of 800nm.

SENSOR DEVELOPMENT

The fabrication process flow of the sensor is depicted in figure 4. Initially, aligned PVDF nanofibers are collected on an aluminium foil substrate. Later on, the fibers are carefully transferred to a $25\mu\text{m}$ thick flexible LCP layer of dimensions 10mm in width, and 20mm in length. Gold electrodes of 2mm in width and 10mm in length are fixed on two ends of the sensors and fibers are protected using carbon tape.

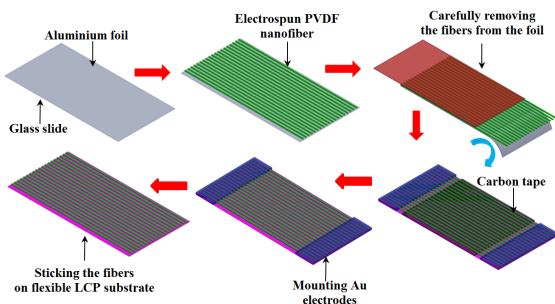


Figure 4. Fabrication process of the ultra-sensitive, stretchable strain sensor based on PVDF electrospun nanofibers.

DYNAMIC PRESSURE DETECTION USING DIPOLE STIMULUS

In order to evaluate the performance of the proposed sensor under dynamic pressure a vibrating sphere (dipole) is used to generate oscillatory pressure and the sensor output is acquired at various frequencies of vibration. The details of the vibrating sphere oscillator system are described in [16]. The dipole is positioned at the distance of 2mm above the sensor. The amplitude of vibration is kept constant (250mVrms) while the frequency is varied in steps from 0.5Hz to 5 Hz. Figure 5 shows the schematic of the experimental set-up. To ensure the repeatability

of the results, the experiment is repeated on four different sensors. Figure 5 shows the sensor output as a function of time for various frequencies. In order to ensure that the voltage generated is actually from the PVDF nanofibers, a dummy sensor with the same electrode set-up but with no nanofibers is tested under the same experimental conditions as that of the nanofiber sensor and the output of the device without sensing element (marked as paper in figure 5) is recorded. The experimental results conducted using the dipole stimulus is shown in figure 5.

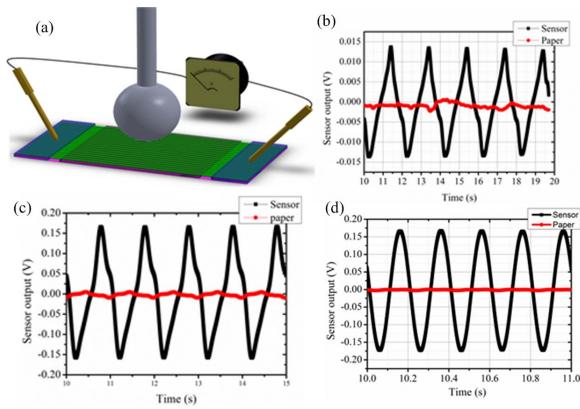


Figure 5. Testing the sensor under low frequency dynamic loads. (a) schematic diagram of the experimental setup (b) experimental result when the dipole is excited at frequency of 0.5Hz and amplitude of 250mVrms.

APPLICATIONS IN ARTIFICIAL LIMBS

There is immense need for producing myoelectric limbs that could help amputees to regain independence in their everyday lives. Myoelectric sensors are required to provide signals for control of artificial limbs. In order to investigate the performance of the proposed sensor in detecting the movement of human limb joints we developed a smart glove by mounting the sensors on the fingers of the glove (figure 6). This glove is integrated with a data acquisition system that can transfer the sensor output to a computer. Two sensors are mounted on index and middle fingers of the glove. Figure 7 shows the sensor output in response to the bending of the index and middle fingers. For example, in the first case, the middle finger is bent while the index finger is kept straight. The sensor on the index finger generated a clear voltage peak (plotted by red) due to the displacement of this finger while the sensor output on the index finger (plotted in black) remained unchanged. Increased bending of the fingers lead to an increase in mechanical stress induced on the nanofibers which led to a higher sensor output. Similar explanation can be applied for the other cases when the middle finger remained straight, both fingers stayed unchanged and for both fingers bend together (see figure 6). The sensor exhibited an excellent stability, response speed, and repeatability.

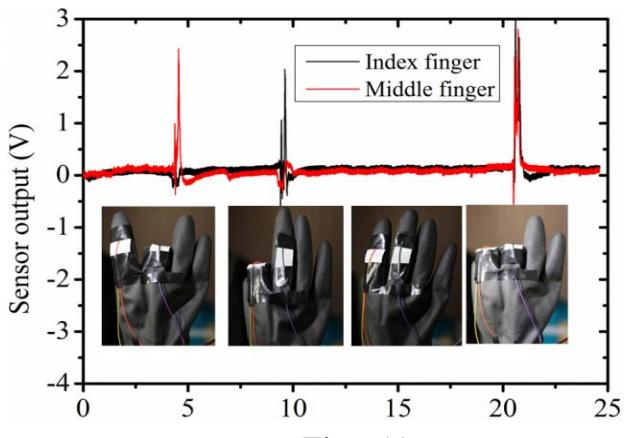


Figure 6. Human motion detection by using the proposed nanofiber sensor. Each case shows the response of the strain sensor to the bending of corresponding finger.

CONCLUSION

In this work, we developed piezoelectric PVDF nanofibers by using electrospinning process. We developed a flexible strain sensor with high sensitivity, stretchability with simple and low cost of fabrication process by using PVDF nanofiber as the sensing element. Performance of the proposed sensor under low frequency dynamic load and in artificial limbs presented. The sensory feedback provided by these devices can open-up new avenues in rehabilitation engineering and brings a sense of touch to myoelectric limbs.

ACKNOWLEDGEMENT

This research was funded by Singapore National research foundation (NRF) through the Singapore-MIT Alliance for Research and Technology (SMART) Centre, Centre for Environmental Sensing and Modeling (CENSAM) IRG

REFERENCES

- [1] M. Asadnia, A. G. P. Kottapalli, J. M. Miao, A. B. Randles, A. Sabbagh, P. Kropelnicki, *et al.*, "High temperature characterization of PZT(0.52/0.48) thin-film pressure sensors," *J. Micromech. and Microeng.*, vol. 24, Jan 2014.
- [2] M. Asadnia, A. G. P. Kottapalli, Z. Shen, J. Miao, and M. Triantafyllou, "Flexible and Surface-Mountable Piezoelectric Sensor Arrays for Underwater Sensing in Marine Vehicles," *Ieee Sensors J.*, vol. 13, pp. 3918-3925, 2013.
- [3] M. Asadnia, A. G. P. Kottapalli, Z. Shen, J. M. Miao, G. Barbastathis, M. S. Triantafyllou, *et al.*, "Flexible, zero powered, piezoelectric MEMS pressure sensor arrays for fish-like passive underwater sensing in marine vehicles," in *26th IEEE MEMS' 13, Conference*, Taipei, January 20-24, pp. 126-129, 2013.

- [4] J. Dusek, A. G. P. Kottapalli, M. E. Woo, M. Asadnia, J. Miao, J. H. Lang, *et al.*, "Development and testing of bio-inspired microelectromechanical pressure sensor arrays for increased situational awareness for marine vehicles," *Smart. Mater. Struc.*, vol. 22, 2013.
- [5] C. Chang, V. H. Tran, J. Wang, Y.-K. Fuh, and L. Lin, "Direct-Write Piezoelectric Polymeric Nanogenerator with High Energy Conversion Efficiency," *Nano Letters*, vol. 10, pp. 726-731, 2010.
- [6] Y.-F. Goh, I. Shakir, and R. Hussain, "Electrospun fibers for tissue engineering, drug delivery, and wound dressing," *J. Materials Science*, vol. 48, pp. 3027-3054, 2013.
- [7] D. Mandal, S. Yoon, and K. J. Kim, "Origin of Piezoelectricity in an Electrospun Poly(vinylidene fluoride-trifluoroethylene) Nanofiber Web-Based Nanogenerator and Nano-Pressure Sensor," *Macromolecular Rapid Communications*, vol. 32, pp. 831-837, 2011.
- [8] J. Chang, M. Domnner, C. Chang, and L. Lin, "Piezoelectric nanofibers for energy scavenging applications," *Nano Energy*, vol. 1, pp. 356-371, 2012.
- [9] D. H. Reneker, A. L. Yarin, H. Fong, and S. Koombhongse, "Bending instability of electrically charged liquid jets of polymer solutions in electrospinning," *J. Applied Physics*, vol. 87, pp. 4531-4547, 2000.
- [10] E. Hollenstein, M. Davis, D. Damjanovic, and N. Setter, "Piezoelectric properties of Li- and Ta-modified (K_{0.5}Na_{0.5})NbO₃ ceramics," *Applied Physics Letters*, vol. 87, Oct 31 2005.
- [11] Z. H. Liu, C. T. Pan, L. W. Lin, and H. W. Lai, "Piezoelectric properties of PVDF/MWCNT nanofiber using near-field electrospinning," *Sensors and Actuators A-Physical*, vol. 193, pp. 13-24, Apr 15 2013.
- [12] D. H. Sun, C. Chang, S. Li, and L. W. Lin, "Near-field electrospinning," *Nano Letters*, vol. 6, pp. 839-842, Apr 2006.
- [13] H. S. Nalwa, "Ferroelectric Polymers: Chemistry, Physics, and Applications," *CRC Press*, vol. 20 Jun 1995.
- [14] C. Ribeiro, V. Sencadas, J. L. Gomez Ribelles, and S. Lanceros-Mendez, "Influence of Processing Conditions on Polymorphism and Nanofiber Morphology of Electroactive Poly(vinylidene fluoride) Electrospun Membranes," *Soft Materials*, vol. 8, pp. 274-287, 2010.
- [15] A. Baji, Y.-W. Mai, Q. Li, and Y. Liu, "Electrospinning induced ferroelectricity in poly(vinylidene fluoride) fibers," *Nanoscale*, vol. 3, pp. 3068-3071, 2011.
- [16] A. G. P. Kottapalli, M. Asadnia, J. M. Miao, G. Barbastathis, and M. S. Triantafyllou, "A flexible liquid crystal polymer MEMS pressure sensor array for fish-like underwater sensing," *Smart. Mater. Struc.*, vol. 21, Nov 2012.

CONTACT

*M. Asadnia, Tel: (+65) 6790 4264, School of Mechanical & Aerospace Engineering, Nanyang Technological University, mohs0002@e.ntu.edu.sg