

NANOSTRUCTURED MATERIALS AND DEVICES FOR SENSING AND ENERGY HARVESTING APPLICATIONS

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MATERIALS SCIENCE AND NANOTECHNOLOGY PROGRAM

By
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August, 2015

I certify that I have read this thesis and that in my opinion it is fully adequate, in scope and in quality, as a thesis of the degree of Doctor of Philosophy.

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ABSTRACT

NANOSTRUCTURED MATERIALS AND DEVICES FOR SENSING AND ENERGY HARVESTING APPLICATIONS

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Ph.D. in Materials Science and Nanotechnology

Supervisor: Prof. Dr. Mehmet Bayındır

August, 2015

A closer look into the fundamental challenges of the modern world reveals that the increasing demand for energy threatens the evolution of science and technology. Energy-efficiency is thus a fundamental issue in engineering nano-devices. An important path to achieve high efficiency is to convert the mechanical energy into electrical energy using piezoelectric and triboelectric energy harvesting circuitries, hence enabling self-powered systems at nanoscale. The utilization of novel piezoelectric and triboelectric energy harvesting materials introduces the opportunity of manufacturing flexible, wearable and stretchable self-powered devices.

In this thesis, we introduced a new fabrication technique, new strategies and practical approaches for developing high performance triboelectric and piezoelectric materials and devices for flexible electronics, artificial skin and energy harvesting applications.

The first part of the thesis focuses on the development of piezoelectric nanoribbons. Poly (vinylidene fluoride) and its copolymer Poly (vinylidene fluoride)-co-tri (fluoroethylene) were used to fabricate spontaneously high piezoelectric nanoribbons. We measured the record-high piezoelectric charge coefficient from our ribbons, because the high stress and high temperature used in the fabrication can enhance their properties. In addition, proof of principle devices for energy harvesting and sensing were fabricated using nanoribbons. The achievements in this part of the thesis can be listed as: i) We obtained extraordinary high aspect ratio, globally oriented, polymer encapsulated, and high piezoelectric microribbon and nanoribbon arrays. ii) Due to process conditions (shear stress and temperature) used in thermal fiber drawing, as-produced micro and nanoribbons contain high amount of polar phase without requiring

any electrical poling. iii) We developed a new technique for characterizing and analyzing multiferroic characteristics of nano-objects, which consist of parallel evaluation of instrumental, numerical and analytical data. iv) To our knowledge, we achieved the highest piezoelectric charge coefficient from our ribbons in the literature. v) We enhanced stability of the piezoelectric ribbons by increasing the Curie temperature above its melting point due to processing conditions. vi) We observed and explained a new phase transformation mechanism in polymer piezoelectric ribbons. vii) The state-of-the-art ab initio calculations, which explain the phase transformation mechanism of molecules during the fiber drawing with the effect of shear, tensile forces and temperature, were included in detail.

The second part is about developing high energy output triboelectric generators. A high performance multi-layered triboelectric generator was developed using chalcogenide nanostructures. This part of the thesis details the following achievements: i) We demonstrated that not only polymer, but also semiconductor chalcogenide materials can be used in triboelectric applications, for the first time. ii) For the first time, we proposed and demonstrated that the fluorination of nanostructured surfaces increases triboelectric performance significantly. iii) We introduced a multi-layered triboelectric generator which is very promising for real applications such as acoustic wave and vibration detection, and energy harvesting with very high power output (0.51 Watt) in comparison with the literature. iv) We used a 3D printing technique to produce our device, which is low-cost and appropriate for rapid prototyping and mass production. v) We explained the device theory for the triboelectric nanogenerator, which aligned well with our experimental results.

Keywords: Iterative size reduction technique, energy harvesting, triboelectricity, piezoelectricity, poly (vinylidene fluoride), flexible electronics, nanoelectronics.

ÖZET

ENERJİ ÜRETİMİ VE SENSÖR UYGULAMALARI İÇİN NANO YAPILI MALZEMELER VE NANO AYGITLAR

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Malzeme Bilimi ve Nanoteknoloji, Doktora

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Modern dünyanın temel sorunlarına yakından bir bakış attığımızda, artan enerji ihtiyacının bilim ve teknolojinin gelişimini tehdit ettiğini görmekteyiz. Süregelen problemlerin, düşük enerji gerektiren cihazlar üreterek ve kayıp enerjiyi geri dönüştürerek çözülmesi hedeflenmektedir. Düşük enerji sarf eden cihazlar ile piezoelektrik enerji üretim devreleri kullanarak mekanik enerjinin elektrik enerjisine dönüştürülmesini sağlayarak kendi enerjisini üretebilen sistemlerin entegre edilmesi mükemmel bir çözüm olarak görülmektedir. Daha da ötesi, yüksek performanslı triboelektrik ve piezoelektrik malzemelerin kullanımına ihtiyaç duyulduğu organik piezoelektrik ya da yüksek performanslı triboelektrik nano-jeneratörlerin üretilmesi ile esneyebilir, giyilebilir ve sünebilir, kendi enerjisini kendi üreten cihazların geliştirilmesi fırsatını ortaya koymaktadır.

Bu tezde yeni bir üretim tekniği, esnek elektronik, yapay deri ve enerji üretimi uygulamaları için, yüksek performanslı triboelektrik ve piezoelektrik malzemelerin geliştirilmesinde yeni stratejiler, pratik yaklaşımlar anlatılmaktadır. Bu tez iki ana kısımdan oluşmaktadır. Birinci kısım piezoelektrik nano şeritlerin üretimini içermektedir. Poly (vinylidene fluoride) ve onun kopolimeri olan Poly (vinylidene fluoride)-co-tri (fluoroethylene) malzemeleri kendinden yüksek piezoelektrik özelliği gösteren nano şeritlerin üretiminde kullanılmıştır. Ardışık fiber çekme yönteminde kullanılan yüksek sıcaklık ve stres gibi parametrelerin etkisiyle, ürettiğimiz şeritlerden rekor yükseklikte piezoelektrik yük katsayısı ölçtük. Ayrıca, nano şeritler kullanılarak enerji üretimi ve sensör amaçlı cihazlar geliştirildi. Bu tezin birinci kısmında elde edilen kazanımlar şöyle sıralanabilir: i) Sıra dışı uzunluk oranlarına sahip, aynı oryantasyonda dizilmiş, polimer içerisine gömülü, yüksek piezoelectric özelliği

gösteren mikro ve nano şeritler elde ettik. ii) Termal fiber çekme parametreleri (kayma gerilmesi ve sıcaklık) sebebiyle, üretilen mikro ve nano şeritlerde, elektriksel polarizasyon işlemi gerektirmeksizin, yüksek oranda polar faz elde edilmiştir. iii) Nano objelerin çoklu ferroik karakteristiklerini incelemek için, enstrümantal, sayısal çözümleme ve analitik tekniklerin paralel olarak kullanıldığı, yeni bir yöntem geliştirdik. iv) Bilgimiz dâhilinde, literatürde bildirilen en yüksek piezoelektrik katsayı bizim nano şeritlerimizden ölçülmüştür. v) Üretim parametreleri sayesinde, Curie sıcaklığını erime sıcaklıklarının üzerine çıkararak piezoelektrik şeritlerin kararlılığını arttırdık. vi) Polimer piezoelektrik şeritlerde yeni bir faz dönüşüm mekanizması gözlemledik ve bu mekanizmayı açıkladık. vii) Modern ab initio hesaplamaları kullanılarak, kayma gerilimi, çekme gerilimi ve sıcaklık gibi fiber çekme parametrelerinin etkisi ile moleküllerde oluşan faz dönüşümü detaylı olarak açıklandı.

İkinci kısım ise, yüksek enerji üretimine sahip triboelektrik jeneratörlerin geliştirilmesini hakkındadır. Kalkojen nano yapılar kullanılarak yüksek performanslı, çok katmanlı triboelektrik nano jeneratör geliştirildi. Tezin bu kısmı aşağıda listelenmiş yönleri ile tanımlanabilir: i) İlk kez, sadece polimerlerin değil, yarı iletken kalkojenlerinde triboelektrik jeneratör uygulamalarında kullanılabileceğini gösterdik. ii) Nano yapıları yüzeylerin flor ile kaplanması sonucu triboelektrik özelliklerinin önemli miktarda artacağını ilk kez önerdik ve gösterdik. iii) Akustik dalgaların ve titreşimin algılanması, literatürde ki eş denekleri ile karşılaştırıldığında, çok yüksek çıkış gücüne (0.51 Watt) sahip enerji üretici gibi gerçek uygulamalarda kullanılabilecek, çok katmanlı triboelektrik bir triboelektrik jeneratör geliştirdik. iv) Bahsi geçen cihaz, düşük maliyetli, hızlı üretim ve seri üretime uygun, 3D yazdırma tekniği ile üretildi. v) Triboelektrik nano jeneratörlerin teorisini açıkladık ve deneysel sonuçlarımız ile analitik sonuçlarımızın mükemmel şekilde örtüştüğünü gösterdik.

Anahtar kelimeler: Ardışık boyut küçültme tekniği, enerji üretimi, triboelektrik, piezoelektrik, poly (vinylidene fluoride), esneyebilir elektronik, nanoelektronik.

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To my mother

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Chapter 1

Introduction

Developments led by materials science and engineering have revealed the importance of flexible electronics [1]–[7]. Organic solar cells, flexible displays and cameras, artificial skin, smart surfaces and transistors were recently demonstrated on circuitries made by flexible components [1], [8]–[10]. Fabricating high efficient flexible devices with multi-functionalities requires using different types of materials such as conductive polymers, semi-conductive self-assemble films and resistive layers [7], [11], [12]. Although conventional electronic materials represent very high electronic performances, integration and fabrication of circuits on flexible, stretchable and curved surfaces is not an easy task. Especially, interfacing electronic devices with organs and living tissues requires non-invasive, flexible and multi-functional devices. Transmitting light and electric signals through the brain and other organs for recording real time information from organs can be possible by using flexible electronic and soft electronic fiber devices [13]–[17]. Fabricating all polymer flexible electronic devices seems more promising and inexpensive, where there is a greater demand for developing new organic high performance materials in terms of electronic properties such as mobility, conductivity and piezoelectricity. Researchers study on improving the performance of organic materials such as conductive inks, sheets and semiconductors by playing size, shape and composition of used organic substances [18], [19]. In addition to these organic materials used in flexible electronics, there is an emerging need to develop organic piezoelectric materials that can be used in many different applications such as energy harvesting, sensing and actuation, artificial skin and artificial muscle [19]–[25].

This thesis focuses on two main subjects, piezoelectricity and triboelectricity. In the first part, we developed nanoribbons from Poly (vinylidene fluoride) (PVDF) and its copolymer Poly (vinylidene fluoride)-co-tri (fluoroethylene) (PVDF-TrFE).

Although recent articles were reporting that PVDF was not compatible with fiber drawing process for obtaining polar phase nanostructures [11], we proved that γ polar phase PVDF can be spontaneously induced during the fabrication of PVDF nanoribbons via fiber drawing. Furthermore, we obtained the highest piezoelectric coefficient from our nanoribbons in comparison with the reported values in the literature. Table 1.1 represent a detailed analysis of the piezoelectric coefficient of polymer and ceramic piezoelectric materials with respect to their shapes, phases, fabrication methods and post-processing techniques. The highest reported piezoelectric coefficient was -7 pm/V from pure γ phase PVDF/Clay nanocomposites produced by solution based methods without requiring and post-processing such as polarization under high electric field [26]. Our γ phase PVDF nanoribbons, which doesn't require any post processing for obtaining polar phase, represent 8.35 times higher piezoelectric coefficient (-58.5 pm/V). The piezoelectric coefficient of the γ phase PVDF can be increased by shaping it in nanoribbons and mixing the phase composition with the β phase PVDF. So, the reported highest piezoelectric coefficients for β/γ mix-phase PVDF nanoribbons and thin films are 16.02 pm/V and 10.62 pm/V, respectively. This reported values were still far behind of our results [22]. There are several reasons that we obtained a very high piezoelectric coefficient: (1) non-clamping boundary conditions are valid for nanoribbons in the piezoelectric characterization, which means that the measured piezoelectric coefficient corresponds to effective piezoelectric coefficient; (2) nanoribbons are produced using a solvent free fabrication technique and display better piezoelectric properties.

Piezoelectric characterizations of nano-scale objects are extremely challenging. There are two basic techniques for measuring piezoelectric coefficient of materials: direct and indirect measurements, which are based on the applied force and the applied electric field, respectively. The indirect measurement techniques are very useful for characterizing piezoelectric properties of nano-materials. In this type of measurements, the displacement of the material with respect to the applied electric

field can be measured using very precise displacement sensors such as laser beam interferometers or atomic force microscopy, which have angstrom level sensitivity.

Table 1.1: Comparison between the piezoelectric coefficient of PVDF, PVDF-TrFE and other ceramic piezoelectric materials. PVDF and PVDF-TrFE nanoribbons have the highest piezoelectric coefficient among other reported measurements from those polymers and ceramic piezoelectric materials. *ISR: Iterative Size Reduction. **PZT: $(\text{Pb}_x\text{Zr}_{1-x}\text{Ti})\text{O}_3$ ***PVD: Physical Vapor Deposition.

Material	Phase	$ d_{33} $ (pm/V)	Type	Method	Poling	Reference
PVDF	γ	58.5	Nanoribbon	ISR*	No	Our Study
PVDF	β / γ	16.02	Nanoribbons	Template	Yes	[27]
PVDF	β / γ	10.62	Thin Film	Solution	Yes	[27]
PVDF	γ	7	Nanocomposite	Solution	No	[26]
PVDF	β	57.6	Nanowire	Electrospinning	Yes	[28]
PVDF	β	33	Thin Film	Stretching	Yes	[29]
PVDF	β	8	Nanowires	Template	No	[30]
PVDF	β	6.5	Nanowires	Template	No	[31]
PVDF-TrFE	β	384	Nanoribbon	ISR	No	Our Study
PVDF-TrFE	β	72.7-210.4	Nano-grass	Template	Yes	[32]
PVDF-TrFE	β	48 - 81	Nanoribbons	Template	Yes	[33]
PVDF-TrFE	β	13 – 19	Thin Film	Solution	Yes	[33]
PVDF-TrFE	β	25-45	Nanowire	Template	No	[34]
PVDF-TrFE	β	16-23	Thin Film	Solution	No	[34]
PVDF-TrFE	β	22	Nanowires	Template	No	[30]
PVDF-TrFE	β	8	Nanowires	Template	No	[31]
**PZT	Perovskite	200	Thin Film	Sol-Gel	Yes	[35]
PZT	Perovskite	145	Nanoribbon	Lithography	Yes	[36]
PZT	Perovskite	90	Nanoshell	Template	Yes	[37]
PZT	Perovskite	80	Nanowire	Sol-Gel	Yes	[38]
PZT	Perovskite	50	Nanowire	Sol-Gel	Yes	[39]
PZT	Perovskite	17 – 26	Powder	Sol-Gel	Yes	[40]
ZnO	c-Oriented	110	Thin Film	***PVD	No	[41]
ZnO	c-Oriented	14.3 – 26.7	Nanoribbon	PVD	No	[42]
ZnO	c-Oriented	7.5	Nanopillar	Template	No	[43]
NaNbO ₃	Orthorhombic	0.85-4.26	Nanowire	Solution	Yes	[44]
KNbO ₃	Orthorhombic	3 – 13	Nanowire	Solution	Yes	[45]
BaTiO ₃	Single Crystal	16.5	Nanowire	Solution	Yes	[46]
GaN	Wurtzite	12.8	Nanowire	Solution	Yes	[47]

However, in the study by Pu, J, et al. [28], the authors reported a high average piezoelectric coefficient (57.6 pm/V) from β phase nanowires produced by electrospinning, which is close to our γ phase PVDF nanoribbons properties. However,

the authors used a very primitive measurement technique based on optical microscopy observation for measuring piezoelectric coefficient of a single nanowire, with ~20% accuracy. Basically, they measured the bending of a suspended nanowire with respect to the applied bias using a calibration background. Therefore, it can be concluded that such technique is not very convenient for nano-materials, as it does not include many influencing factors, such as mechanical vibrations, thermal effects and electrostriction. When these effects are considered, their d_{33} coefficient will dramatically decrease. For instance, when the electrostriction effect was ignored in our study for the piezo-response of PVDF nanoribbons, the measured piezoelectric coefficient increases up to -72.8 pm/V, which doesn't reflect pure and real piezo-response. Therefore, the determination of piezoelectric properties of nanomaterials requires high precision evaluation of the measured data as well as very sophisticated instruments. So, we performed a very precise quantitative piezoelectric characterization technique using AFM as a sensitive displacement sensor and Radiant Premier II as a piezo-evaluation system. Before the nanoribbon measurements, we confirmed our measurements using a commercial PVDF film. In addition, we considered the other parameters (ferroelectric, ferroelastic, electrostriction, and dilatation) which can influence the quantitative evaluation of piezoelectric measurement. For instance, we calculated the indentation of AFM tip (0.3 nm) under 60 nN the applied force by conducting a COMSOL simulation. Besides, the thermal effects were also simulated. Ferroelastic motions can be ignored due to constant local contact loading during the measurements as shown by the finite element simulations in Chapter 3. The value of the piezoelectric coefficient (d_{33}) was calculated by a theoretical fitting to the experimental data, which is explained in Chapter 3. We concluded that 87.4 % of the deflection resulted from pure piezoelectric effect and 12.6 % of the deflection is a result of electrostriction, which corresponds to -58.5 pm/V effective average piezoelectric coefficient measured with 76 % accuracy. PVDF nanoribbons can be considered as potential replacement to the lead-based and lead-free piezoelectric ceramic materials. Although the lead-based ($\text{Pb}_x\text{Zr}_{1-x}\text{Ti}$) O_3 (PZT) systems can represent better piezoelectric coefficients and known as the most favorable ceramic piezoelectric material, they contain plenty amount of Pb. According to Restriction Hazardous Substances Directive (RoHS), Pb was banned from usage in household, consumer, IT-telecommunication, lightning, electronic, medical, etc. equipment, because it is extremely toxic. So, a new research area was appeared as "lead-free piezoelectric". However, the performance of the lead-

free piezoelectric materials such as ZnO, NaNbO₃, KNbO₃, BaTiO₃ and GaN still suffers [42]–[47]. Therefore PVDF nanoribbons are a perfect candidate for the replacement of ceramic piezoelectric materials.

A copolymer of PVDF, PVDF-TrFE was considered as a better piezoelectric material due to extra fluorine in its molecular structure. Extra fluorine increases the polarization and the dipole moment, thus causes a direct nucleation in β phase as explained in Chapter 4. We obtained the highest piezoelectric coefficient (-384 pm/V) from PVDF-TrFE nanoribbons ever measured, as shown in Table 1.1. In the reference [32], the researchers achieved to obtain -72.7 pm/V piezoelectric coefficient from PVDF-TrFE nano-grass structures before polarization under electric field. After the polarization of the structures they obtained -210.4 pm/V piezoelectric coefficient. However, they performed this polarization process using an atomic force microscope tip on a single grass nanostructure and could not show any practical application with this piezoelectric structure. In the references [33] and [34], nanoribbons and nanowires were produced using the solution based template methods, yielding piezoelectric coefficients up to 81 pm/V. Despite the researchers could achieve higher piezoelectric constants in PVDF-TrFE thin films [34], compared to the PVDF [28], they could not beat the ceramic piezoelectric materials [41], particularly PZT [35]–[39]. Among these results obtained from PVDF, PVDF-TrFE, PZT and other ceramic nanostructured piezoelectric materials, our PVDF-TrFE nanoribbons apparently displayed the highest piezoelectric coefficient (-384 pm/V) without requiring an electrical polarization process, due to high stress and high temperature during the fabrication.

In the second part of the thesis, a triboelectric generator working in contact mode was developed, displaying a very high short-circuit current and output power, in comparison to the recent literature on the contact mode triboelectric generators (

Table 1.2). Such performance was achieved using surface fluorination, in order to achieve very high surface charge, in analogy to TEFLON, which is known as the highest negatively charged triboelectric material. However, the processing and surface modification of TEFLON are challenging and require costly processes. Here, we characterized a wide range of materials to understand their triboelectric responses with respect to their chemical content. We concluded that increasing fluorine content in materials also increases their triboelectric response. In addition, for the first time, we

also showed that the inter-metallic semiconductor As_2Se_3 can be used as a triboelectric material. Such devices can generate up to 396 V and 1.62 mA open circuit voltages and short-circuit currents, respectively. They can power up to 38 commercial LEDs, detect low frequency acoustic signals (10 - 100 Hz) and can be excited by small vibrations in a moving car. Hence our devices can be utilized as pocket-size power generators in future nano-electronic devices, and can also be used for vibration and acoustic detection.

Table 1.2: Comparison of the recently-developed triboelectric generators made of different materials, with respect to their open circuit voltages, short circuit currents, output voltage, working mechanisms and working frequencies.

Material Set	Working Mode	Voltage (V)	Current (mA)	Power (W)	Working Frequency	Reference
PEI / F- As_2Se_3	Contact	396	1.600	0.51000	Low	Our Study
TEFLON/Al	Contact	215	0.66	0,14190	Low	[48]
PDMS/Al	Contact	232	0.0165	0.00382	Low	[49]
TEFLON/Al	Contact	100	0.0016	0.00016	Low	[50]
TEFLON/ SiO_2	Contact	88.0	0.0610	0.00530	Low	[51]
TEFLON/Cu	Contact	72.0	0.0320	0.00230	High	[52]
TEFLON/ TiO_2	Contact	21.3	0.032	0.00068	Low	[53]
TEFLON/Cu	Sliding	850	3.0000	1.50000	High	[54]
PVC/Al	Sliding	800	0.0337	0.02700	Low	[55]
TEFLON/Al	Sliding	250	0.250	0.06250	Low	[56]

Since, As_2Se_3 is compatible with the iterative fiber drawing technique and has no toxic reactivity, we rather preferred to use As_2Se_3 in the nanowire form, after the fluorination process. A quick comparison of this study with the previous works on 3D integrated multilayer generators reveals that the power output of our devices is significantly high (Table 1.2), even in comparison to TEFLON. For example, Peng Bai, et al. [48] built a multilayer generator. Although some of the materials (TEFLON, Kapton, Al) that they used in their device were similar with the materials used in this study, the maximum output of their device (215 V and 0.66 mA, powered 9 LEDs) is very low when compared with the output here (396 V and 1.616 mA, powered 38 LEDs).

1.1. Piezoelectricity

Piezoelectricity is an important natural phenomenon which is extensively utilized by a myriad of applications in the field of sensing [57], [58], actuation [59]–[61], and energy harvesting [22], [62]–[64], where a transformation between mechanical and electrical energy is inherently required. Piezoelectricity can be observed in various materials including biological substances [65], [66], but only some of ceramics and polymers are considered to have high piezoelectric coefficients enough to be useful [22], [64], [67]. Besides, a closer look into applications of piezoelectricity such as bio-sensing, pressure sensing, energy generation, artificial muscle and skin discloses that not only high performance piezoelectric, but also flexible, lightweight, and biocompatible materials are demanded [22], [68]–[72]. In addition, intriguing alternative production methods for these piezoelectric materials with advantageous post-processing integration steps are needed to be developed or devised in order to circumvent the main barrier before their large scale exploitation. Although many ceramic materials are known to be good piezoelectric, they suffer from high brittleness, low cyclic endurance, high processing temperatures, and high production cost as well as toxic elemental composition [73]. On the other hand, having none of these drawbacks, piezoelectric polymers such as Poly(vinylidene fluoride) (PVDF) are promising candidates for the replacement of ceramic piezoelectric materials, due to their high piezoelectricity, flexibility, and chemical resistance [22], [74], [75]. A simple evaluation through the literature about PVDF reveals that the form of nanowire brings on many advantages such as higher piezoelectric coefficient, higher electro-mechanical coupling efficiency, and better mechanical properties in contrast with the form of thin films [22]–[24], [76]. The prominent processes for the production of PVDF nanowires are all solution based and they are not superior in all properties considering aspect ratio, uniformity, geometry control, yield, and large area device integrability. The challenging problems confronted in the field can be solved by introducing fundamental changes, starting from the fabrication technique.

1.1.1. Piezoelectric Effect

Piezoelectric materials are differentiated from the other dielectric materials by responding applied force with electric signals. There are two type of piezoelectric

effects available, which are known as direct and converse piezoelectric effect (Figure 1.1). In direct piezoelectric effect, applied force changes the polarization and changes the distance between crystal planes and this change in the polarization induces potential difference on coated electrodes. Direct piezoelectric effect mostly desired in energy harvesting and sensing applications. When an electrical potential applied, a change in the shape occurs in the piezoelectric materials. This phenomena known as indirect or converse piezoelectric effect and mostly desired in actuator applications. Piezoelectric effect was discovered by French physicists Jacques and Pierre Curie brothers [22], [77]–[79].

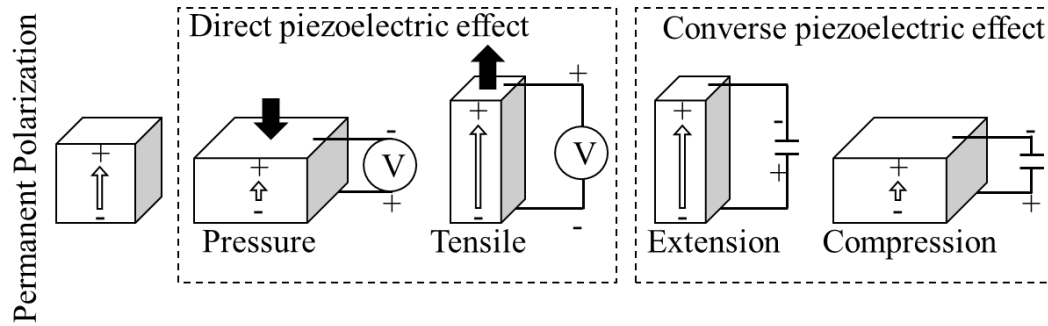


Figure 1.1: There is a permanent polarization in piezoelectric materials after poling process. In direct piezoelectric effect, when there is a mechanical force applied such as pressure or tensile, charges are induced in the coated electrodes with inverse polarity of the dipoles. Indirect effect is the vice versa. Applied potential difference causes extension or compression according to dipole polarity.

Piezoelectric materials carry technologically high importance by interfacing mechanics and electronics. Usually, they are used in electromechanical applications and devices, which play major role in our life, such as electro-mechanic energy converters, pressure sensors, memories, microphones, sonars, headphones, micro-balancers, focusing of optical assemblies in cameras and etc. [71], [80], [81].

Piezoelectric materials are the crystalline materials, which doesn't have inverse symmetry. Therefore, most of the piezoelectric materials are ceramics and many of them have very complex and toxic chemical composition. This complexity also makes piezoelectricity an anisotropic effect, which means direction dependent. These materials can be shaped in rod, slab or films by mixing required elements in specific compositions. However, producing high performance piezoelectric materials requires complex post processing. The post process (Figure 1.2) includes electrical poling

process under high electric field strengths after the materials heated above a critical temperature, which is known as Curie temperature [82], [83].

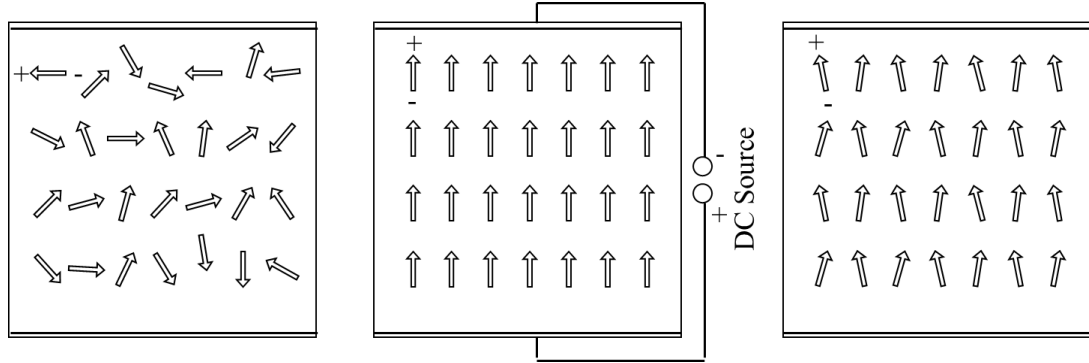


Figure 1.2: Polarizing mechanism of a piezoelectric material. Initially, dipoles are randomly oriented. After poling the material under high electric field above the critical temperature dipoles are saturated. Remnant polarization obtained after removing the electric field.

After this post processing, dipoles can be oriented in the same direction. After electric field removed, forced dipoles create a remnant polarization in the material. In addition, a relaxation in the polarization can be observed after electric field removed [83].

1.1.2. Piezoelectric Constants and Linear Piezoelectric Equations

Materials that reveal piezoelectric property are anisotropic, which means that the piezoelectric properties are different in different crystal plane directions. Response of the piezoelectric material is also dependent on the direction of the applied force as well as the alignment of the dipoles. Irrelevant with the applied force or sensing direction, according to IEEE Standards on piezoelectricity polarization direction is always termed the “3” direction. Detailed explanation was given in Figure 1.3.

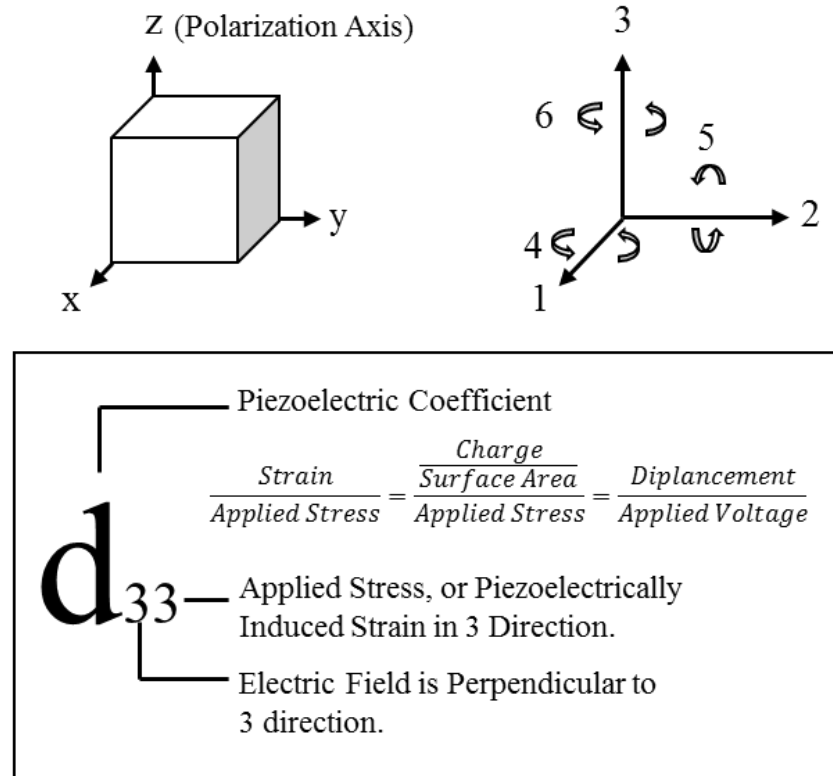


Figure 1.3: Direction of polarization and applied forces in a piezoelectric crystal. The letter “d” known as piezoelectric coefficient or charge constant and can be identified with two indices. The first indice correspond to polarization direction and the second tells the direction of the applied force.

Piezoelectric constants generally have written with two tensors related to direction of the applied force, induced strain, applied electric field, dipole orientation. In an x, y, z coordinate system for defining crystal directions as shown in Figure 1.3, each direction corresponds to 1, 2 and 3 directions, respectively. Shear directions in the crystal showed with 4, 5 and 6. Most used piezoelectric constants were defined below [22], [77], [79], [84], [85].

Piezoelectric Charge Constant or Piezoelectric Coefficient: Piezoelectric coefficient can be shown by “d” and defined as induced polarization per applied stress (T) or induced strain (S) by applied voltage. Therefore units of “d” are pC/N or pm/V. It can be represented by two indices such as d₃₃. Here, the first tensor corresponds to direction of the polarization or the direction of applied field strength and the second one is the applied stress of induced strain.

Piezoelectric Voltage Constant: The voltage constant can be represented by letter “g” and defined as induced electric field by applied stress or induced mechanical strain

by applied electric displacement. It can be represented by two tensors such as g_{33} . Here, the first subscription corresponds to direction of the electric field or the direction of applied electric displacement and the second one is the applied stress of induced strain.

Elastic Compliance: It is represented by “s” letter and defined as the induced strain with applied stress.

Young Modulus: Defined as the stiffness/elasticity of a material. “E” or “Y” used to represent it.

Electromechanical Coupling Factor: Shown as “k” and it is important for transducer applications by characterizing the response of a piezoelectric crystal, whose square is defined as $k^2 = \frac{\text{mechanical energy stored}}{\text{electrical energy stored}}$ proportion of stored mechanical and electrical energy.

Indirect and direct piezoelectric effect can be characterized by polarization hysteresis and displacement curves as shown in Figure 1.4.

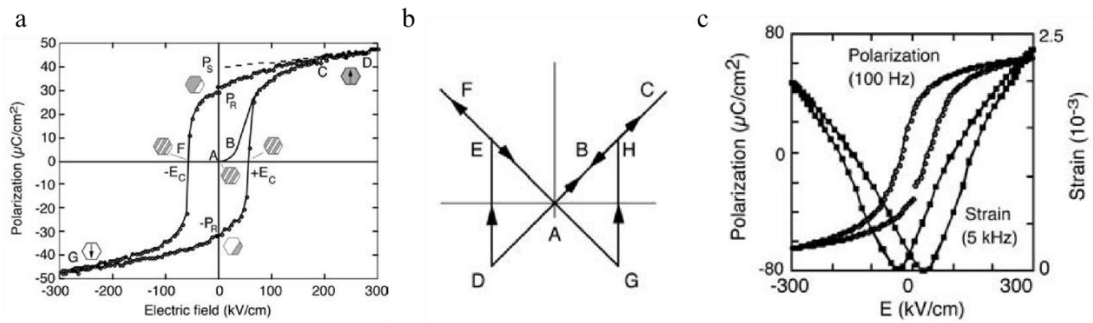


Figure 1.4: Important curves to characterize piezoelectric properties. a) Change in the polarization and polarization switching with respect to applied electric field. b) Strain – electric field curve to characterize expansion and contraction of the piezoelectric crystals with respect applied electric field. c) Real piezoelectric characterization curves are more complex than theoretical representations [86].

When an alternating electric field strength applied to a piezoelectric material, polarization starts to increase between A-B as shown in Figure 1.4a. Increasing electric field switch the polarization between B-C. All domains become the full switch position when electric field further increased in C-D segment. This segment known as saturation region “ P_s ”. Decrease in the electric field relaxes dipoles and when the

electric field removed, polarization doesn't decrease to zero but it remains at remnant polarization point “P_R”. Zero polarization can be obtained at F point, where further change observed in electrical field. The field at this point known as the coercive field E_C, which corresponds to required opposite electric field to neutralize the polarization. Increasing the field in negative direction changes the alignment of the dipoles at G point. A good hysteresis loop is symmetric and absolute values of coercive fields and remnant polarizations are equal. Applied field also increases the strain due to piezoelectric effect [86], [87].

Polarization switch as shown in Figure 1.4a causes a strain as shown in Figure 1.4b-c. So that means, polarization – electric field curve in piezoelectric materials are also related to displacement (strain) – electric field curve. Strain curve is also known as butterfly curve because of its shape. In Figure 1.4b, polarization is zero at zero point. Total strain reaches the maximum at point C. This point corresponds to P_S in polarization curve. When the field decreases, curve follows the same line in opposite direction. After point A, the crystal switches from expansion to contraction. At the point D, polarization switches and it goes to point E. Increasing the field saturates the crystal strain between E-F. At the E point strain becomes in the same direction with field. Decreases in the field, drives the curve to the switching point G. A real strain – electric field and polarization – electric field curves were shown in Figure 1.4c [77], [79], [86], [87].

Basic governing linear equations for piezoelectricity were established by IEEE Standards in 1987. As I mentioned before, piezoelectricity is an anisotropic effect and required to be formulized with indices.

$$D_i = \varepsilon_{ij}^\sigma E_j + d_{im}^d \sigma_m \quad (1.1)$$

$$e_k = d_{jk}^c E_j + s_{km}^E \sigma_m \quad (1.2)$$

This formulations can be rewritten in matrix formulations:

$$\begin{bmatrix} D \\ e \end{bmatrix} = \begin{bmatrix} \varepsilon^\sigma & d^d \\ d^c & s^E \end{bmatrix} \begin{bmatrix} E \\ \sigma \end{bmatrix} \quad (1.3)$$

Here the electrical displacement D (Coulomb/m²) and applied electric field E (Volt/m) are 3x1 vectors. The strain is e and it is a dimensionless 6x1 vector. σ (N/m²) is 6x1 stress vector. Dielectric permittivity ε^σ (Farad/m) is 3x3 matrix. d_{im}^d (m²/N) (6x3) and d_{jk}^c (m/V) (3x6) are direct and converse piezoelectric coefficients, which assumed to be equal. Piezoelectric coefficient d can be written in 3 dimension:

$$d = \begin{bmatrix} 0 & 0 & d_{31} \\ 0 & 0 & d_{32} \\ 0 & 0 & d_{33} \\ 0 & d_{24} & 0 \\ d_{15} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad (1.4)$$

Piezoelectric coefficients related to normal strain at 1, 2, 3 directions and 3 poling direction are d_{31} , d_{32} and d_{33} . d_{15} is related to shear strain at 1-3 directions and 1 polarization direction. Similarly, d_{24} is related to shear strain at 2-3 directions and 2 polarization direction. It should be noted that no shear can be induced in 1-2 direction. Stress compliance for cubic symmetries and permittivity are 6x6 and 3x3 matrices, respectively as given below:

$$s^E = \begin{bmatrix} S_{11} & S_{12} & S_{13} & 0 & 0 & 0 \\ S_{12} & S_{22} & S_{23} & 0 & 0 & 0 \\ S_{13} & S_{23} & S_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & S_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & S_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & S_{66} \end{bmatrix} \quad (1.5)$$

$$\varepsilon^\sigma = \begin{bmatrix} \varepsilon_{11}^\sigma & 0 & 0 \\ 0 & \varepsilon_{22}^\sigma & 0 \\ 0 & 0 & \varepsilon_{33}^\sigma \end{bmatrix} \quad (1.6)$$

To ease the calculations shear and normal stress vectors can be written as:

$$\sigma = \begin{bmatrix} \sigma_{11} \\ \sigma_{22} \\ \sigma_{33} \\ \sigma_{23} \\ \sigma_{31} \\ \sigma_{12} \end{bmatrix} = \begin{bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \sigma_5 \\ \sigma_6 \end{bmatrix} \quad (1.7)$$

As I mentioned before, direct piezoelectric effect equations are used for actuators and converse piezoelectric effect equations are used for sensor applications. In sensor applications, external electric field is zero and there is stress applied to the piezoelectric materials which causes dielectric displacement and generation of charges on coated electrodes with opposed polarity compared to poling direction.

$$\begin{bmatrix} D_1 \\ D_2 \\ D_3 \end{bmatrix} = \begin{bmatrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{24} & 0 & 0 \\ d_{31} & d_{32} & d_{33} & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \sigma_5 \\ \sigma_6 \end{bmatrix} \quad (1.8)$$

Since applied dielectric displacement and induced charge is related:

$$q = \iint \begin{bmatrix} D_1 & D_2 & D_3 \end{bmatrix} \begin{bmatrix} dA_1 \\ dA_2 \\ dA_3 \end{bmatrix} \quad (1.9)$$

Here, A_1 , A_2 and A_3 are the areas of the electrodes in 1, 2 and 3 directions respectively. From capacitance of the device and the charge calculations above, we can calculate induced potential.

$$V_c = \frac{q}{c_p} \quad (1.10)$$

Therefore, a linear charge measurement from a piezoelectric sensor device, help us to calculate applied stress with respect to generated charge. Furthermore, we can also calculate the total induced strain by using compliance matrix [77], [79], [83].

In Figure 1.5, relation between ferroelectricity, piezoelectricity, and pyroelectricity was demonstrated. As expected, smart materials are very complex materials and they have multi-functional stimuli responsive properties such as sensing temperature, chemicals, mechanical and acoustic pressure and static electricity. In ferroelectric materials, there is a spontaneous polarization their crystal system and this polarization can be reversed by applying an external electric filed. This property known as flip-flop change in the dipole orientation. Because of this property of ferroelectric materials, they are mostly used in memory applications. BaTiO₃ and Pb(Zr, Ti)O₃ are the most known ferroelectric materials. ZnO and AlN are known as polar pyroelectric materials. Pyroelectric materials not necessarily contain a flip-flop change and they can sense applied temperature difference as result of charge displacement. Similarly piezoelectric materials also doesn't provide flip-flop action as observed in ferroelectric materials. Besides, in some cases, thermal changes are not enough to induce charge displacement in piezoelectric materials. So, a piezoelectric material not also necessarily provide pyroelectric properties. In most of the piezoelectric applications, in order to obtain a pure piezoelectric charge displacement, pyroelectric effects required to be eliminated.

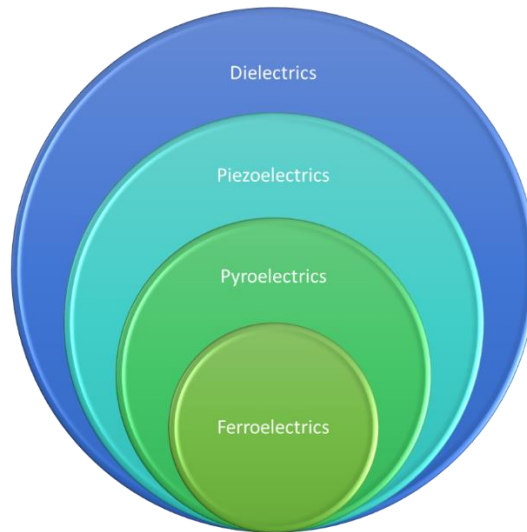


Figure 1.5: Relation between ferroelectric, pyroelectric and piezoelectric effect in a multiferroic material.

There are several disadvantages of using piezoelectric materials. The major part of the piezoelectric materials are very brittle. Besides, the most used piezoelectric materials are toxic. In addition, good piezoelectric materials are also reveal multiferroic effects. Multiferroic effect means coupling between multiple hysteresis effects. For example, PVDF is a polymer piezoelectric material, but in the same time it is a ferroelectric and pyroelectric and ferroelastic material. Besides, co-polymers and terpolymers of PVDF represent relaxor ferroelectric properties. In addition it is a perfect charge storing triboelectric materials [88].

1.2. Triboelectricity and Source of the Static Charges

Triboelectric effect has been known since thousand years and it can be observed only on the surface of dielectric materials such as polymers [23], [89]–[94]. To my knowledge, there is no universal theory that can explain the complete mechanism of triboelectricity. There are speculations about the mechanism of this effect, but none of them are proven yet. Three important phenomenon are considerably strong to explain triboelectric effect, which are direct charge transfer, ion transfer and material transfer from surface to surface [89], [91]–[93]. Although mechanism of triboelectric effect is a conundrum, a closer look into recent studies, which partially explain the mechanism of triboelectric effect reveals that one can facilitate from this effect as a sensor or energy harvesting device [23], [49], [50], [54]–[56], [95]–[98]. It has high capacity to drive electricity from contact and sliding of dielectric materials on their surfaces. This contact and separation phenomenon also causes separation in charges and thus induction of free charges on the electrodes coated on the surface of the dielectrics. Researchers succeeded to harvest over 1 kV and 1 mA from surrounding environmental motions [54]. Surface structure and triboelectric polarity of materials play a major role to build high performance energy harvesting and sensor devices [23], [99], [100]. Interestingly, not only solid materials but also pure water and liquid compounds were also prior to use in triboelectric devices [51], [52], [101], [102]. Many studies has been published that proving water waves are a good source of energy when freely move on a dielectric substrate. The mechanism is related to chemical polarity of the liquid as well as the surface and triboelectric properties of the dielectric substrate.

1.2.1. Triboelectrification

All the mechanical and electronic devices requires many different type of materials to be working together in a harmony. Especially, moving mechanical parts made of different metals and dielectrics seemingly exposed to contact and separation and sliding motions, which consequences in charging of the part surfaces. Moreover, not only solids but also liquids containing lubricant particles or polarizable liquid can cause frictional charging during flow over a metal or dielectric. These mechanisms were investigated by many scientists [89], [101]. Here, I will make a brief introduction to charging mechanism of materials. Before explaining the charging mechanisms, one should note that the final charges of the materials are limited by their electrical breakdown.

Contact charging is one of the most observed materials charging mechanism happened under intimate contact of two dielectrics or metal-dielectric surfaces [89], [93]. Dielectric – liquid metal contact triboelectrification: Dielectric materials are charged when they are immersed in liquid mercury [93]. This experiment is convenient to eliminate frictional forces between dielectric surface and the metal, because of the surface energy of the mercury is too high for wetting to surface of the dielectric materials.

To prove the contact electrification occurs when a dielectric in contact with another dielectric, I conducted an experiment using a faraday cage and an electrometer for measuring charges of two polymer films. Polyether imide (PEI) and TEFLON was cut in equal pieces and their charges were measured after they are grounded for 5 minutes. As shown in Figure 1.6, although the same measurement protocol was applied (5 minutes grounding before measurement) total charges are doubled.

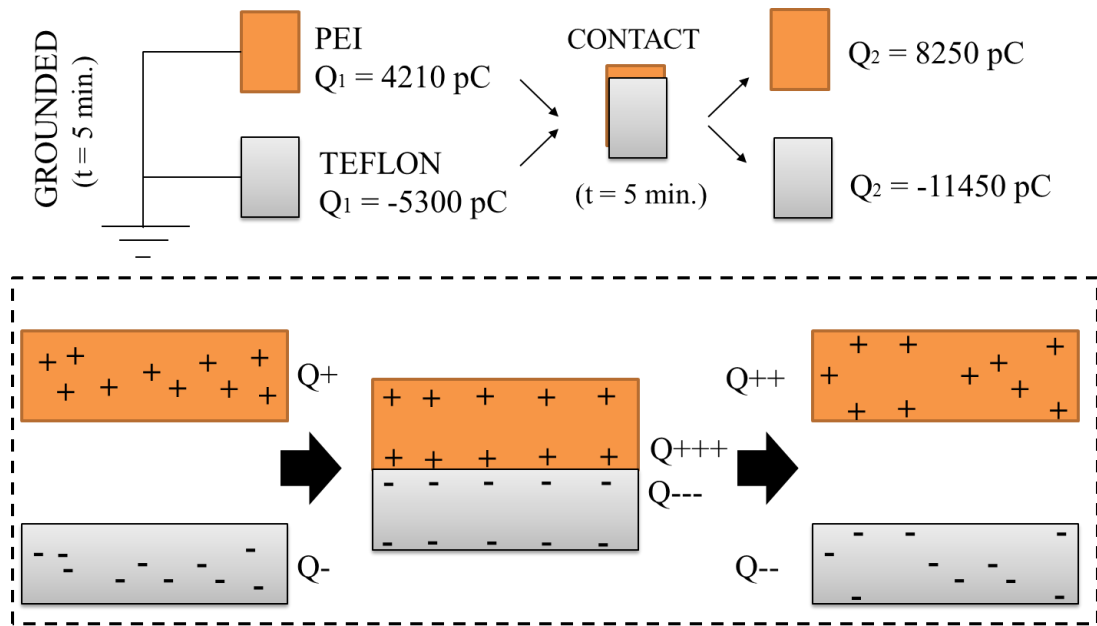


Figure 1.6: Change in the contact electrification after two dielectrics with oppositely charged become in contact and then separation.

Naturally positively charged PEI became more positive and naturally negative charged TEFLON became more negative after contact and separation.

In dielectric metal contacts similar phenomenon occurs, while the metal considered as a floating charging element or source. However, induced charges can be flow through external circuit due to increased external electric field and thus change in the electric displacement. As shown in the Figure 1.7, when I coat the surfaces of PEI and TEFLON with metals, charge separation during their contract induces charge in the metal electrode.

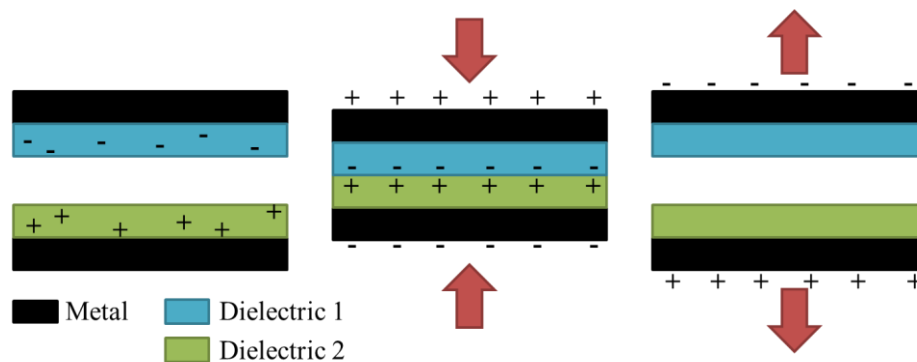


Figure 1.7 : Case of dielectric – dielectric contact when a metal electrode coated on their surfaces.

Here, the total charge of the electrodes are infinite and constant and they are freely moving charges.

When two dielectrics or one dielectric with another metal come to close, they also become charged because of static electricity. To prove this I prepared Cu electrodes in different shape as shown in Figure 1.8.

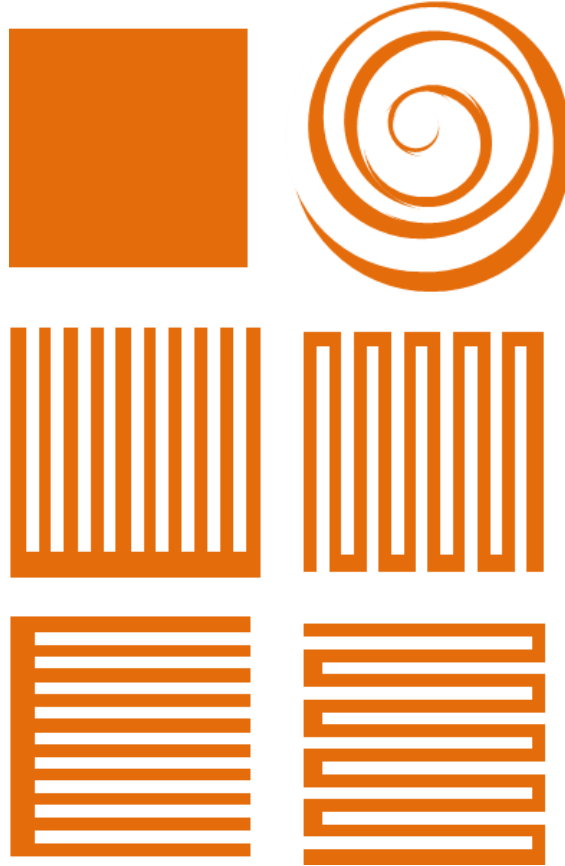


Figure 1.8: Type of Cu electrodes used to prove non-contact electrification.

A TEFLON plate was hanged to 1 cm above of the electrodes. It is released to 15 cm above from the electrodes and freely oscillating TEFLON induced charges on electrodes. This oscillations recoded using an oscilloscope as shown in Figure 1.9

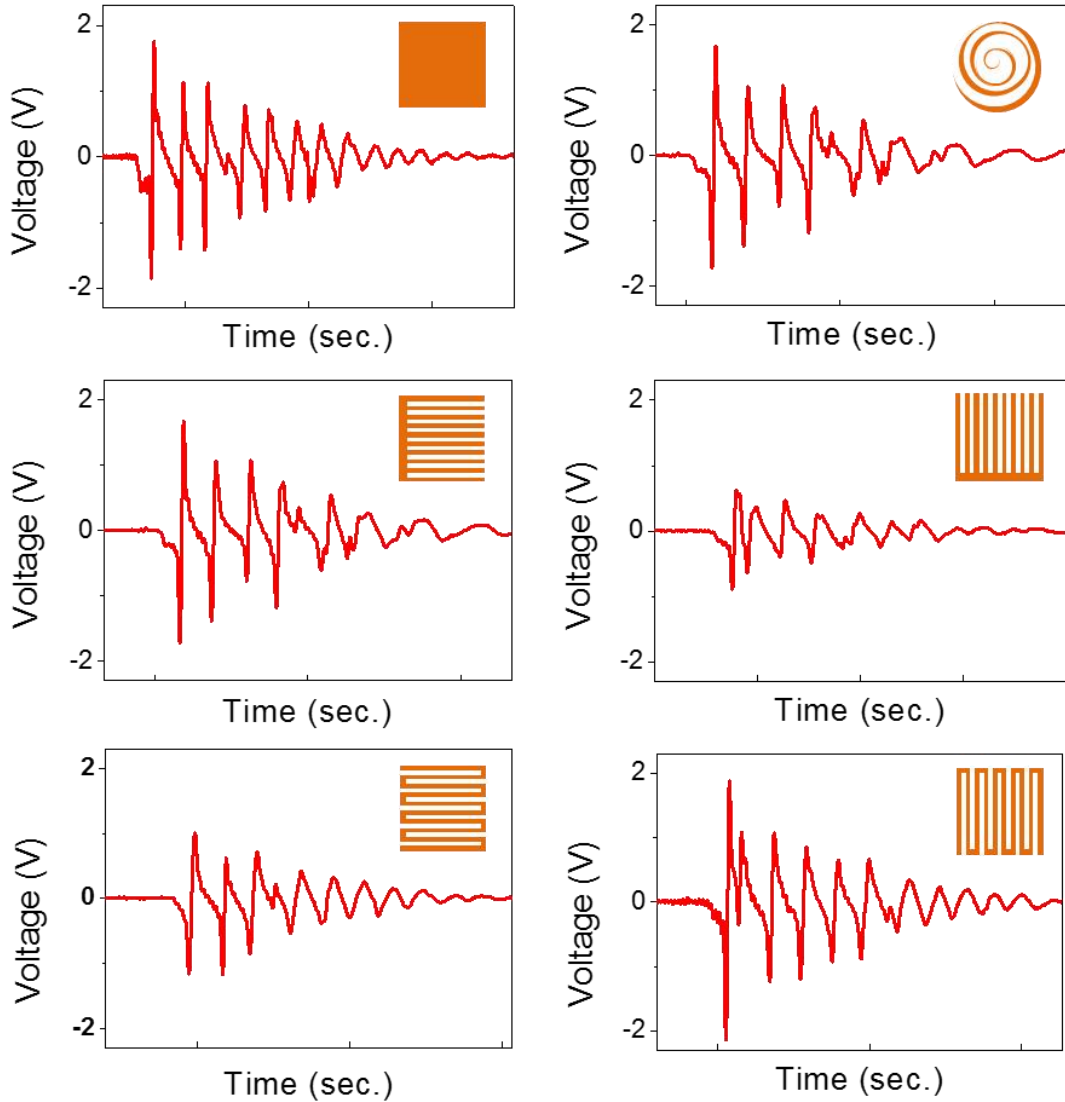
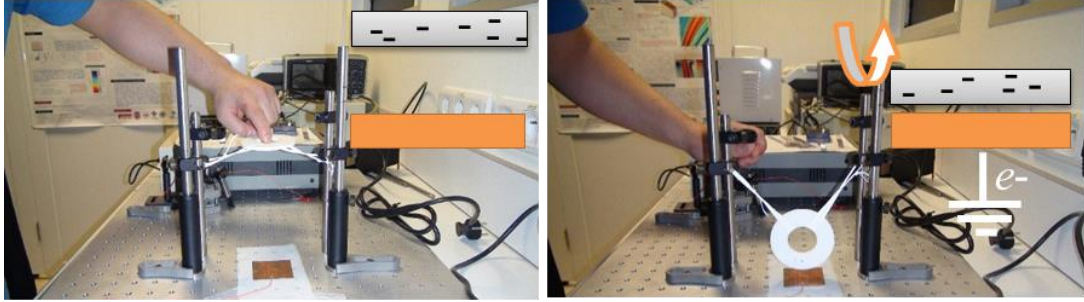


Figure 1.9: Experimental results showing that an oscillating charged plate can induce charges on a Cu electrodes with other any contact to the electrodes.

This non-contact charge induction phenomena briefly explained by COMSOL simulations in Figure 1.10. In this simulation an Al electrode and a TEFLON film approaching to each other from 1m distance. TEFLON set to - 200 V potential and Al electrode was defined as floating potential. There is no significant electric field

enhancement observed, when the distance is 1 m. At 50 cm, the field is still regular. However, a strong electric field enhancement was observed when two materials brought close to each other as 1 cm and 5 mm. Finally, metal electrode compensate the TEFLON and the field become homogenized, when materials come to intimate contact position.

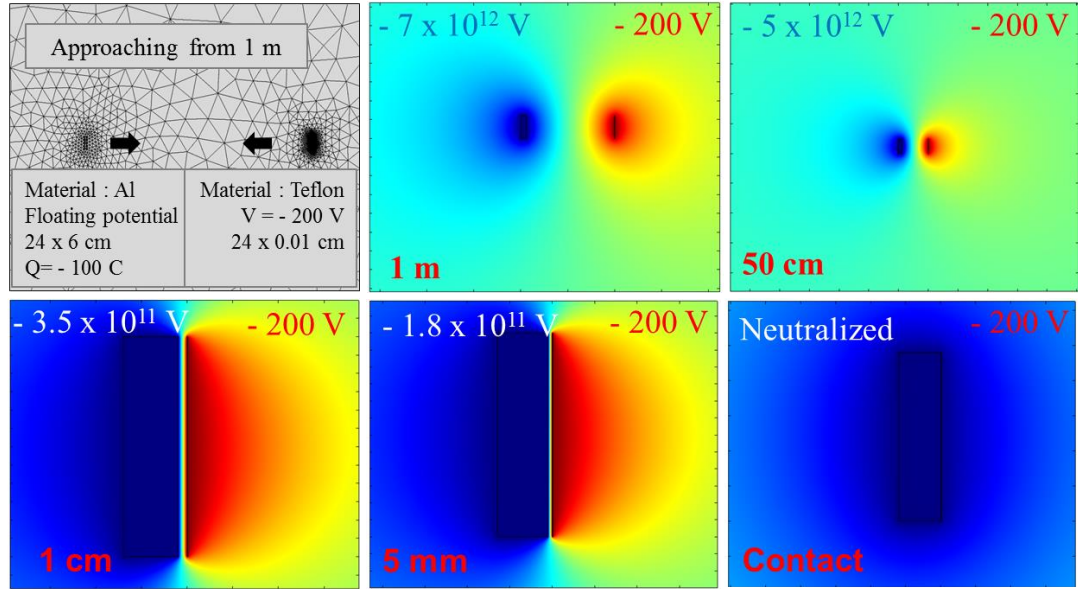


Figure 1.10: COMSOL Multiphysics simulation to show the change in the electric field, when a metal and dielectric approaches to each other. Here the TEFLON has a stable potential while Al electrode set as a floating potential connected to an external circuit. Gradually decrease in the floating potential correspond to charge flow from Al to external circuit because of the approaching potential.

Similar to the COMSOL simulations, in the experiment shown in Figure 1.9, irrespective to electrode shape, oscillating TEFLON causes a floating potential on Cu electrodes. Indeed, it is a simple pendulum and in every return of the object total traveling distance decrease. This effect is a function of the time and was observed as decreasing in the amplitude of the induced voltage.

We are able to explain the way for charging and discharging of materials by controlled experiments. Theoretical details of triboelectric effect and nanogenerators devices explained in detail in chapter number 5.

1.3. Thesis Outline

This thesis organized as follows:

Chapter 1: A detailed literature survey and a comparative analyses of the thesis are given here. The importance of this study is discussed. A brief introduction to piezoelectricity is also explained. In addition, the governing equations for piezoelectric sensor applications are listed. Finally, a brief introduction to triboelectricity by explaining the controlled experiments on the source of the static charges are also given here.

Chapter 2: The details of the iterative size reduction as a new top-down fabrication are given in this chapter. Moreover, the production of nanowires, nanotubes and core-shell structures are detailed.

Chapter 3 and Chapter 4: Obtaining piezoelectric ribbons from Poly (vinylidene fluoride) and its copolymer Poly (vinylidene fluoride)-co-tri (fluoroethylene) is explained in these chapters. A detailed instrumental analysis with ab-initio calculations is also given. Finally, a proof-of-principle energy harvesting device is demonstrated.

Chapter 5: In this chapter, the fabrication and analysis of the 3D-printed multi-layered triboelectric nanogenerators are demonstrated. 3D surface modification using fluorine monolayers are also explained in detail.

Chapter 6: The thesis is summarized and a brief outlook for future work is given.

Chapter 2

Iterative Thermal Size Reduction Technique for Multi-material Nanostructure Fabrication

Nanowires are arguably the most studied nanomaterial model to make functional devices and arrays [103], [104]. Although there is remarkable maturity in the chemical synthesis of complex nanowire structures [105], [106], their integration and interfacing to macro systems with high yields and repeatability [7], [107], [108] still require elaborate aligning, positioning and interfacing and post-synthesis techniques [109], [110]. Top-down fabrication methods for nanowire production, such as lithography and electrospinning, have not enjoyed comparable growth. Here we report a new thermal size-reduction process to produce well-ordered, globally oriented, indefinitely long nanowire and nanotube arrays with different materials. The new technique involves iterative co-drawing of hermetically sealed multimaterial in compatible polymer matrices similar to fiber drawing. Globally oriented, endlessly parallel, axially and radially uniform semiconducting and piezoelectric nanowire and nanotube arrays hundreds of meters long, with nanowire diameters less than 15 nm, are obtained. The resulting nanostructures are sealed inside a flexible substrate, facilitating the handling of and electrical contacting to the nanowires. Inexpensive, high-throughput, multimaterial nanowire arrays pave the way for applications including nanowire-based large-area flexible sensor platforms, phase-change memory, nanostructure-enhanced

photovoltaics, semiconductor nanophotonics, dielectric metamaterials, linear and nonlinear photonics and nanowire-enabled high-performance composites.

2.1. Top-Down and Bottom-Up Fabrication

One-dimensional nanostructures such as nanowires, nanotubes and nanoribbons are continuing to be at the forefront of nanoscience and nanotechnology. Two distinct approaches for the fabrication of these structures are the top-down and bottom-up philosophies [111]. During the past decade, chemical synthesis demonstrated the impressive success of the bottom-up approach in achieving controllable composition and morphology [105], [106] and prototype functional devices [103], [104], [111], but less so for the integration of high-density device assemblies. Post-synthesis assembly techniques, designed for this end, such as electric, magnetic-field-assisted alignment and dielectrophoresis [107], optical and optoelectronic tweezers [112], laminar flow in microfluidic channels [113] and micro contact printing [114] still do not achieve low cost, high throughput, and good reproducibility with high-precision addressability. For some applications chemical synthesis is simply not a fitting choice; for example, it is still difficult to produce very long aligned nanowires [115]–[117], and to obtain nanowires on large area substrates [118], or polymer substrate nanowire integration, requires separate high-temperature nanowire synthesis and subsequent transformation.

On the top-down side, patterning by lithography is a powerful but costly micro- and nanofabrication tool perfected by the semiconductor industry. However, for one-dimensional nanostructure fabrication, it is not much favored owing to scientific challenges such as resolution, surface roughness, limited chemical composition and its low throughput [111]. Various hybrid techniques are developed for nanowire fabrication to expand the toolkit, such as using photonic crystal fibers [119] as microfluidic reactors [116] to synthesize nanowires and meniscus-controlled solution evaporation [117] (growth and winding process) to obtain very long nanowires. A few other successfully fabricated top-to-bottom micro- or nanostructures are the photonic crystal fiber, which consists of microtubular enclaves inside a silica fiber [119] for optical guiding, thermally drawn composite fibers integrating semiconductors, metals and insulators featuring micro- and nano-sizes for advanced functionality [120], [121], and silica nanofibers obtained by tapering [122]. Direct attempts to produce very long

metallic [123] and semiconducting [124], [125] micro- and nanowires inside viscoelastic matrices using thermal size reduction similar to the Taylor wire process [126] could not produce ordered structures. Arbitrarily distributed filaments are obtained, making it impossible to identify/address each filament as single nanostructures.

2.2. Iterative Fiber Drawing Technique

Here we report the first successful fabrication of arrays of millions of ordered indefinitely long nanowires and nanotubes in a flexible polymer fiber. Using a new iterative size-reduction process, semiconducting nanowires and hollow-core piezoelectric polymer nanotubes, with diameters below 15 nm, are obtained as well-ordered high-density arrays. The nanostructure sizes are uniform for hundreds of meters along the fiber and radially homogeneous in the cross-section. Unique multimaterial core-shell nanowire arrays were obtained and nanowires and nanotubes can be extracted to obtain extremely long free-standing slivers [22]–[24], [76], [127].

To fabricate nanowires that bridge the macroscopic and the nanoscopic world, we designed a multistep iterative thermal size-reduction process inspired from composite-fiber drawing from polymer reels. We start with a macroscopic polymer rod with an annular hole which is tightly fitted with a thermoelastically compatible material that is to become nanowires on multiple axial elongation and radial reduction. Millimetric fibers obtained from the first thermal size-reduction step are cut and arranged in hexagonal lattices inside a protective jacket, vacuum consolidated and redrawn. This second step reduces the wire size to a few micrometers. The drawing step is repeated a third time with the fibers obtained from the previous step to obtain nanometer-sized wires (Figure 2.1). Typically, macroscopic rods are reduced by 25- to 300-fold within each step. Using a reduction factor of 50–100 for three iterative steps, a 10 mm initial rod is reduced to hierarchically ordered 10 nm wires. The total number of nanowires and their ultimate size distribution is determined by the number of packed fibers after each step, the total number of iterative steps and the reduction factor as shown in Figure 2.1.

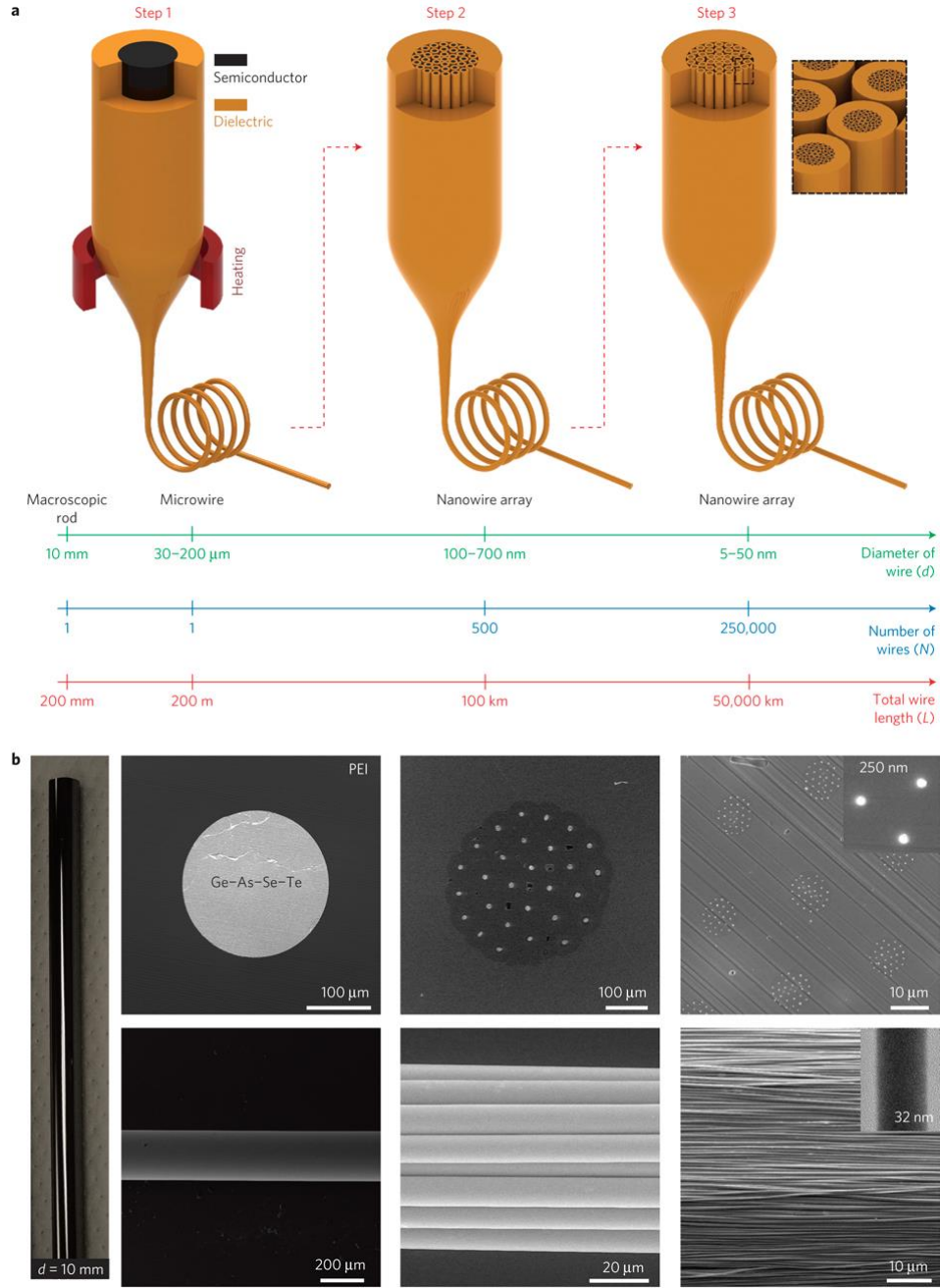


Figure 2.1: a) A macroscopic multimaterial rod is reduced to ordered arrays of nanowires by thermal size reduction in a protective polymer matrix in successive steps. Each step starts with structures obtained from a previous step, resulting in geometrical size reduction and increment in wire number and length. Using the technique, we produced millions of kilometer-long nanowires with sub-10 nm diameter and an aspect ratio of 10. b) As an example, a 10 mm amorphous semiconducting rod (Ge–As–Se–Te) is reduced to hundreds of meters of single 200 μm wire (reduction factor $\times 50$), ~ 30 wires of 5 μm diameter (reduction factor $\times 50$) and $\sim 1,000$ wires of 250 nm (reduction factor $\times 50$). Nanowire arrays are obtained as embedded in a dielectric polyetherimide encapsulation. Wire-array cross-sections with well-ordered wires and extracted, globally oriented slivers are shown after each step. Inset: Transmission electron microscopy image of a single 32-nm-thick nanowire obtained by further scaling down the third-step nanowires.

We demonstrate nanowire production using chalcogenide semiconducting glasses in Figure 2.1. Stable glass-making non-oxide chalcogenide compounds have low softening points, making them amenable for thermal co-drawing inside polymer matrices owing to their excellent match of thermomechanical properties. We synthesized a 10 mm diameter glass making chalcogenide $\text{Ge}_{15}\text{As}_{25}\text{Se}_{15}\text{Te}_{45}$ (GAST, $T_g \sim 190^\circ\text{C}$) from high-purity elemental constituents using the conventional melt-quenching technique (see Chapter 5). Around the glass rod, a high-temperature engineering polymer (polyetherimide, $T_g \sim 220^\circ\text{C}$) is rolled and thermally consolidated in vacuum. The composite structure is then thermally drawn to reduce radial size. Typically, the process is carried out at 50 cm min^{-1} drawing speed while feeding the macroscopic rod at 1.5 mm min^{-1} into a furnace at 275°C . The ‘fiber wires’ obtained from the first drawing are then packed and vacuum consolidated to prepare a second-step macroscopic rod. Vacuum consolidation ensures structural homogeneity and purity from defects that may adversely affect the subsequent thermal drawing process. Beginning with a 10-mm-diameter GAST rod, the diameter is successively reduced to $200\text{ }\mu\text{m}$, $5\text{ }\mu\text{m}$ and 250 nm within each drawing step. Further reduction in the third step results in sub- 50 nm nanowire arrays. In Figure 2.1, we show a perfectly ordered array of GAST micro- and nanowires in the polyetherimide polymer cross-section. It is remarkable that the macroscopic structure is undistorted after the drawing steps. We have also demonstrated that the micro- and nanowires can be extracted from the polymer matrix retaining their global alignment simply by exposing the polymer section to organic etching agents (dichloromethane (DCM) or dimethylacetamide). Resulting free-standing micro- and nanowire slivers are shown in Figure 2.1.

Finally, we investigated the size-dependent photoconductivity of selenium micro- and nanowire arrays fabricated using the described technique. Elemental selenium has phase-dependent electrical conductivity and photoconductivity properties, making it suitable for phase-change memory, optoelectronics and photodetection applications. In a three-step drawing process, we obtained a $56\text{ }\mu\text{m}$ wire, an array of $100 \times 8\text{ }\mu\text{m}$ wires and an array of $10,000 \times 190\text{ nm}$ nanowires. The structure of the nanowires inside the polyethersulfone polymer matrix is conserved after the drawing steps (Figure 2.2). The uniformities of the selenium nanowires from the second and third steps are found to be $\pm 3\%$ and $\pm 11\%$ respectively. Factors contributing to the overall size distribution are

slight variations in the fibers that are used to make the macroscopic composite, and the total accumulated size variation from each previous step. Amorphous selenium wires are obtained after drawing, as revealed by X-ray diffraction and transmission electron microscope diffraction (FEI, Tecnai G2 F30). The wires are crystallized through heat treatment, by annealing above the crystallization ($T_x=110\text{ }^{\circ}\text{C}$) but below the melting temperature [124], [128] and by exposing to the organic reagent pyridine (Figure 2.2a). After crystallization we observe that the conductivity increases to 10^{-4} S cm^{-1} consistent with bulk selenium conductivities. Electrical measurements were carried out with nanowire arrays by cleaving fiber ends with a razor blade and electrical contacting was achieved using silver paint on the facets of the fiber. Step 3 nanowires were chemically crystallized after extraction from the polymer matrix. Electrical gain due to photoconductivity is measured by shining white light (50 W) while applying voltage bias (Figure 2.2b). Step-3 wires make Ohmic contact and feature photoconductivity after crystallization (Figure 2.2c). The photoconductance of the nanowires is observed to be a function of the nanowire number and size in the array. We observed that the I/I_0 gain (photocurrent versus dark current) was an order of magnitude larger for step-2 wires and two orders of magnitude larger for step-3 wires with respect to the single selenium microwire from the first drawing (Figure 2.2d). The switching between on/off states is also faster with the smaller nanowire sizes. We attribute the logarithmic increase in photoconductance to the high absorption of selenium, increased surface-area-to-volume ratio and enhanced scattering of the incoming beam.

We have demonstrated a unique, high-throughput, lithography-free nanofabrication method to produce macroscopically large nanowire and nanotube arrays. The nanostructures are indefinitely long, ordered, uniform, high-density arrays embedded in a flexible polymer fiber matrix. Diverse multimaterial sets and disparate combinations are used to obtain crystalline semiconducting nanowire arrays, chalcogenide nanowire array waveguides, piezoelectric polymer nanotubes and cylindrical core-shell structures.

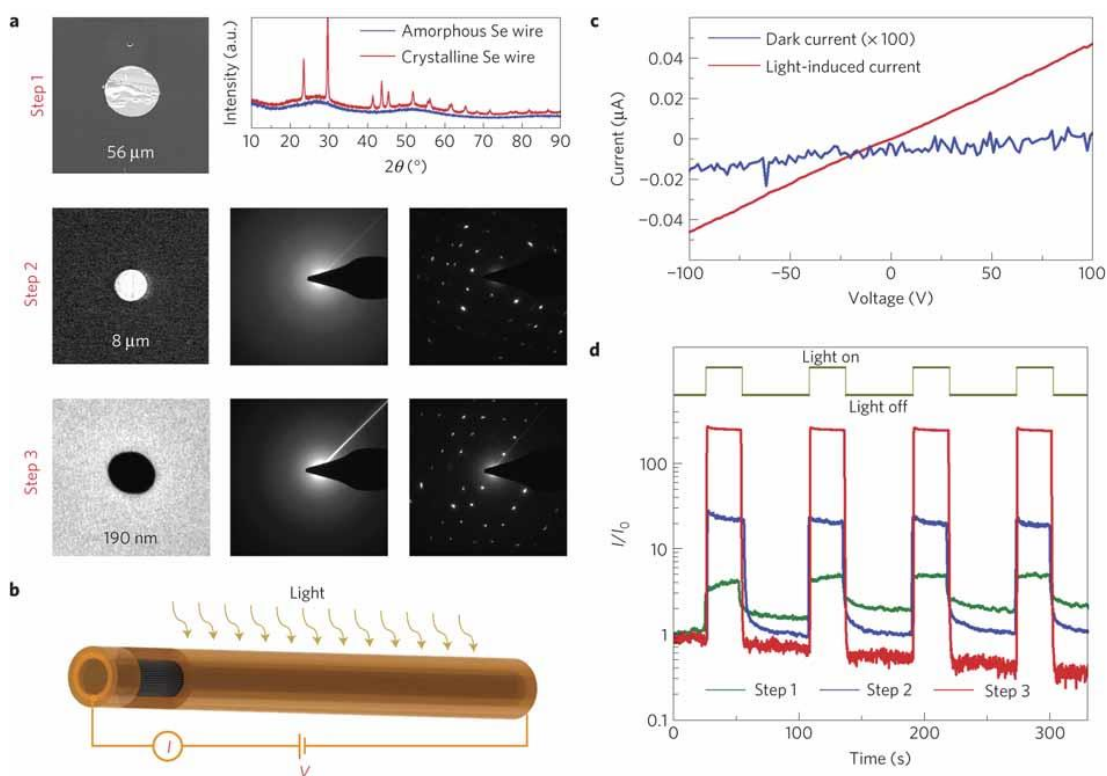


Figure 2.2: a) Amorphous selenium wires are crystallized through heat treatment or by exposing to the organic reagent pyridine. SEM images of regularly scaled-down individual selenium wires. The electrically conductive hexagonal crystallographic phase is obtained by X-ray and electron diffraction. b) A schematic representation of the photoconductance measurement geometry. c) The photoconductance from a selenium nanowire in the dark and on white-light illumination. d) A logarithmic increase in the ratio of photocurrent versus dark current (I/I_0) and a reduction in switching time (τ) with reducing nanowire diameter are observed. The performance increase is attributed to the high optical density of selenium, increased surface-area-to-volume ratio and enhanced scattering in the polymer matrix.

It is an open question if molecular wires can be obtained using the method. The ultimate size reduction for the nanowires needs to be studied by optimizing drawing parameters for thermoviscous materials and materials that melt during drawing separately. On the other hand, the material set can also be widened to include semiconductors, such as Si and Ge that soften/melt at higher temperatures using suitable glassy matrices.

2.2.1. Possible Applications of Nanofibers

This type of produced nanofibers have versatile application areas (Figure 2.3). Here I will mention just a few of them;

- Bio sensing
- Chemical sensing
- Artificial skin
- Large area detection
- Photonic filters
- Photonic band gap fibers
- Intelligent textile etc.



Figure 2.3: Application of fiber that produced by drawing technique.

We expect that a whole new family of radically novel nanowire applications will be enabled owing to the unique geometry and material set used. We identify a number of enticing applications that are of current and rigorous scientific and technical interest. For example, these nanostructures can be exploited in nanowire electronics, as large-area conformal photodetectors, large-area flexible nanowire sensors [115], scalable high-density nanowire-based phase-change memory [129] and in high-speed reconfigurable field-effect transistors [72]; in energy harvesting, large-area cylindrical hetero-structure nanowires can be used as active cells [130], [131] but also for passive light enhancement in resonance-enhanced third-generation photovoltaics [132]–[134]; in semiconductor nanophotonics, polymer-embedded chalcogenide nanowires can be used as high-refractive-index dielectric structures for size-dependent absorption [133], structural coloring [135] and biomimicry, and as dielectric metamaterials [136]; in nonlinear photonics, ordered nanowires can be used as high-power zero-dispersion optical arrays for new frequency generation [137] and in discrete optics [138]; in mechanics, nanowire-embedded high-strength composites [126]; in acoustics, flexible piezoelectric nanowires and nanotubes can be used as sensors and actuators [11], as pumps, in energy harvesting [62] and as nanochannels in nanofluidics.

2.3. Kilometer-long Nanotubes and Nano-shells

Recently developments in organic and flexible electronics emerged new investigations and applications of piezo-polymers. We realized a proper fabrication method will bring on the opportunity of manufacturing highly efficient all polymer flexible devices and developed a new method depends on iterative fiber drawing in order to fabricate kilometer long ordered PVDF nanotube, nanoshell and nanoribbon arrays, which can be used for large area flexible sensor, high energy density capacitor, energy harvesting, non-volatile memory, artificial skin and muscle applications. In the fabrication, we start with preparing the preform structure which is an exact macroscopic copy of the final fiber structure, and then we thermally shrink down the size as small as 20 nm using iterative fiber drawing method. Cross sectional characteristics of our nanostructures can be squared or tubular depends on the shape of the macroscopic core material [22], [24].

Detail information about structure and phase transformation of PVDF also given in Chapter 3 and Chapter 4. Since, Kawai discovered the piezoelectric property of PVDF in 1969, it is widely used in organic electronics. PVDF has the highest piezoelectric coefficient among the all organic materials. Moreover, high flexibility and chemical stability with high piezoelectric coefficient make PVDF one of the best replacement candidates of ceramic piezoelectric materials. Electronic and mechanical properties of PVDF depend on its molecular conformation and chain density in its unit cell (see Figure 2.4). Normally there is a strong interaction between CF_2 molecules, but there are CH_2 groups statistically located between CF_2 groups which makes it form different chemical structures such as combinations of Trans (T) and Gauche (G) strings in different regions of the polymer chain (TGTG, TTTT, TTTGTTTG). Different stoichiometry in PVDF result in different crystals known as α (II), β (I), γ (III) and δ (IV) phases. However, only form I or β crystals of PVDF reveal piezoelectric properties [11], [22], [74], [75], [29], [83], [139]–[141].

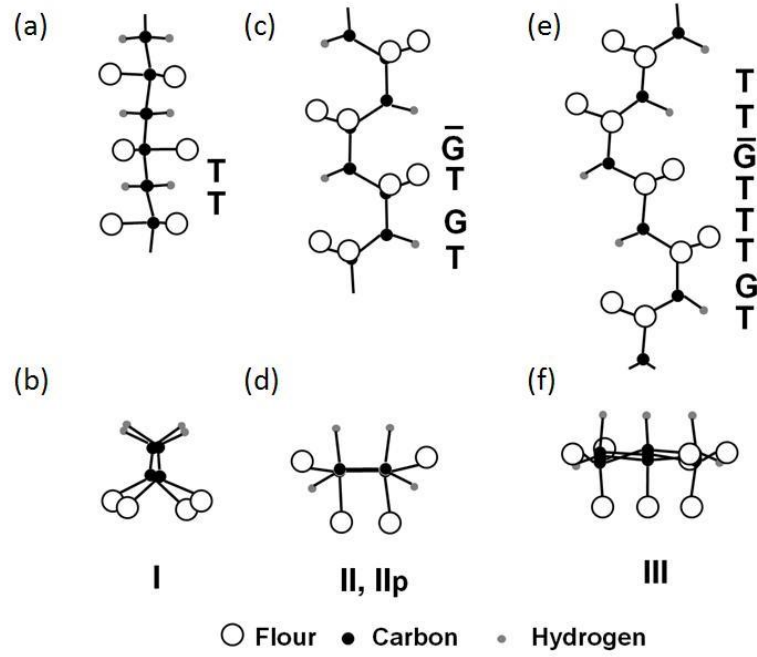


Figure 2.4: Different crystal structure of PVDF. a-b) Piezoelectric form I chain TT structure. c-d) α -phase PVDF which can be polarized, but it doesn't reveal any piezoelectric effect. e- f) Form III PVDF.

Crystallographic structure of form I PVDF is defined as planar zigzag orthorhombic. However, some of the researchers put forward that it can stay stable in monoclinic and triclinic structure. Form I PVDF space group number is $2mCm-C_v$. The group theory information for all phases of PVDF is given in Table 2.1.

Table 2.1: Unit cell parameters, space group numbers and molecular chain data for all of the phases of PVDF.

	Unit Cell Parameters	Space Group	Molecular Chain	*N
Form I	$a=8.85 \text{ \AA}$, $b=4.91 \text{ \AA}$, c *(f.a.) = $2,56 \text{ \AA}$	$2mCm-C_v$	**Zigzag	2
Form II	$a=4.96 \text{ \AA}$, $b=9.64 \text{ \AA}$, c (f.a.) = $4,96 \text{ \AA}$, $\beta=90^\circ$	$P2_1/c-mC_{2k}$	TGT $\bar{G}$	2
Form II _p	Almost same with form II	$P2_1cn (?)$	TGT $\bar{G}$	2
Form III	$a=4.96 \text{ \AA}$, $b=9.58 \text{ \AA}$, c (f.a.) = $9,23 \text{ \AA}$, $\beta=92,9^\circ$	$Cc-C^4$	TTTGT $\bar{G}$	2

*N: Chain number in a unit cell; (f.a.): fibril axis, ** slightly helix planar zigzag

Phase changes characteristics in PVDF may vary depending on environmental factors such as cooling, heating, mechanical stress, stretching and pressure (see Figure 2.5). Usually, PVDF is heated at 95 °C for a while and polarized at that temperature in order to obtain form I phase. Polarization requires high electric field strengths. So that making PVDF at nanoscales greatly alters the polarization process required for phase transformation to β crystals. Besides with decreasing thickness, motion of molecular change becomes easier, also helping obtain the piezoelectric phase. The importance of nanoscale effects has been demonstrated by fabricating PVDF ferroelectric memory and nanogenerators where electro spinning, nano-imprinting, alumina template methods are employed. However, none of these fabrication methods are capable to obtain ordered, polymer encapsulated, ultra-long, PVDF nanostructures[22], [28], [83], [142], [143].

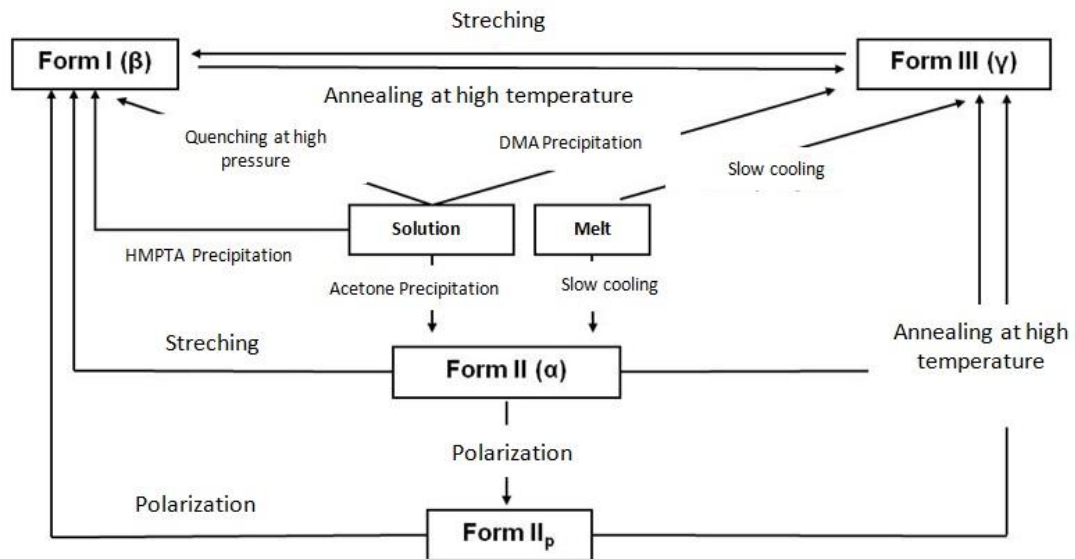


Figure 2.5: PVDF phase transformation mechanisms. Piezoelectric β phase can be obtained by several ways: quenching under high pressure from the PVDF solution, stretching α -phase PVDF (Generally 1 to 4 or more stretching result in high amount of phase transformation), and polarization of form one under electric field. We prefer to apply last option for phase transformation for out fibers because stretching may harm nanotube structure.

Here we introduce a new fabrication method in order to obtain highly flexible and kilometer long, polymer encapsulated PVDF nanotubes, nanoribbon and nanoshell arrays which rely on the thermal fiber drawing technique. Nanoribbons fabrication techniques were discussed in Chapter 3 and Chapter 4 with all details.

The thermal drawing process is a very well-known standard process which utilizes the glass transition temperature or softening temperature of materials in order to create effortless and controlled plastic deformation. Fiber drawing technique is not only applicable for telecommunication silica glass fiber manufacturing but also appropriate for composite multi-material fiber production which is made with polymers, chalcogenides and metals. Our technique is based on drawing fibers iteratively, so we can easily control the diameters of fibers between 200 μm to 20 nm. Since, we can produce our nanotubes, nanoribbons and nanoshells in a macroscopic polysulfone (PSU), polyethersulfone (PES) and polycarbonate (PC) polymer encapsulation layers respectively; it can be easily handled and integrated with any macroscopic desired device. Cross-sections of our nanostructures can be square or tubular depends on the shape of the core material. In addition, by dissolving cladding layer using dichloromethane (DCM) we can extract PVDF nanostructures on any flexible, curved or rigid surface. The advantage of using the square cross sectional nanoshells is creating high density packed arrays which can enhance the performance of any built devices by using PVDF.

2.3.1. Fabrication Process

Our top-down fabrication technique introduces many advantages for PVDF nanotubes and nanoshells such as ordered structure, precise controlled dimensions, ultra-high aspect ratio and polymer encapsulation jacket; each can only be obtained using different fabrication processes.

Fabrication of Nanotubes: The fabrication procedure starts with a preform structure which is an exact macroscopic copy of final fibers Figure 2.6. A 50 μm thick and 25 mm wide PSU film are rolled around a 10 mm in diameter Teflon coated glass tube. Inner diameter of the preform may change in order to the diameter of the Teflon coated glass tube. PSU roll that used for constructing the cladding layer of the fibers is required to be thick enough to support core material. We held the preform in a vacuum oven for 4 hours at 180 $^{\circ}\text{C}$ and 1×10^{-2} Torr in order to evacuate the air trapped between rolled polymer layers. Because, trapped air lowers the quality of the preform as bubbles accumulate inside of the preform and the preform takes undesired shapes which make it impossible to use for fiber drawing. PSU preform consolidated at 225

°C for 30 minutes under a 1×10^{-2} Torr vacuum condition. A consolidated preform is ready for thermal drawing after machining and flattening the both edges.

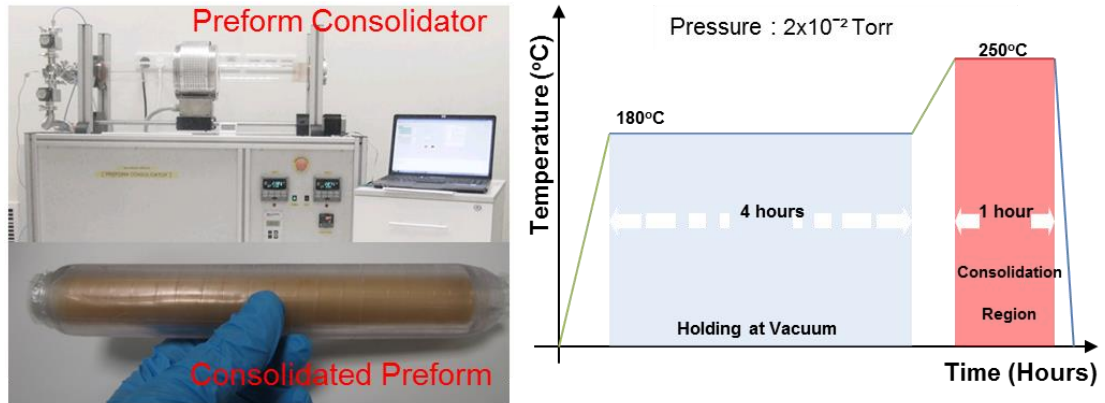
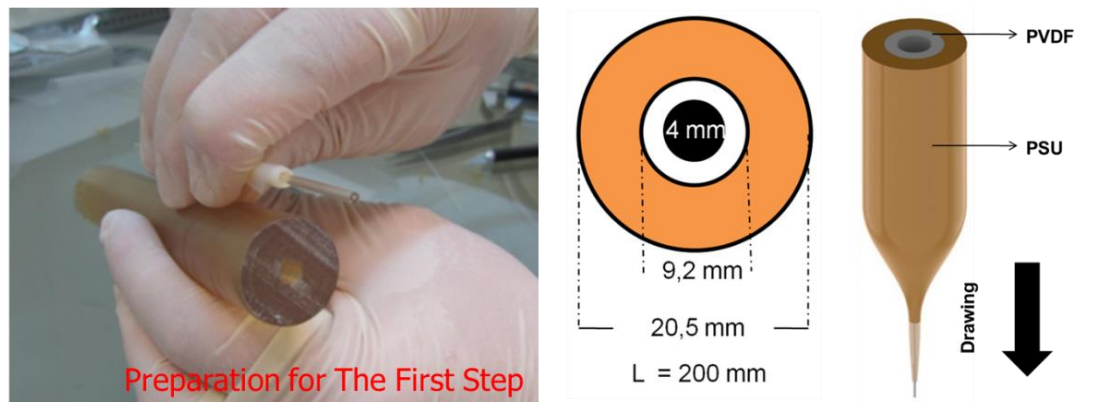


Figure 2.6: Preform consolidation process take place in a tubular oven at elevated pressure and moderate vacuum as shown in the right side. A successfully consolidated preform and the consolidator device shown at the left.

The fabrication of polymer nanotubes by using thermal drawing process comprises several fiber drawing steps, starting with a hollow core PSU preform which is filled with rolled 75 μm thick PVDF films. Iterative fiber drawing process and preparation for each drawing step described in the Figure 2.7.



Preparation for The Second and The Third Steps

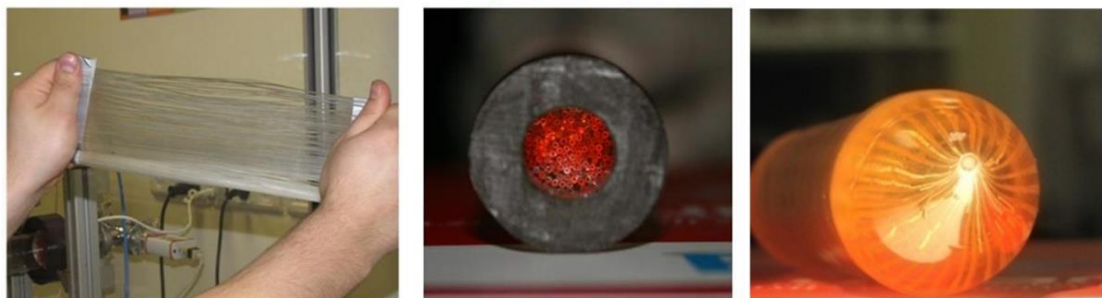


Figure 2.7: Structure of the first step preform and preparation of first step drawing were shown in the schematics. We roll PVDF thin films and directly insert in to the core of the preform. In the preparation for step 2 and 3 fiber drawing: We need to cut, clean and align the fibers before

we start to the next step. We put first step fibers into a new preform and draw the fibers iteratively in order to produce nanotubes.

Fiber drawing process executed in a custom made fiber tower (Figure 2.8), which consist of a vertical tube oven, feeding mechanism and a real time stress, temperature and diameter measurement systems. After gently inserting the preform into the tube oven, a 100 gr load is applied downwards where it pulls the preform. PSU preform takes the fiber shape by the help of the gravitational and applied force when it is heated up to 240 °C above softening temperature.

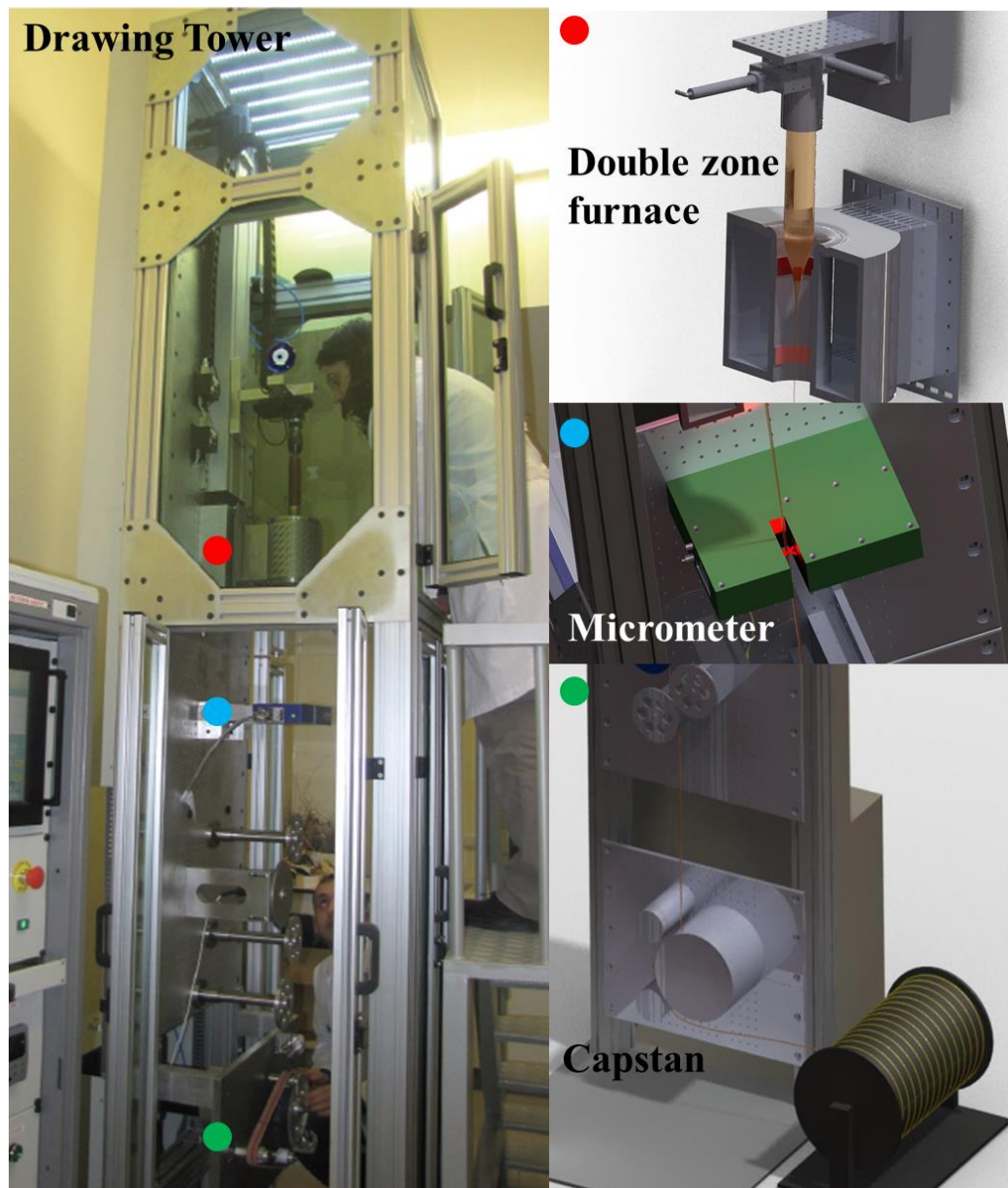


Figure 2.8: A custom made fiber tower, which is used to produce nanoribbon embedded fibers, consists of a preform feeding mechanism, furnace, thickness monitoring system, tension measurement unit, and a capstan.

PVDF microtubes formed in accordance with dimensional changes in PSU cladding and it is mainly a self-assemble tube formation process due to high surface energy of molten PVDF at thermal drawing temperature. In fiber drawing, glass transition temperature of each material that used in preform structure should be considered when a multi-material fiber is produced. Since glass transition temperature of PSU is higher than the melting point of the PVDF, during fiber drawing it causes PVDF films melt and reform tubular structure as it takes the shape of the PSU cladding.

Precise design of a fabrication process (Figure 2.9) is directly related to determination of size reduction factor, total amount of input fibers and their diameters for each step. Fiber drawing process iteratively runs two more times in order to scale down first step microtubes into nanotubes.

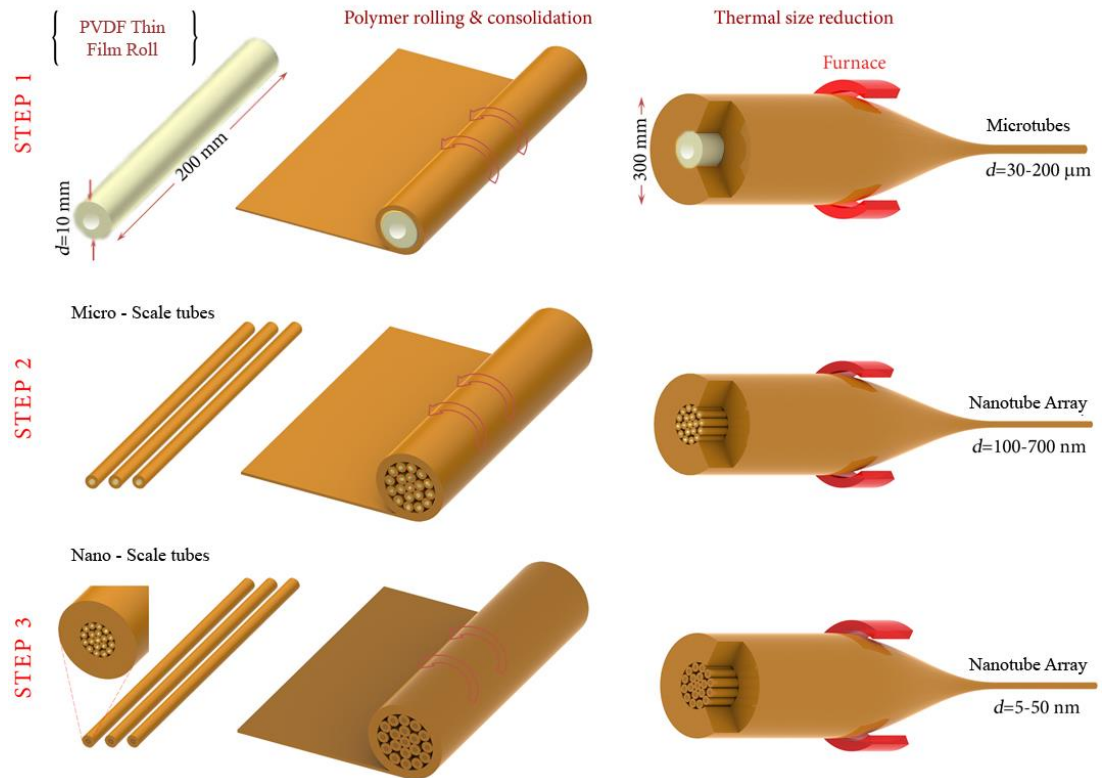


Figure 2.9: Nanotube fabrication takes 3 iterative steps which results in different sizes. Size of a macroscopic rolled thin film reduced down to below 20 nm by using thermal reduction technique in a fiber tower. Rolled PVDF films inserted in the preform and as the preform shrinks at high temperature, PVDF melts and takes the shape of the preform in step 1. Nanotube arrays inserted in the preform scaled down by thermal drawing in step 2 and 3.

First step PVDF fibers with PSU cladding are cut into 15 mm long pieces and arranged in a new PSU preform before redrawing steps. Numbers of the input fibers in second step and third step may vary depend on the core diameter of the preform and

diameter of the first step fibers. In the second step, we generally use about 400 first step fibers with a diameter of 400 μm . In order to achieve nanotubes, we take 400 second step fibers and insert them into a new PSU preform and redraw it. Consequently, we end up with about 160,000 ordered PVDF nanotubes in PSU cladding. PSU cladding can be etched by using DCM in order to extract PVDF nanotubes out of their claddings and PVDF nanotubes can be located or positioned on a rigid or flexible substrate.

Fabrication of Nanoshells: After successfully fabricating nanotubes by using iterative thermal drawing technique, we focused on fabricating square cross sectional nanoshell structures composed of a PC square cross sectional core, PVDF piezo-polymer rolled around the core material and PC cladding layer as shown in Figure 2.10a-c. Fabricating a square cross sectional nanoshell structure requires designing a special multi-material preform which is a macroscopic copy of the final fiber structures. Square cross sectional core PC extracted from a 35 mm thick PC preform which is rolled around a 3 mm glass rod and held in a vacuum oven for 4 hours at 140 $^{\circ}\text{C}$ and 1×10^{-2} Torr before consolidation. PC preform consolidated at 186 $^{\circ}\text{C}$ for 35 minutes under 1×10^{-2} Torr vacuum condition.

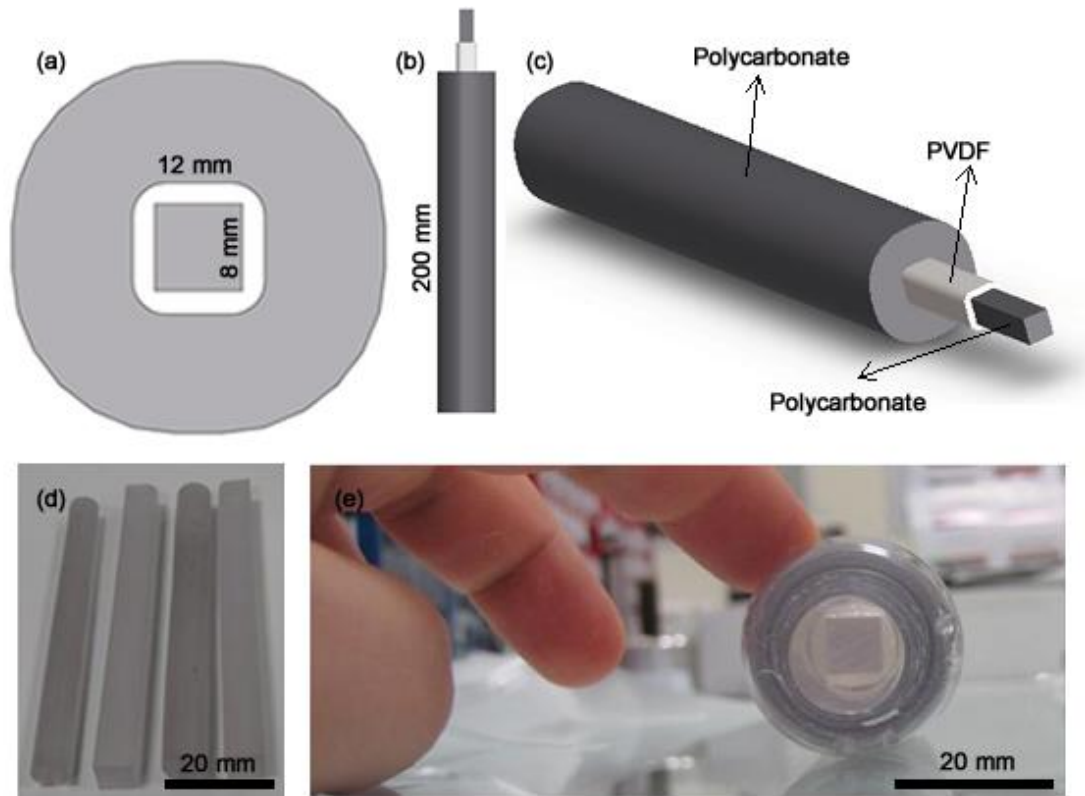


Figure 2.10: Square cross sectional PVDF nanoshell fabrication starts with preparing a square cross sectional macroscopic PC core. a-c) A 2 mm thick PVDF region obtained by rolling PVDF films around 8 mm thick PC square cross sectional core. Finally, PC rolled around the PVDF in order to create the cladding layer. Total thickness of the preform is 35 mm. d) 8 mm thick square cross sectional PC core extracted from a PC preform by using a milling machine. e) Preform consolidated under 1×10^{-2} Torr vacuum at 186 °C for 35 minutes.

Square cross sectional core material extracted from this preform by using a milling machine (See Figure 2.10d). A 75 μm thick PVDF piezo-films rolled around the core material until the total thickness of the PVDF films becomes 2 mm. Then the cladding layer with an overall thickness of 35 mm obtained by rolling 50 μm thick PC film over the PVDF shell. Preform held in a vacuum oven for 4 hours at 140 °C and 1×10^{-2} Torr and consolidated at 186 °C for 35 minutes under a 1×10^{-2} Torr vacuum. A consolidated square cross sectional designed preform is shown in Figure 2.10e. Although we change the structure of the preform except fiber drawing temperature which depends on the used material, there is no change in fiber drawing process. Fiber drawing process is described in Figure 2.11. After the preform inserted in the fiber tower's tube oven, temperature increased up to 215 °C where the PC preform start softening and 100 gr load applied to preform in addition to gravitational force which used for triggering the flow of the preform. First step drawing results in micron scale CP - PVDF core shell structures.

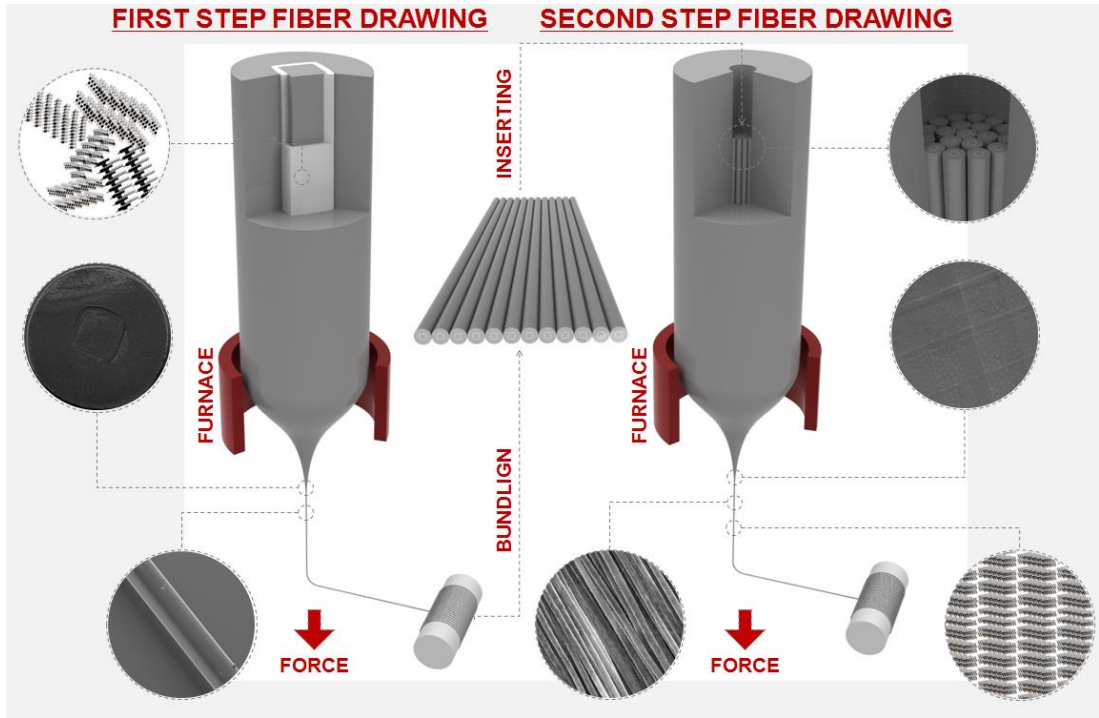


Figure 2.11: Square cross sectional PVDF nanoshell fabrication requires two fiber drawing process. As a result of first step drawing we obtain micro fibers and we put first step fibers in a second step preform and draw them again in order to obtain nanoshells. Although we have a single micro wire in first step, we can obtain a bundle of nanowires after second step drawing.

A second step drawing process is used to further decrease the fiber cross section down to the nanoscale. 400 μm thick, 400 square cross sectional step 1 fibers inserted in a new PC preform after the fibers are cut into 15 mm long pieces. By thermal redrawing the micron sized first step fibers, nanoscale fibers are obtained with ultra-high aspect ratios in conformity with dimensional drop of the second step preform. Size of the second step square cross sectional nanoshells can be controlled by altering the reduction factor that used in fiber drawing process. PC cladding can be etched by using DCM without the damaging the PC core, because DCM cannot dissolve PVDF.

2.3.2. Morphologic Characterization

Many flexible and stretchable devices are designed to be portable requiring self-powering systems such as battery or energy harvesting circuitries. PVDF nanotubes, nanoribbons and nanoshells are promising for supplying electricity to flexible electronic devices due to its excellent piezoelectric properties. Our new top-down approach brings the opportunity of integrating macroscopic world with nano-world. We produced our nanotubes, nanoribbons and nanoshells in a polymer jacket which

keeps them in a parallel order. Therefore, polymer encapsulation layer make it possible kilometers long thousands of nanostructures to be grabbed by hand. Polymer encapsulation can be dissolved by DCM which make possible to extract nanotubes, nanoribbons and nanoshell on any type of substrate without using any special device for alignment of them. First step microtubes which produced in PSU polymer cladding can be not only chemically but also mechanically extracted out of their cladding as shown in Figure 2.12a-c. Diameter of first step tubes can range 30 to 200 μm depending on the reduction factor used in fiber drawing. In the first step, we fabricate a single microtube with 200 m length embedded in polymer. Figure 2.12a-c represents cross-sectional and longitudinal SEM images of step 1 PVDF microtubes in PSU cladding. The outer diameter is about 400 μm . Further drawing steps are required to decrease the size of our microtubes down to nanometer scale. We obtained a bundle of PVDF nanotubes by redrawing of first step microtubes in a new PSU preform as shown in Figure 2.12d-f. Bundles can include up to 500 PVDF nanotubes which can have diameter between 100 - 700 nm with a total length of 100 km. Cross sections of PVDF nanotube array prepared by using cryo-microtome. Unfortunately, microtome diamond knife made damages which hamper the ability to observe cross sections of nanotubes. Moreover, as shown in Figure 2.12f PVDF nanotubes have curling and creases which proves that our structures have hollow cores. Surface smoothing made a devastating effect on cross section of third step PVDF nanotubes. Therefore, we broke the nanotubes in liquid nitrogen after we made a gentle notch on the PSU cladding in order to see hollow cores as shown in Figure 2.12g-i. In the third step, the number of the tubes can be up to 250,000 and their diameters can range from 20 to 70 nm with a total length of 50,000 km.

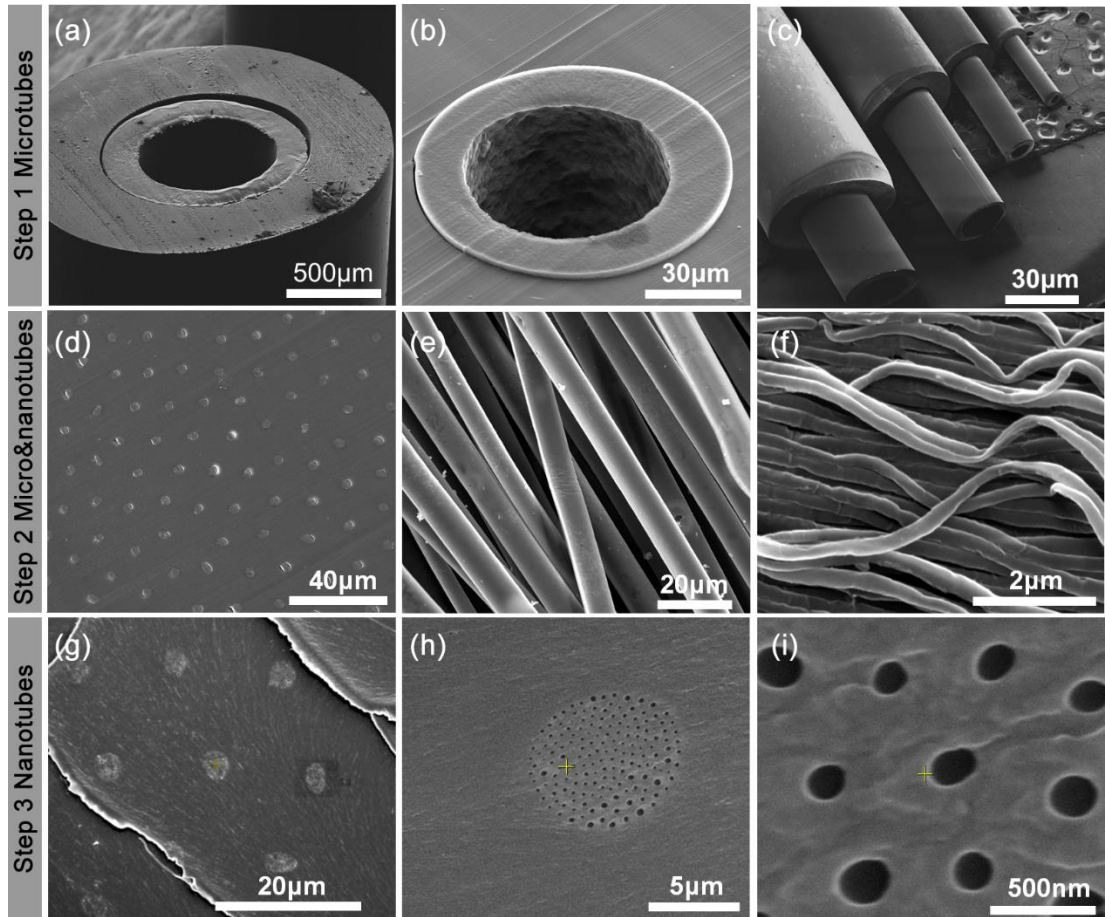


Figure 2.12: a-c) PVDF microtubes obtained by drawing a macroscopic preform in a fiber tower. Step 1 result in microtubes which are in a PSU jacket with diameter 50-50 μm and length longer than 100 m. Mechanically extraction of PVDF first step microtubes is possible. d-f) Step 2 results in micro and nanotubes which are also in PSU jacket with diameter 10 μm to 180 nm depends on the reduction factor. Not mechanically but chemically extraction of second step tubes is possible. g-i) Step 3, results in globally ordered tubes which can have diameter below 20 nm.

The smallest nanotube diameters that we attained were 20 nm which we believe can be reduced down to a fraction of this value. Comparative results for each fiber drawing step for nanotube fabrication are given in Figure 2.13a-e.

We fabricated square cross sectional nanoshells in order to reveal that our iterative fiber drawing technique can be used for different geometries. This is the first report which denotes the fabricating all polymer square cross sectional 1D nanostructure arrays which is also preferable high density packing of such structures. Square cross sectional PC core provides mechanical support to the piezoelectric PVDF shells. That allows us to decrease the size of the shells down to the nanoscale without using very

high reduction factors in fiber drawing process and disrupting continuity of PVDF shells.

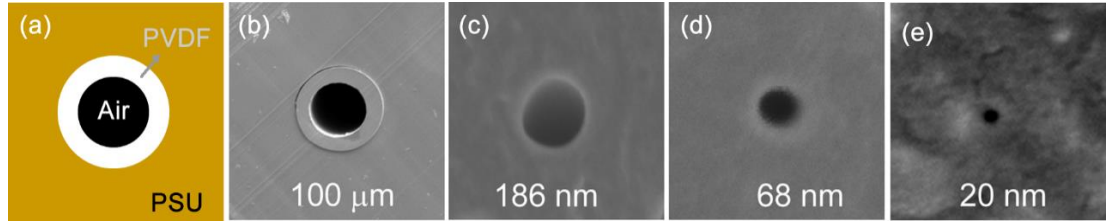


Figure 2.13: PVDF micro and nanotube cross-section scanning electron microscopy (SEM) images. Although, sample preparation is done by using cryotom, there is still a smearing effect which disturbs the image quality. Besides, polymer-polymer combined structure has shown not much contrast for SEM. a) A representative appearance of the PVDF. b) First step microtubes which have a diameter range 30 to 200 μm . c) Second step nanotubes which have a diameter range 100 to 700 nm. d-e) Third step nanotubes which have a diameter range 20 to 100 nm.

Different from the nanotube fabrication, nanoshell fabrication process covers two iterative drawing steps. The total number of the nanoshells embedded in the PC is not more than 500. Although the yield dramatically decreases when the number of drawing steps drop down to two, using less drawing steps appends versatile advantages such as reducing the amount of defects and removing the process complications. First step fibers embody only a single microshell. Edge length of square cross sectional PC supporting core decreases down to below 100 μm and the thickness of the PVDF shell layer scaled down to 10 μm . Edges of PVDF shell have taken a convex shape because of the stress difference applied on the edges and the corners of on PC core during PVDF and PC rolling (See Figure 2.14a). We can extract PVDF square cross sectional microshells out of the PC cladding by using DCM which can't dissolve PVDF shell.

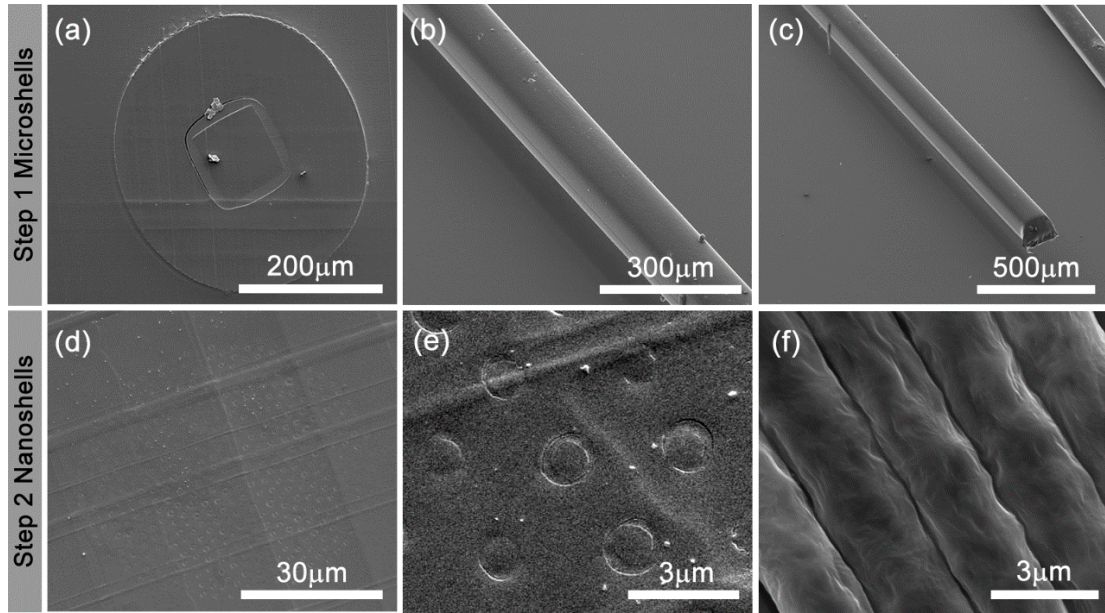


Figure 2.14: PVDF nanoshells are produced by using two step fiber drawing process. a) First step fibers have a single square cross sectional microshell. Thickness of the PVDF shell is below 100 μm . c-d) PC cladding of the microtubes can be etched by using DCM. d-e) Second step drawing results in nanoshells. Unfortunately, nanoshells couldn't maintain perfect square cross sectional shape. f) Even though their cross sections are not perfectly square, adjacent positioning of chemically extracted nanoshells reveals that high density packing of square cross sectional PVDF nanoshells is still possible.

Figure 2.14b-c represents the chemically extracted first step microshells. The second step drawing preparation requires cutting the 300 μm thick first step fibers in 15 mm long pieces and making a bundle of them which contains 500 fibers in order to insert in the second step PC preform. Unfortunately, square cross sectional shape of the nanoshells intend to change to circular (See Figure 2.14d-e). Another reason observing undesired shape changes might be due to the surface smoothing caused by microtome knife in the SEM sample preparation step. Even though the cross sections observed as it lost the perfect square shape, chemically extracted nanoshells still can be precisely stacked as shown in Figure 2.14f. The thickness of the core PC supporting region and PVDF shells diminished below to 1 μm and 100 nm respectively.

2.4. Summary

In conclusion, we have demonstrated a new iterative fiber drawing technique which is capable of fabricating ultra-high aspect ratio, ordered, all polymer nanotubes, nanoribbons, nanoshells, chalcogenide nanowires and core-shell structures. Dissolving the polymer cladding using organic etchants make it possible to extract free standing

PVDF 1D nanostructures on any type of substrates such as curved, flexible, stretchable and rigid. Ordered kilometer long piezoelectric PVDF nanoribbons, nanotubes and square cross sectional nanoshells are unusual nanostructures and are expected to bring new perspectives to energy harvesting, high energy density capacitors, artificial muscle and skin research. Future work may be required to produce in-fiber devices by including new materials such as conductive polymer electrodes, insulating layers and semiconductors into the research.

Chapter 3

Spontaneous High Piezoelectricity in Poly (vinylidene fluoride) Nanoribbons Produced by Iterative Thermal Size Reduction Technique

We produced kilometer-long, endlessly parallel, spontaneously piezoelectric and thermally stable Poly (vinylidene fluoride) (PVDF) micro and nanoribbons using iterative size reduction technique based on thermal fiber drawing. Owing to high stress and temperature used in thermal drawing process, we obtained spontaneously polar γ phase PVDF micro and nanoribbons without electrical poling process. Based on X-ray Diffraction (XRD) analysis, we observed that PVDF micro and nanoribbons are thermally stable and conserve the polar γ phase even after exposed to heat treatment above to the melting point of PVDF. Phase transition mechanism is investigated and explained using ab initio calculations. We measured an average effective piezoelectric constant as -58.5 pm/V from a single PVDF nanoribbon using a piezo evaluation system along with an atomic force microscope. PVDF nanoribbons are promising structures for constructing devices such as highly efficient energy generators, large area pressure sensors, artificial muscle and skin, due to the unique geometry and extended lengths, high polar phase content, high thermal stability and high piezoelectric coefficient. We demonstrated two proof of principle devices for energy

harvesting and sensing applications with a 60 V open circuit peak voltage and 10 μ A peak short-circuit current output.

3.1. Introduction

Utilization of the unique material properties represented by flexible, lightweight and biocompatible piezoelectric polymeric materials such as PVDF [143] and its copolymer poly (vinylidene fluoride tri-fluoroethylene) (PVDF-TrFE) [144] is expected to bring on new horizons for sensor, actuator, and energy harvesting applications where piezoelectric ceramic materials have been employed hitherto. A closer look into the applications of piezoelectricity including bio-sensing,[68] energy generation, [69], [70], [145] pressure sensing, [146] high precision positioning, [147] artificial muscle and skin [71], [72] reveals that thermally stable, flexible, and stretchable piezoelectric materials are required to be produced with high yields and in a cost effective way for the fabrication of commercially feasible, large area, self-powering, and highly efficient devices. Although ceramic piezoelectric materials can present higher piezoelectric coefficients, they suffer from high brittleness, low cyclic endurance, high processing temperature and high production cost as well as toxic elemental composition in contrast to properties of polymer piezoelectric materials [73], [148].

3.1.1. Piezoelectric Properties and Phases of Poly (vinylidene fluoride)

Since the discovery of PVDF $(\text{CH}_2\text{-CF}_2)_n$, which has the highest piezoelectric coefficient among all polymers,[143] PVDF and copolymers have been a subject of intense research which initiated development of many fabrication methods for PVDF thin film [149] and nanowires [62]. Regardless of the production method, piezoelectric properties are dependent on the amount of polar phase of PVDF [29], [150]. Four commonly known forms of PVDF are α , β , γ and δ phases, which are represented by different stereochemical structures with alternating s-Trans and s-Gauche C-C bonds ($\text{TGT}\bar{\text{G}}$, TTTT , $\text{TTTGT}\bar{\text{T}}\bar{\text{G}}$, and $\text{TGT}\bar{\text{G}}_{(\text{polar})}$), respectively [29], [141]. The most stable and easily obtained form of PVDF is the non-polar α phase which can also be in a rarely found polar form named δ phase. On the other hand, β and γ phases are the most desirable forms of PVDF due to their high polar molecular conformations [62], [75],

[26], [32], [151]. High polarity of the β phase as a result of all trans C-C bonds makes PVDF a promising candidate for piezoelectric, pyroelectric and ferroelectric applications [62], [75], [32], [146]. Transitions between phases of PVDF are possible under specific nucleation and processing conditions (Figure 3.1). Irrespective of the initial phase, the amount of the β phase in PVDF thin films can be increased by adding inorganic additives or stretching more than 80 % at 95 °C following with an electrical poling [29], [152]. Transition mechanisms resulting in γ phase are crystallization at high temperature or applying high shear on molten polymer; long term annealing at high temperature or polling at low electric field from α phase; and low rate evaporation from high temperature polymer solutions [26], [150], [151], [153]. Fiber drawing can be considered as a new method which produces γ phase PVDF nanostructures.

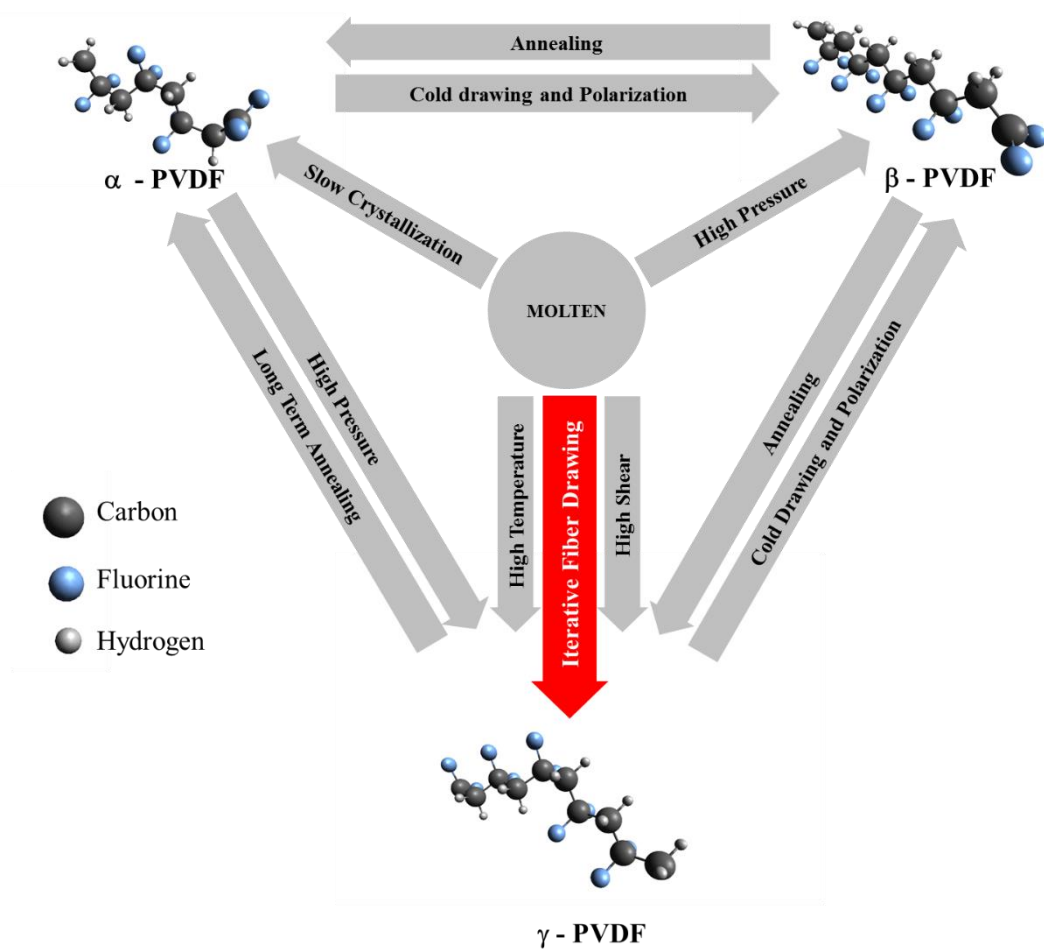


Figure 3.1: Transition into α , β , and γ phases from the molten state or other phases of PVDF are possible by using versatile processes. γ phase transition from the molten PVDF requires to combine specific processing conditions such as high temperature and high shear. Iterative size reduction by fiber drawing, which stands as a new method for nanotechnology, triggers the polar γ phase transformation by providing the two conditions concurrently.

Although, γ phase has lower polarity when compared to β phase, its piezoelectric coefficient still stands better than those of other polymers [75], [32], [141], [151]. Besides, the higher Curie temperature of γ phase makes it less vulnerable to harsh environmental conditions. Due to the decay of remnant polarization of β phase PVDF and PVDF-TrFE at lower Curie temperatures, these materials are not good candidates for production of thermally stable long endurance devices [154]. Owing to superior properties, γ phase is highly desirable. Unfortunately, it is known to be hard to access experimentally [151].

3.1.2. Fabrication Methods Triggering to Polar Phase Transition

The most common way of triggering polar phase transitions is applying a high strength electric field at elevated temperatures [62], [155], [156]. In addition, diminishing the feature size of PVDF lowers the cost and energy required for the polarization process [157]. In accordance with the developments in nanotechnology, scientists have been trying to facilitate nanoscale effects to improve the piezoelectric properties of PVDF and copolymers by altering their composition, [26], [152], [158], [159] size and shape [32], [140], [151], [153], [157], [160]. Initial attempts were focused on developing PVDF piezoelectric thin films by using spray coating, [161] spin coating, [141] physical vapor deposition, [162] and the Langmuir-Blodgett thin film coating methods [163]. Although shaping the PVDF in the form of thin film can disclose elevated piezoelectric properties, PVDF nanowires lead to superior piezoelectricity, due to the one-dimensional nanoscale confinement [62], [146]. Results of nano-confinement effects such as spontaneous polarization can eliminate external electrical poling process for polar phase transition [75], [140], [151].

Beyond the controversy, nanowires have made great impacts on many disciplines including solar cells, biosensors and phase change memory devices [110], [164]–[166]. A similar impact is also expected on piezoelectric applications using PVDF nanowires. The prominent piezoelectric PVDF nanowire fabrication methods are anodized alumina (AAO) template molding, [75], [151], [167] electrospinning, [62], [146], [168], [169] and nanoimprint lithography (NI) [32], [140], [153], [157] which are all solvent dependent. Even though these techniques are appropriate to produce PVDF nanowires, they are not superior in all aspects considering the nanowire aspect

ratio, uniformity, geometry control, yield, and device integrability in order to produce large area, low cost and high throughput devices. Table 3.1 is the comparison of prominent PVDF nanowire fabrication methods with iterative size reduction technique in terms of aspect ratio, uniformity, size control, geometry control, multi material compatibility, yield and large area device integration.

Table 3.1: Comparison of PVDF nanowire production techniques considering as-produced nanowire properties in terms of aspect ratio, uniformity, size and geometry control, multimaterial production compatibility, yield and device integration

	Electrospinning	Lithography	AAO	Iterative Size Reduction
Aspect Ratio	+++	+	+	+++
Uniformity	+	+++	+++	+++
Size control	++	+++	++	+++
Geometry Control	+	+++	+	+++
Multi-material Compatibility	+	++	+	+++
Yield	+++	+	+	+++
Large Area Device Integrability	+	++	+	+++

Despite the fact that high aspect ratio nanowires can be produced with high yield by using electrospinning, diameter uniformity and geometry control capability of this technique are not fulfilling the requirements of current state of the art technology. Tuning the diameter of nanowires can be better accomplished by using AAO and NI techniques. However, nanowires produced by these methods are not feasible to carry out the production of flexible, large area devices. Above all, unlike electrospinning, AAO, and NI techniques, a fabrication technique which provides PVDF nanowire production with high aspect ratio, excellent uniformity, desired geometry, and high yield in a multi-material fashion can pave the way for in situ assembly of nanowires with metallic, semiconductor and dielectric components of the macroscopic devices [24].

3.2. Fabrication of Kilometer-long Piezoelectric Nanoribbons

Compatibility of iterative fiber drawing based size reduction technique for a wide range of materials in nanowire shape has been demonstrated [24], [76]. On the contrary to a recent study,[11] it is possible to produce micro and nanostructured PVDF in polar phase spontaneously induced by fiber drawing process as we showed in this study for the first time. Here, we produced kilometer-long, PVDF arrays in novel forms such as nanoribbon and square cross-sectional nanoshell (Figure 3.2) structures.

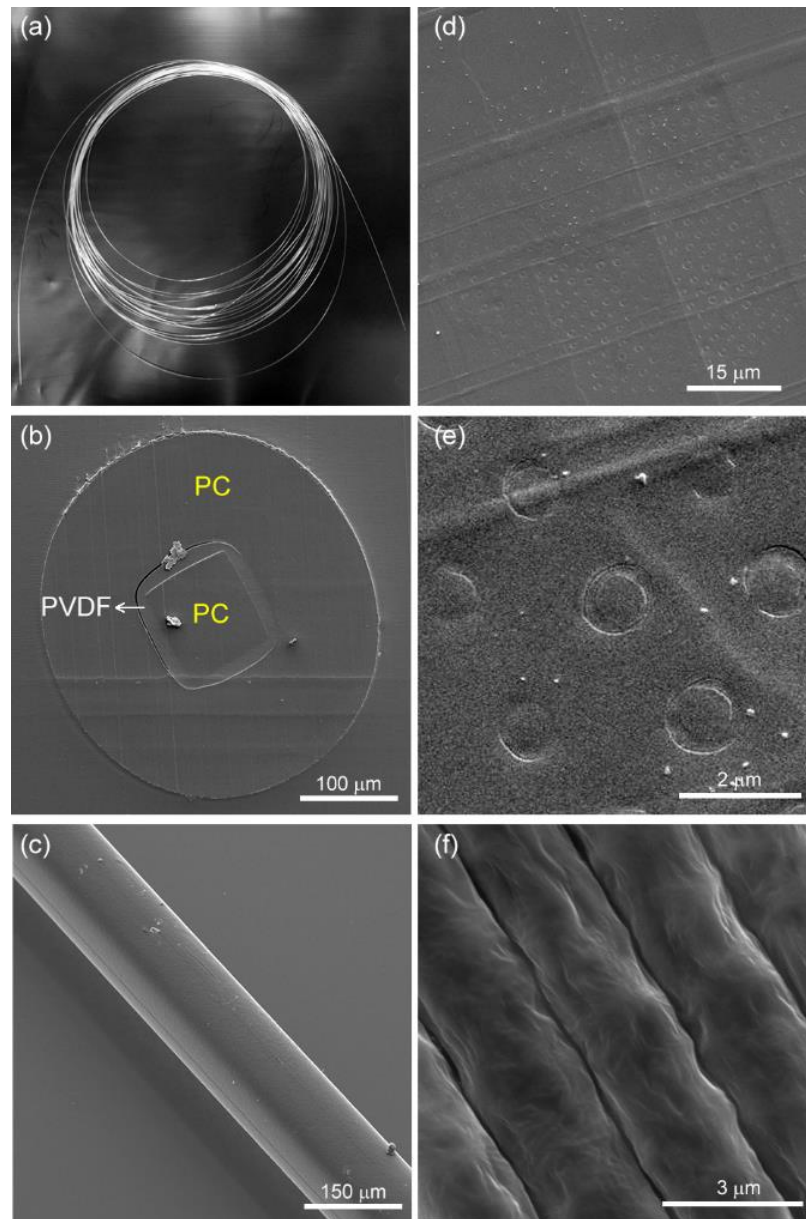


Figure 3.2: SEM micrographs of PVDF nanoshells produced as a result of two iterative fiber drawing processes. (a) Photograph of meters-long as-drawn square cross sectional fiber. (b)

The first step fiber drawing results in a single square cross sectional microshell in a fiber. Thickness of the PVDF shell is below 10 μm . (c) First step microshells after their Polycarbonate (PC) cladding was etched by using DCM. (d-e) The second step fiber drawing results in nanoshells having rounded square cross sectional shape. (f) High density packing of chemically extracted PVDF nanoshells.

We rather prefer ribbon shape with planar contact areas, which poses a unique advantage for piezoelectric measurements, unlike the nanowires with cylindrical symmetry.

3.2.1. Temperature and Shear Induced Phase Transformation

Fiber drawing process favors the transformation of the molten PVDF into polar γ phase due to the shear stress and the high temperature applied during the process. The shear stress occurred in the fiber drawing process, due to the 3 MPa tensile force, is simulated by using finite element methods (Figure 3.3).

We achieved highly polar γ phase PVDF nanoribbons from the fiber drawing technique simultaneously utilizing high temperature and shear stress triggered by tensile forces (Figure 3.3). In order to simulate the phase transformation in iterative fiber drawing process, we performed ab initio calculations based on density functional theory in which the effects of both temperature and shear stress are included.

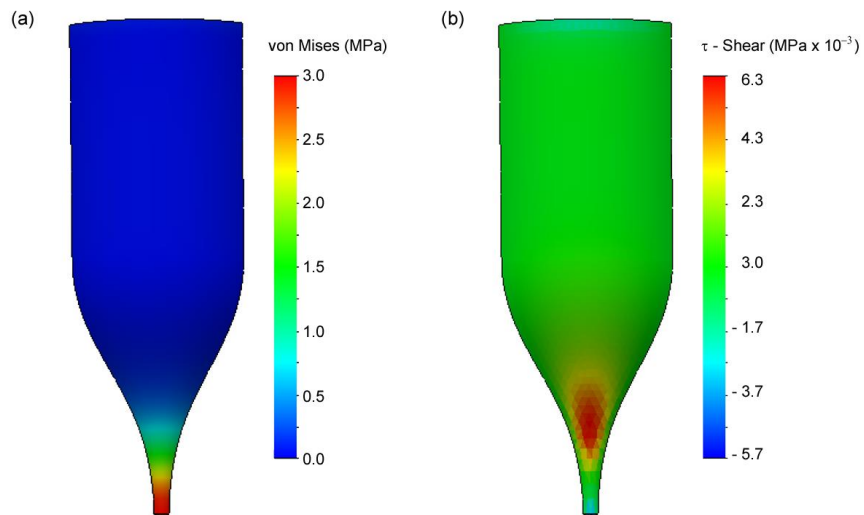


Figure 3.3: Results of the finite element simulation for the process of all-polymer fiber drawing. (a) The stress distribution in the preform drawn by a 3 MPa tensile stress. (b) Demonstrating the shear stress distribution which triggers γ phase transition in PVDF nanoribbons at high temperatures.

Using the software SolidWorks 2013 Simulation, three dimensional numerical finite element method is conducted to show the distribution of normal and shear stress when a 3 MPa triggering stress is applied through the fiber drawing axes for polymer materials. Effect of the gravity (9.81 m/s^2) is also taken into account. Simulation temperature is considered constant at fiber drawing temperature ($258 \text{ }^\circ\text{C}$). To find out the yield characteristics in fiber drawing process, the maximum von Mises stress ($\sigma_{vonMises}$) criterion which is based on the von Mises-Hencky theory is applied to the system using following governing equation.

$$\sigma_{vonMises} = \left[\frac{(\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_1 - \sigma_3)^2}{2} \right]^{\frac{1}{2}} \quad (3.1)$$

Where σ_1, σ_2 and σ_3 are the principle stresses. The Cauchy stresses, shear stress caused by applied tensile stress, strain and displacement with respect to the initial parameters are also investigated. Frictional forces due to air in the environment and free body forces are ignored. In order to be able to simulate fiber drawing, we used a linear elastic isotropic model type with large displacement option. Curvature based mesh used with 4 Jacobian points.

3.2.2. Preform Fabrication

We produced one PVDF and three PES preforms. PVDF films (Ajedum Films – Solvay Plastics) with a thickness of $60 \text{ }\mu\text{m}$ are used for the fabrication of PVDF preform which is 30 mm in diameter and 20 cm in length. The nanoribbon fabrication procedure starts with preparation of a multimaterial preform, which is an exact macroscopic copy of the final fibers. The easiest way to produce a preform is rolling polymer films, degassing the air trapped in the roll under vacuum at a temperature below the glass transition temperature of the films and lastly consolidating in a vacuum oven at the glass transition of the films. Following the mentioned procedure, a PVDF preform is prepared by rolling $60 \text{ }\mu\text{m}$ thick PVDF films around a glass tube and consolidated in a tube oven at $180 \text{ }^\circ\text{C}$ for 30 minutes under 2×10^{-2} Torr vacuum. Next, a slab ($3 \text{ mm} \times 10 \text{ mm} \times 10 \text{ cm}$) is mechanically extracted from this PVDF preform. Afterwards, a PES preform with 35 mm in diameter and 25 cm in length is made by

rolling 100 μm thick PES films around a 3 mm glass tube and consolidated at 255 $^{\circ}\text{C}$ for 35 minutes under 2×10^{-2} Torr vacuum. The PES preform is split in two halves and machined in the center to open a niche for inserting the PVDF slab (Figure 3.4).



Figure 3.4: The fabrication steps of the PVDF ribbon embedded in PES preform which is a macroscopic copy of the final nanoribbons. As an initial step, (1) a PVDF preform is built by rolling PVDF sheets and (2-3) a slab is mechanically extracted out of the PVDF preform. (4-5) Next, the PVDF slab is inserted into a PES preform which is then sealed by heating in a consolidator oven. (6) The final multimaterial product turns into a PVDF ribbon embedded PES matrix. Dimensions and design specifications of the preform directly affect the size and shape of the final product of the drawing process.

3.2.3. Iterative Fiber Drawing

Fiber drawing processes are executed in a custom made fiber tower which consists of a vertical tube oven, a preform feeding mechanism, and a real time monitoring system measuring applied stress, temperature, and thickness of the drawn fiber.

Figure 3.5 summarizes the nanoribbon fabrication technique. The fabrication of PVDF nanoribbon arrays, which comprises several fiber drawing steps, starts with the drawing of PVDF slab embedded PES preform.

Heating the preform above the glass transition temperature of PES and melting point of PVDF, and applying approximately 3 MPa tensile force are required in order to trigger plastic deformation in fiber drawing process. Optimized preform feeding speed is found to be 8 mm/sec. Since drawing temperature (285 $^{\circ}\text{C}$) or the temperature

in the core of the preform ($\sim 200\text{ }^{\circ}\text{C}$) is higher than the melting point of PVDF ($T_m = 165\text{ }^{\circ}\text{C}$), the molten slab flows and shrinks in the PES cladding during fiber drawing. Fibers in thermal drawing process results in PVDF micro and nanoribbons with various thicknesses by adjusting the process temperature, applied stress, drawing and feeding speed.

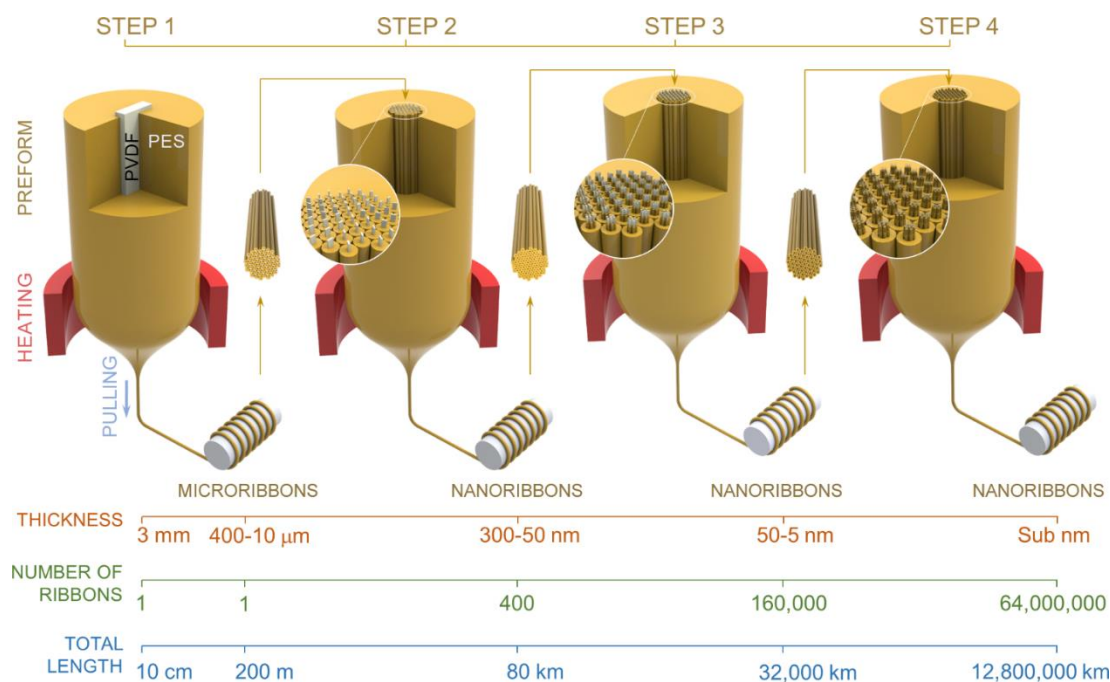


Figure 3.5: A novel top-to-bottom nanofabrication technique for producing kilometer-long piezoelectric nanoribbons. An iterative fiber drawing scheme allows to achieve nanometer structures. A macroscopic PVDF slab is inserted, thermally sealed in a PES matrix, and drawn thermally to produce first step fibers. At high temperatures, molten PVDF flows together with softened PES cladding, producing tens of meters long PVDF microribbon encapsulated in PES. First step fibers are stacked and redrawn in a new preform for the second step fiber drawing in order to decrease the size of the ribbons down to nanometers. Further size reduction can be accomplished by following same stacking and redrawing cycles. From the first step to the last step, total number and length of the ribbons in the fiber increase as the size of each nanoribbon decreases.

The thickness of the ribbons ranges between $400\text{ }\mu\text{m}$ to $10\text{ }\mu\text{m}$ in the first step, 300 nm to 50 nm in the second step and 50 nm to 5 nm in the third step. Approximately 400 fibers are used in the second and third steps.

3.2.4. Morphological Characterization

PVDF ribbons are confirmed by morphological characterizations conducted with scanning electron microscopy (SEM). Figure 3.6a shows as drawn step 1 fibers and Figure 3.6b represent cross sectional and longitudinal SEM images of $30\text{ }\mu\text{m}$ thick

microribbon embedded fibers, which are produced in the first step with a preform feeding speed 8 mm/sec. For the second drawing step, approximately 400 first step fibers are stacked and inserted into cylindrical hollow core of a new PES preform which becomes a multifunctional jacket protecting and keeping the PVDF nanoribbons together. Sequential thermal drawings of the preform prepared for the second step result in thicknesses ranging from 300 nm to 50 nm (Figure 3.6c-d). Similarly, 400 nanoribbon embedded fibers obtained in previous steps are inserted in new PES preforms produced for the third step fiber drawing processes. After drawing the third step preform, nanoribbons result in thicknesses ranging from 50 nm to 5 nm (Figure 3.6e-f).

The distance between nanoribbons is well defined with cladding thicknesses of the input fibers. In addition, the macroscopic encapsulation polymer makes it practicable to manually manipulate kilometers long, perfectly aligned, millions of nanowires. Number and total lengths of the nanoribbon embedded fibers are progressive in conformity with the growing number of drawing steps. For instance, despite a 200 meter long in-fiber single ribbon is obtained after the first step drawing, nanoribbons are achieved in kilometers of length and thousands of number in following drawing steps.

We extracted PVDF nanoribbons out of the PES cladding by using dichloromethane (DCM), which can't dissolve PVDF. SEM images are taken using FEI Quanta 200 FEG Electron Microscopy with low voltage - high contrast detector (vDS) under vacuum at 6×10^{-4} Pa chamber pressure. We used 5 kV acceleration and 4 kV deceleration (bias) beam voltage within 4 mm working distance. Lateral PVDF nanoribbon images are taken after the PES cladding of fibers are etched using DCM and 4 nm Au/Pd conductive film is sputtered on to the surface.

Cross sectional characterization of nanoribbons requires a special sample preparation using ultra-microtome for SEM imaging. Firstly, fibers are embedded in a resin (Technovit 7100). Using a Leica EMUC6 – EMFC6 Ultra-microtome with a diamond knife, fiber cross sections are smoothed after the cryogenic chamber of the ultra-microtome is cooled down to -125 °C using liquid nitrogen. Before SEM images are taken, 4 nm Au/Pd conductive film is coated on the smoothed surfaces. To enhance

the electrical conduction, each sample is painted using silver paste. However, diamond knife of the ultra-microtome causes defects which hamper observing the exact cross sectional shape of the nanoribbons. In addition, even state of the art electron microscopy techniques are used, imaging of nanometer scale polymer features are very difficult due to fast degradation of polymers under high energy electron beam [170].

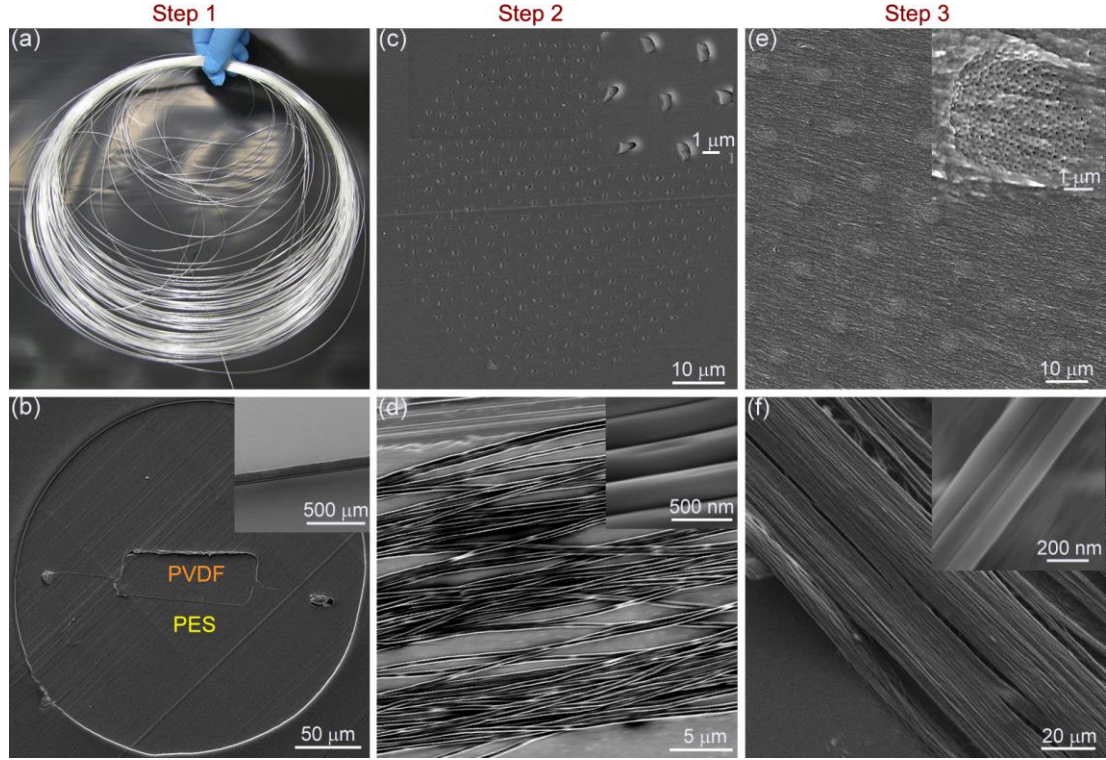


Figure 3.6: SEM micrographs of PVDF micro and nanoribbons produced by using iterative size reduction technique in each drawing step. (a) Photograph of tens of meters long PDVF nanoribbon array embedded in PES cladding. (b) Cross sectional image of first step PVDF microribbon in the PES cladding. Inset: Free-standing PVDF microribbon obtained by etching PES cladding using chemical etchants. (c) Cross sectional image of second step fiber with ~400 nanoribbons. Inset: Close-up image of nanoribbons. (d) Lateral image of second step nanoribbons. Inset: Close-up image of aligned nanoribbons. (e) Cross sectional image of third step nanoribbon bundles in fiber. Close-up image of a single bundle. (f) SEM of third step nanoribbons extracted out of their cladding. Inset: Close-up image of aligned nanoribbons.

Alternatively, a better SEM observation of the ribbon shape is accomplished using two different sample preparation methods; breaking the fibers after a liquid nitrogen treatment (Figure 3.7) and direct cutting of the fibers longitudinally. Size distribution for second step PVDF nanoribbons is given in Figure 3.8. Standard deviation normalized with respect to the mean of the nanoribbons size distribution is found to be ~11%.

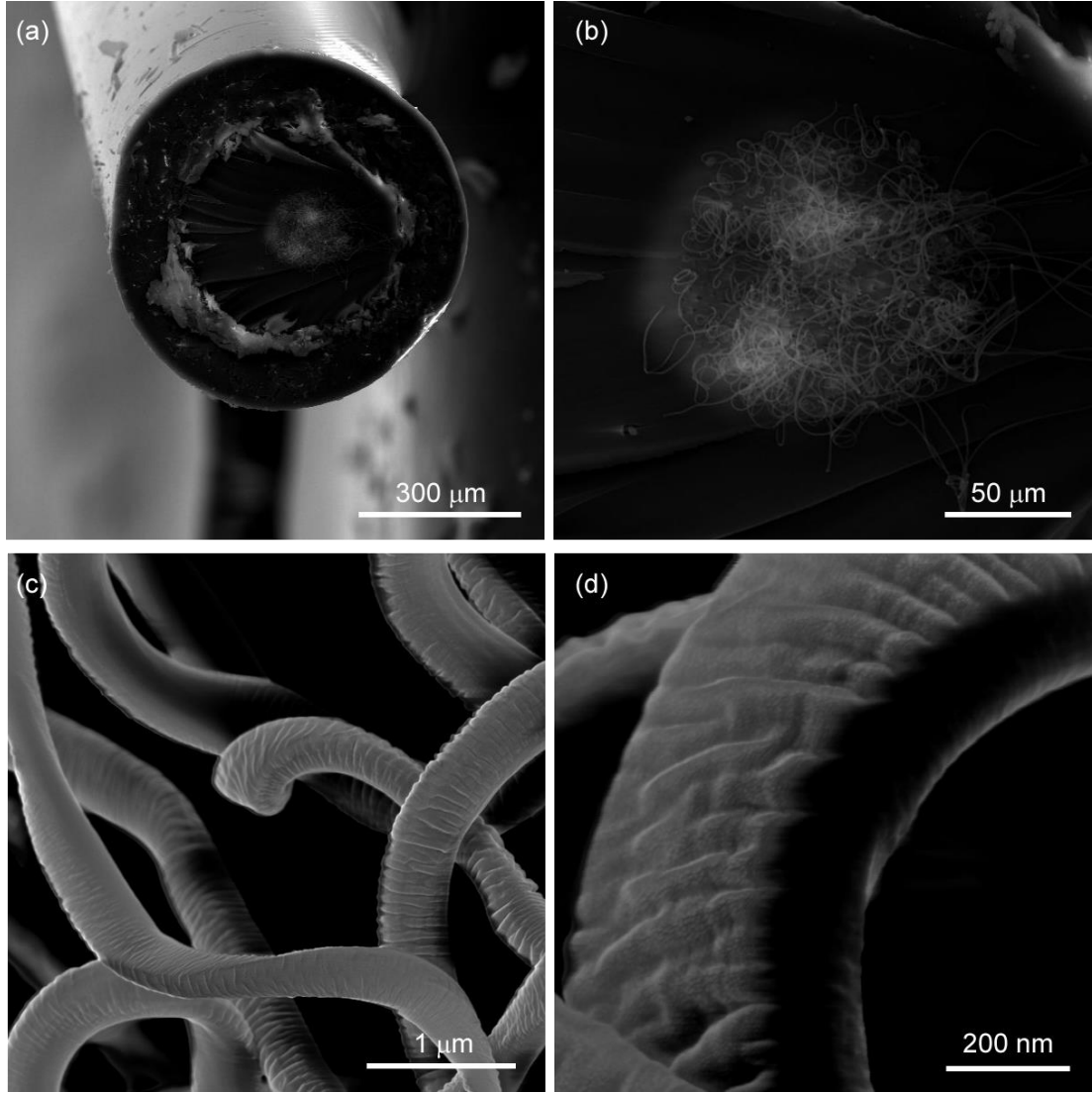


Figure 3.7: (a) Cross sectional SEM images of the second step nanoribbons embedded in PES fiber prepared by breaking just after liquid nitrogen cooling. (b) PVDF nanoribbons are extracted out of the PES cladding due to uniaxial pulling force for breaking the fiber. (c) A preferential buckling is observed due to the rectangular cross sectional shape of the nanoribbons. (d) A closer look at the PVDF nanoribbons proves that ribbon shape is perfectly preserved.

Dimensions of the first step slab and preform, overall reduction ratio, and the number of steps in iterative fiber drawing processes determine the final size of nanoribbons. Besides, ribbon shape is inherited by next generation ribbons from the fibers produced in previous steps.

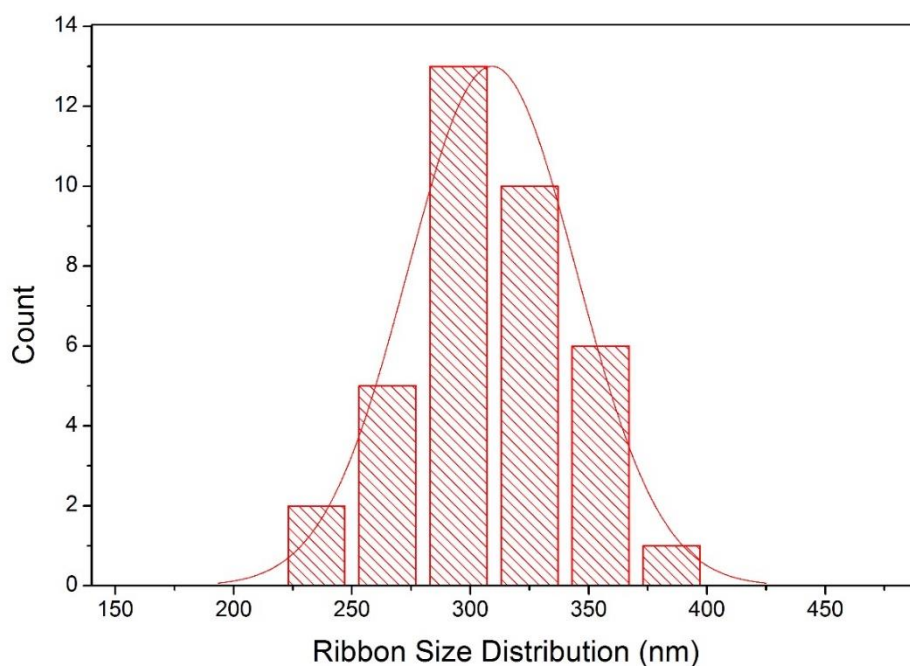


Figure 3.8: Mean of size distribution in nanoribbon width is calculated from SEM images as $\langle w \rangle = 309$ nm. Standard deviation of size distribution is $\sigma = 35$ nm. Standard deviation normalized with respect to the mean is $\sigma / \langle w \rangle \approx 11$ %.

3.2.5. Molecular Nanowire Bundles

As for the fourth step fibers, calculations using reduction ratio parameters reveal that thicknesses of the fourth step nanoribbons are diminished to sub-nanometer scales. Although the existence of the fourth step bundles can be observed via dark field optical microscopy (Figure 3.9), size verification is experimentally impossible, since PVDF sub-nanoribbons dissolve in DCM when intended to extract them out of the PES cladding. In addition, state of the art electron microscopy techniques are not essentially capable of measuring sub-nanometer polymer features due to fast degradation of polymers under high energy electron beam.

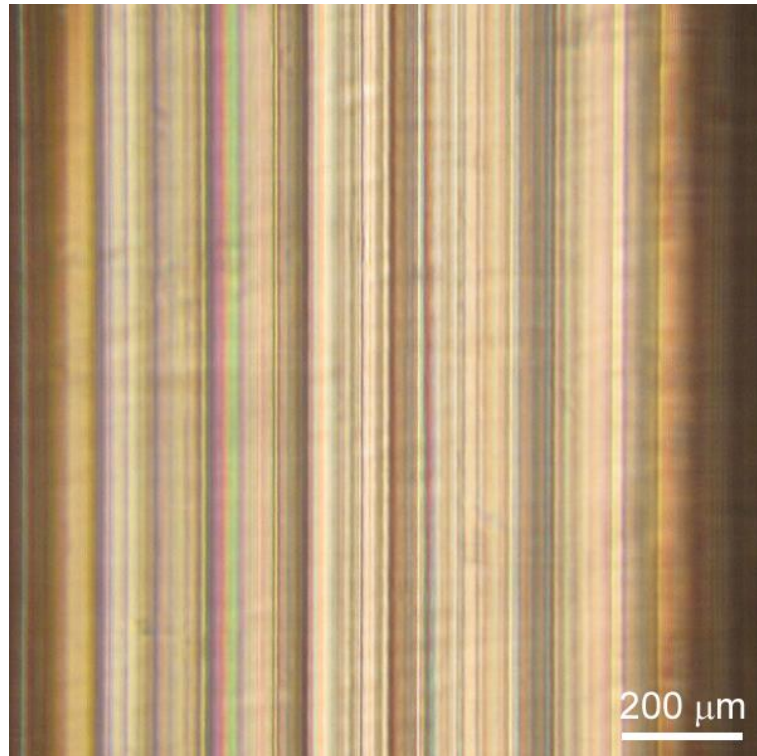


Figure 3.9: Dark field optical microscopy of a fourth step fiber containing sub-nanometer millions of PVDF ribbons. The sub-nanometer ribbons can't be extracted by etching PES cladding, but dissolved in DCM. Bundles can be seen clearly under optical microscope.

3.3. Phase Analysis and Theoretical Proof of Phase Transformation Mechanism

We compared the phase transition at 0 °K and 470 °K (above the melting temperature of PVDF) from α and β phase to γ phase under varying compressive and tensile strain. γ phase in the as produced PVDF nanoribbons is observed to be still exist after annealing at high temperatures up to 175 °C. α , β and γ phase distribution in PVDF ribbons are investigated as a function of size using XRD and Attenuated Total Reflectance - Fourier Transform Infrared (ATR - FTIR) spectroscopy techniques.

3.3.1. XRD Phase Characterization

XRD patterns of the PVDF nanoribbons are taken by Pananalytical X'pert Pro XRD with the diffraction angle 2θ scanned between 5 to 75 degrees by using a step size of 0.01 degrees and a dwell time of 800 second per step. Nanoribbons without polymer

claddings are annealed in a furnace at various temperatures in order to investigate thermal stability of the γ phase.

Molecular conformation of α , β and γ phases are shown in Figure 3.10a. Predominance of the polar γ phase ribbons produced in first, second, and third drawing steps is clearly observed by using XRD. PES claddings of nanoribbons are etched in DCM before XRD measurements in order to eliminate amorphous background arising from the PES cladding, and to increase the signal intensity. In the literature, characteristic peak positions (2θ) of PVDF are tabulated as 17.7° , 18.4° , 19.9° , 26.5° , 27.8° , 35.7° , 39° , and 57.4° for α phase; 20.7° , 20.8° , 35° , 36.6° , and 56.1° for β phase; 18.5° , 19.2° , 20.1° , 20.3° , 26.8° , 36.2° , and 38.7° for γ phase [26], [29], [150], [151].

Starting from the PVDF macroscopic slab, we have analyzed change of phase content for all fabrication steps (Figure 3.10b). The slab includes a minor amount of β ($2\theta = 20.7^\circ$) and α ($2\theta = 27.8^\circ$) phases and a transition trend to the γ phase is persistent starting from the first step ribbons. Although, suppressed α phase peaks are still exist at 17.7° , 26.5° and 27.8° peak positions, dominance of the γ phase is obvious from the peaks at $2\theta = 18.5^\circ$, 20.1° and 26.8° . For the second step nanoribbons, except shifts observed in γ peak positions from 20.1° to 20.3° , and 18.5° to 18.6° , other peaks preserve their positions. Characteristic peaks of γ phase in the third step nanoribbons are located at the same peak positions of the first step microribbons. Broadening in the γ phase peaks and drastic fall in $2\theta = 26.8^\circ$ peak intensity indicate a slight decrease in amount of γ phase in step 2 and 3.

3.3.2. FTIR Phase Characterization

Another tool that we used to confirm the existence of the γ phase in the nanoribbons is Fourier Transform Infrared Spectroscopy (FTIR) with an ATR attachment (Thermo Scientific Nicolet 6700). Considering the reflection bands at 840 cm^{-1} (overlapping with β PVDF) and 885 cm^{-1} (non-overlapping characteristic γ phase), the γ phase content in the PVDF ribbons can be recognized for all steps. FTIR reflection data are taken with a wavelength scan resolution of 0.482 cm^{-1} and a total of 256 scan steps.

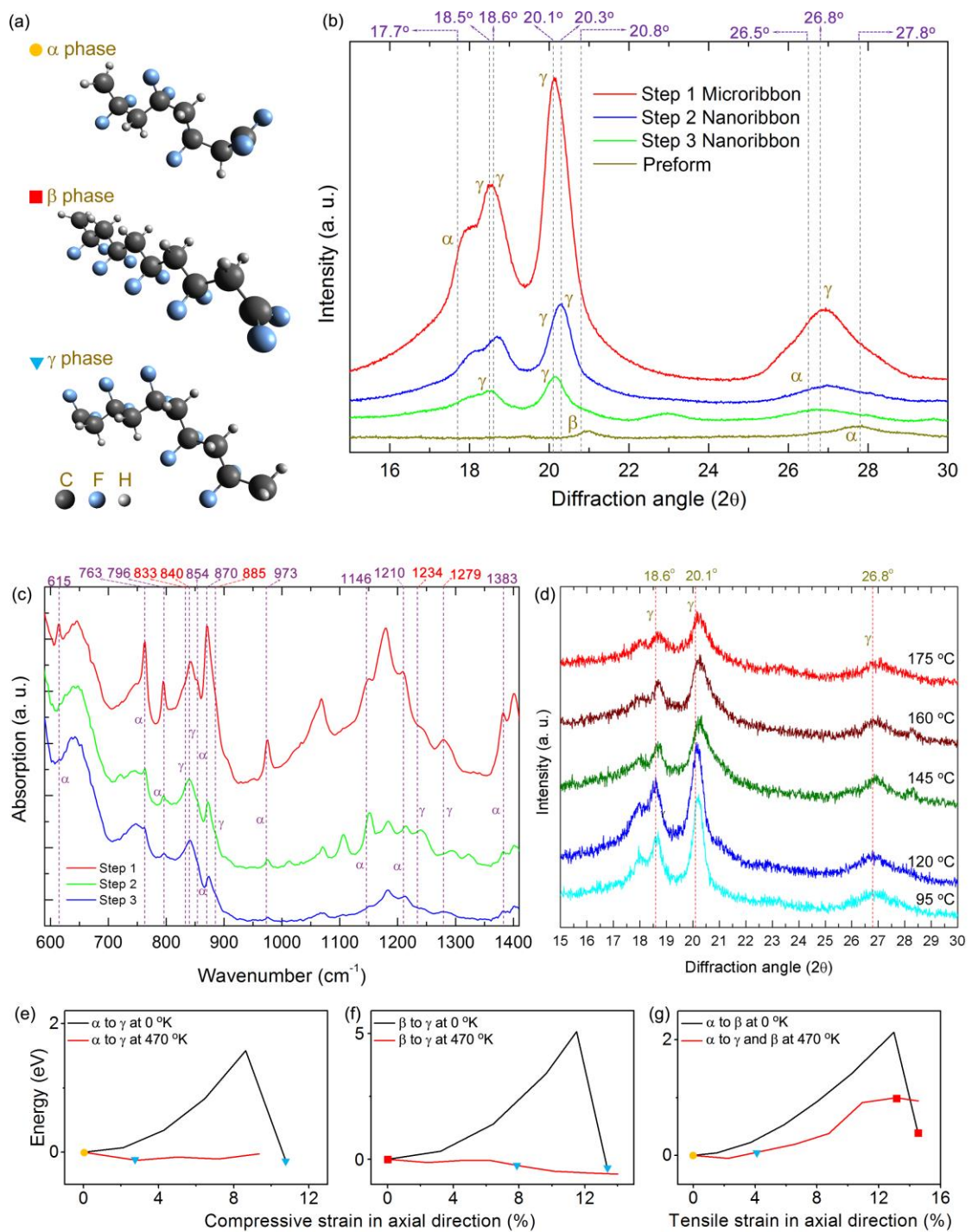


Figure 3.10: XRD and ab initio simulation results representing γ phase transition from PVDF slab via fiber drawing process. (a) PVDF has three main forms which are known as nonpolar α phase, polar β and γ phases. (b) XRD data of PVDF slab extracted from a preform, microribbon and nanoribbon are taken after removing the PES cladding. Peaks observed at 18.5° and 18.6° , 20.1° and 20.3° , 26.8° correspond to the planes of γ polar form (020), (002)/(110) and (022), respectively. α phase peaks at 17.7° , 26.5° and 27.8° are collected from (100), (021) and (111) planes. Peak at 20.8° , is the only β peak observed in the slab. Spontaneous polar form (γ phase) is achieved after the thermal size reduction in all fiber drawing steps. (c) ATR-FTIR peaks from the first, second and third step PVDF microribbons and nanoribbons representing α and γ phases. 833, 840, 885, 1234, 1279 and 1286 cm^{-1} are characteristics of the γ phase PVDF. 615, 763, 796, 854, 870, 973, 1146, 1210 and 1383 cm^{-1}

are the FTIR peaks of α phase PVDF. Fraction of the γ phase is 74 % in first step microribbons whereas it decreases 72 % in third and second step nanoribbons. (d) XRD patterns showing the characteristic peaks of the second step PVDF nanoribbons at different annealing temperatures. Although the temperature is increased above the melting point of PVDF, dominance of γ phase is obvious from the peaks at 18.6°, 20.1° and 26.8° positions. (e) Transition from α (yellow circle) to γ phase (blue triangle), (f) transition from β (red square) to γ phase with compressive strain and (g) transition from α to β phase with tensile strain on the unit cell with 6 monomers of PVDF in axial direction are simulated considering fiber drawing parameters (high temperature and shear stress) using ab initio calculations. 0 °K results are corresponding to the case where temperature effects are excluded.

Absorption band characteristics of α , β , and γ phases of PVDF are identified as given in literature: 532, 612, 763, 796, 854, 870, 974, 1146, 1210, 1383, and 1423 cm^{-1} for α ; 510, 840, 1279, 1286, 1431 cm^{-1} for β ; 812, 833, 838, 885 and 1234 cm^{-1} bands for γ . However, most of the absorption bands are superimposed for β and γ phases hindering the phase discrimination [26]. Overlapping peak at 840, 1279 and 1286 cm^{-1} with γ and β phases can be assigned for γ phase as long as no β peak is identified using XRD technique for micro and nanoribbons. Figure 3.10c represents ATR-FTIR absorption spectra for PVDF nanoribbons produced in all steps. Fraction of the γ phase is calculated using the following equation:

$$F(\gamma) = \frac{X_\gamma}{X_\alpha + X_\gamma} \times 100 = \frac{A_\gamma}{(K_\gamma/K_\alpha)A_\alpha + A_\gamma} \times 100 \quad (3.2)$$

where the X_γ and X_α are degree of crystallinity, A_γ and A_α are measured absorbance intensity, K_γ and K_α are wavelength dependent absorption coefficient and F_γ is the percentage of γ phase. We calculated γ percentage for 763 cm^{-1} α peak and 833 cm^{-1} γ peak using corresponding absorbance coefficients $K_\gamma = 0.150 \mu\text{m}^{-1}$ and $K_\alpha = 0.365 \mu\text{m}^{-1}$ (Beer – Lambert Law) respectively [26], [151]. γ phase percentage in step 1 microribbons is 76 % whereas step 2 and step 3 nanoribbons γ phase percentage decreased to 72 % as a result of diminishing shear force on nanoribbons exposed to heat retreatment with smaller cross sectional areas [171].

3.3.3. Thermal Stability of Piezoelectric Polymer Nanoribbons

Due to phase transformation into γ phase occurs at high temperatures, stability of the γ phase at harsh conditions is needed to be investigated. We realized from

sequential heat treatments to PVDF nanoribbons that γ phase PVDF produced by iterative fiber drawing technique is quite stable at high temperatures. Nanoribbons extracted out of the PES cladding are annealed at several different temperatures up to 175 °C and it is evident from XRD peaks that there is no significant change in γ phase content (Figure 3.10d). It is clearly observed from the peaks at $2\theta = 18.6^\circ$, 20.1° and 26.8° , γ phase still exist at elevated temperature. Regarding broadening and decreasing intensity of XRD peaks, we observed that crystallinity is slightly diminished due to effect of high temperature.

3.3.4. Ab Initio Calculations (Density Function Theory)

In order to simulate the phase transformation in iterative fiber drawing process and investigate the effect of temperature, ab initio calculations based on density functional theory [172], [173] are carried out using Vienna ab initio simulation package (VASP) [174], [175]. To understand the effect of compressive and tensile strength, α -, β , and γ -PVDF with 6 monomer chains in the unit cell is considered at temperatures equal to and higher than drawing temperature (470 °K) which are compared with ground state results at 0 °K as shown in Figure 3.11.

Transformations α phase and β phase to γ phase PVDF under lattice compression and α to γ and β phase PVDF under lattice tensile at 470 °K given in below.

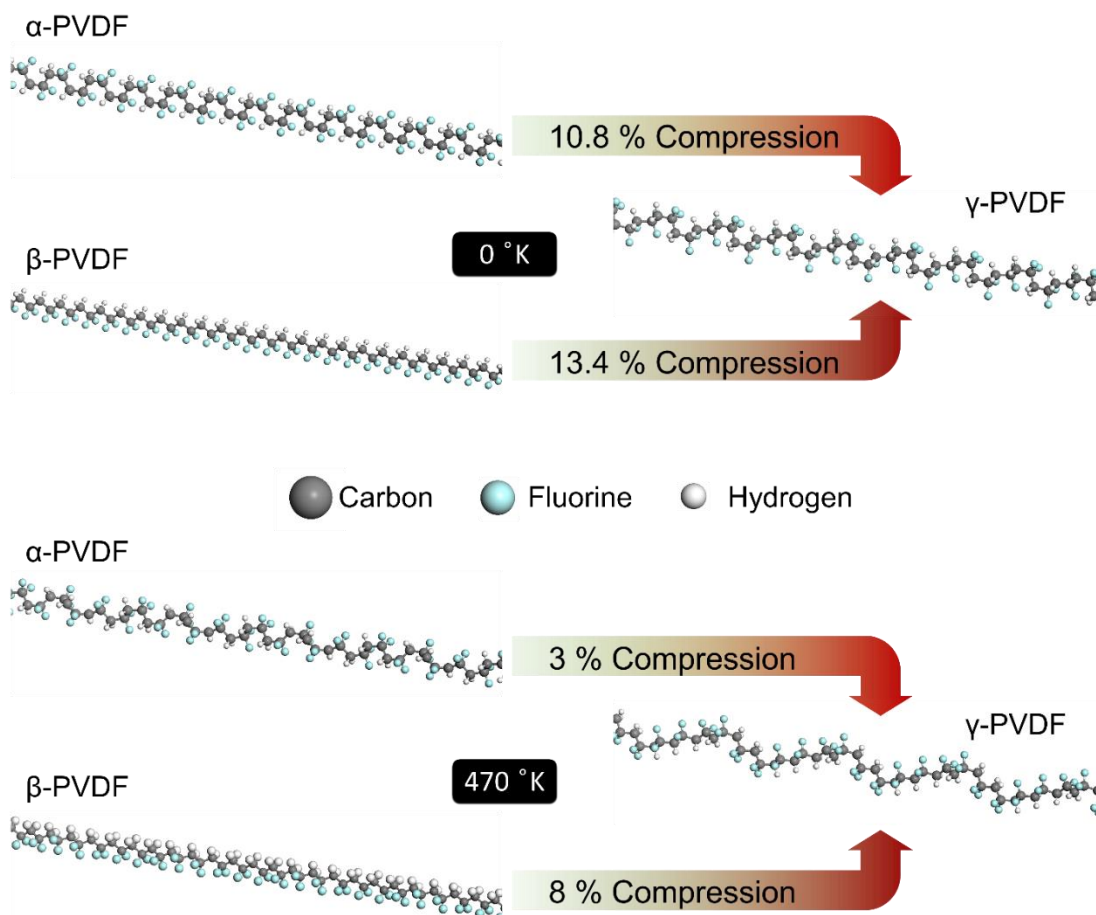


Figure 3.11: Ab-initio calculations reveals that, with the compressive strain in axial direction, alpha and beta PVDF transforms into gamma PVDF both for 0K and 470 °K. The required compression for the transformation from alpha to gamma at 0K is 10.8% and from beta to gamma is 13.4%. The required compression decreases to 3% and 8% at 470 °K.

At 0 °K (or without temperature effects) the atoms are stationary and it is possible to obtain exact energy (within the limits of used methodology) and other relevant properties for instance energy barriers in our case. Accordingly, we considered 0 °K ground state simulations as benchmark calculations and compared the results of higher temperature results with it. When temperature effects are included, the simulation becomes dynamic (which is known as ab initio molecular dynamics). The atoms start to move around their equilibrium positions with a velocity in proportional with the temperature and energy varies at each simulation step. The total energy and atomic positions thus can be obtained by averaging over the total simulation time. In that sense, it is more informative to compare the high temperature results with ground state ab initio calculations in order to reveal the effect of temperature. We consider 470 °K for comparison, firstly because it is well above melting temperature of PVDF and secondly even the applied temperature is higher, our simulations indicate that the

temperature of PVDF inside preform is around 470 °K. This is because, even we preheated the preform, the traveling time of preform in hot zone of the furnace is not enough for thermal saturation. We conducted a time dependent COMSOL Multiphysics finite element simulation to show the temperature distribution inside of a traveling preform in our fiber tower furnace (Figure 3.12).

Temperature distribution in fiber drawing furnace is simulated using COMSOL 4.3 heat transfer model which follows the first rule of the thermodynamics. We ignored viscous heating and pressure work. Therefore, we concluded that:

$$\rho C_p \frac{\partial T}{\partial t} + \rho C_p u \cdot \nabla T = \nabla \cdot (k \nabla T) + Q \quad (3.3)$$

is our governing equation, where C_p is the specific heat capacity, T is the absolute temperature, u is the velocity vector, ρ is the density, Q is the heating term and t is time. We assumed that mass is always conserved in the furnace which means:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho V) = 0 \quad (3.4)$$

where V is the volume. Heat transfer interfaces of the furnace such as out flowing heat boundaries and insulating boundaries use Fourier's law of heat conduction which means:

$$q_i = - \sum_j k_{ij} \frac{\partial T}{\partial x_j} \quad (3.5)$$

where q_i is heat flux, k_{ij} is anisotropic thermal conductivity tensor and x_j is distance.

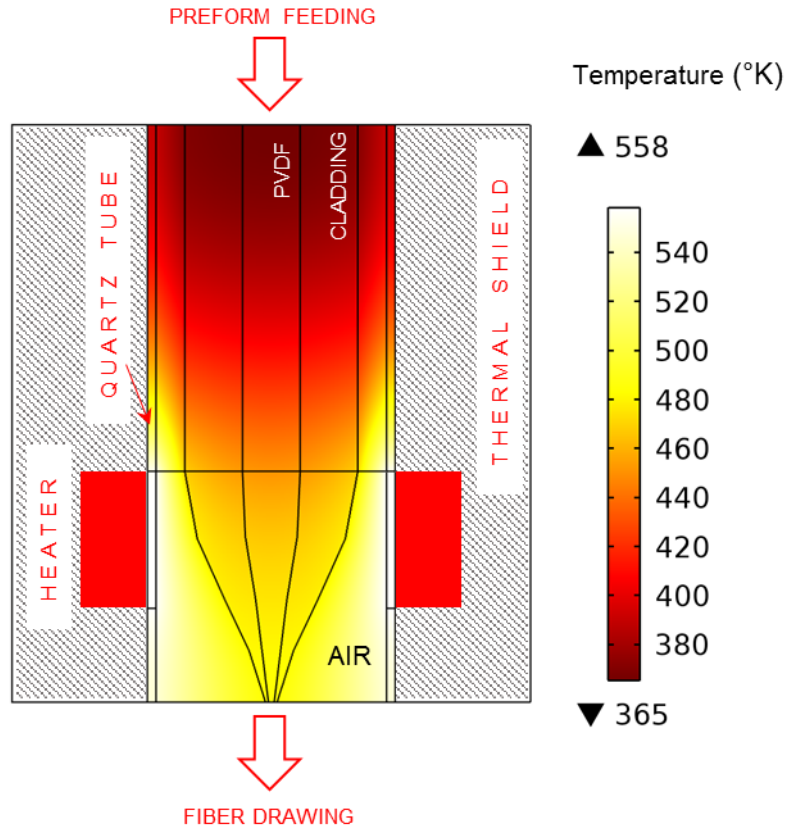


Figure 3.12: Finite element simulation of the temperature distribution in the furnace. The height of the heating zone is 2.5 mm and the temperature of the PVDF in the core is around 470 °K.

Moreover, for higher temperatures the trend is similar and does not contain any new knowledge except the higher temperature decreases the required strain for phase transformation (Figure 3.13).

Correlations between experiment and theory in terms of phase transformation and structural changes: Structural changes due to temperature and induced stress during the fiber drawing is investigated by ab initio calculations which confirm that there is a phase transition trend from α and β forms to γ form under tensile and compressive strain (Figure 3.10e-g, Figure 3.11). The temperature in the simulation is set to 470 °K which corresponding to PVDF core temperature during drawing process (Figure 3.12) and also which is well above the melting temperature of PVDF.

For comparison and to understand the effect of temperature, the calculations are also performed at 0 °K (which is actually corresponding to the case where temperature effects are excluded in ab initio simulations to obtain ground state properties). The

applied force in the fiber drawing axis causes stretching in the same direction whereas compression in the perpendicular directions. As the orientation of the molecules with respect to fiber drawing axis in the bulk PVDF can vary, all strain components that occurred during the fiber drawing should be taken into account in the ab initio model in which we considered tensile and compressive strains in the system as lattice stretching and lattice compression, respectively.

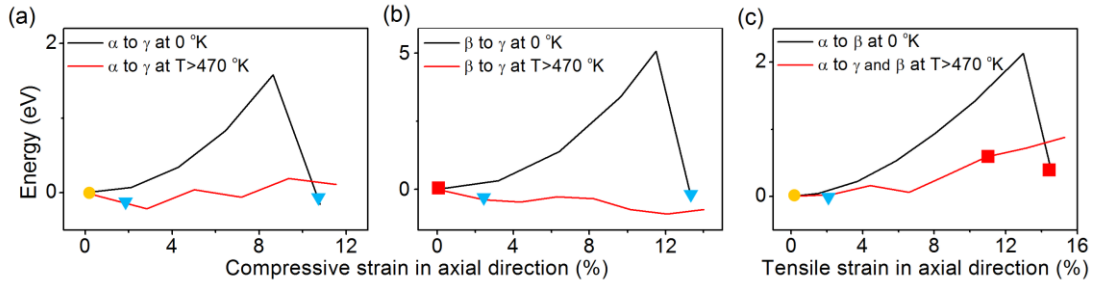


Figure 3.13: Ab initio calculations for explaining phase transformation at higher temperatures. Increasing the temperature decreases the required strain for phase transformation accordingly. (a) Transition from α (yellow circle) to γ phase (blue triangle), (b) transition from β (red square) to γ phase with compressive strain and (c) transition from α to β phase with tensile strain.

The results are summarized in Figure 3.10e-f-g, where yellow circle, red square and blue triangle represent the molecular chains in Figure 3.10a. When compressive strain is applied in axial direction of α and β form PVDF, a transformation from α to imperfect γ phase with longer non-polar parts, and a transformation from β to ideal γ phase are clearly observed at both 0 and 470 °K. Although, a very high activation energy of 1.6 and 5.1 eV, which practically makes the transformation impossible, is required at 0 °K for the transition from α and β to γ phase respectively, the same phase change phenomena occur with almost no energy barrier at 470 °K. The required strain for phase transformation is significantly reduced with temperature as well. While transformations from α to γ occurs at 10.8 % and β to γ at 13.4 % compressive strain at 0 °K, the same transformations are observed at 3 % and 8 % at 470 °K. The similar trends are observed at higher temperatures with a small amount reduction in the required strain (Figure 3.13). These results indicate that the temperature above the melting point of PVDF during the fiber drawing process enables the phase transformation from other phases to γ phase by decreasing the required compressive strain and energy barrier. The peaks obtained at $2\theta = 17.7^\circ$, 26.5° and 27.8° from XRD data, which correspond to α phase PVDF as shown in Figure 3.10b can be explained by imperfect transformation from α to γ phase. In a similar manner, tensile strain in

axial direction is also applied. A direct phase transition from α to β phase is favored at 0 °K when strain exceeds 14.6 % and the required activation energy is 2.1 eV. Interestingly, when the temperature is elevated up to 470 °K or more, instead of direct transition from α to β phase, γ phase appears in the first place at 2.2% transforming into a perfect γ phase at 4.4 % of tensile strain with an energy barrier of 0.07 eV. If strain is further increased and reaches 13.1 %, imperfect β phase can be obtained with an energy barrier of 1.0 eV (The imperfection of the β phase can be due to the requirement of polarization process for the transformation [29]). Therefore, simulation results show that energy barrier for α to γ transition (0.07 eV, blue triangle in Figure 3.10g) under tension is lower than α to β transition (1 eV, red square in Figure 3.10g) under tension.

3.4. Piezoelectric and Electrostriction Characterizations

Using a piezo evaluation system attached to an atomic force microscope (AFM), we observed a large piezoelectric response ($d_{33} = -58.5$ pm/V) from a single 80 nm thick nanoribbon. To our knowledge, this is the first piezoelectric measurement performed on a single PVDF nanoribbon. Besides, here we report the highest effective d_{33} coefficient ever measured from a γ phase single PVDF nanoribbon.

3.4.1. Experimental Method

Electrical characterizations such as piezoelectric displacement and ferroelectric hysteresis curve measurements are performed for PVDF nanoribbons. Utilizing a (Radiant Premier II) piezoelectric evaluation system along with an AFM instrument (Asylum Research MFP-3D AFM) simultaneously functioning as a high precision displacement sensor and a tool for electrical coupling to nano-scale surfaces (Figure 3.14), a large average effective piezoelectric coefficient ($d_{33} = -58.5$ pm/V) is measured from 80 nm thick, 180 nm wide single PVDF nanoribbons isolated from an as-produced bundle (Figure 3.15a). As the exact shape and the size of the tip is unknown, we can only represent a ferroelectric hysteresis curve (polarization vs. voltage) in arbitrary polarization units. But still remnant polarization can clearly be observed (Figure 3.15b). Polarization curve is measured at 100 Hz and up to 25 V.

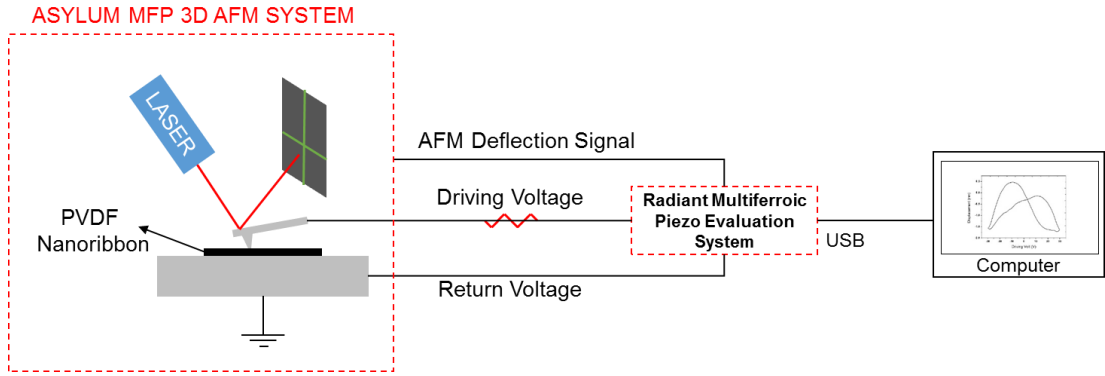


Figure 3.14: Experimental setup for piezoelectric characterization of the PVDF nanoribbons.

Since PVDF is a multiferroic material and piezo-response characterization of nanoscale piezoelectric materials is challenging, characterization of PVDF nanoribbons is inherently multi-physical problem which requires considering internal and external variables such as local temperature changes, electrostriction, pyroelectricity, ferroelasticity, electrostatic effects, indentation regime, applied electrical potential, contact (AFM Tip) sliding and drifting effects. Piezoelectric coefficient measurements using AFM and a piezoelectric evaluation system (virtual ground mode) can be well understood in three sequential stages: sample preparation and mechanical contact with AFM tip, recording piezoelectric response, analyzing the acquired signals for calculating pure piezoelectric displacement. The ribbon structure provides convenience for piezoelectric measurements with AFM since a more conformal contact between the bottom of the nanoribbon and the conductive surface of the substrate diminishes the sliding and drifting adversities during measurements. Before local piezoelectric characterization, we operated a non-contact mode AFM surface imaging for locating a PVDF single nanoribbon among dispersed nanoribbons on a 60 nm silver coated silicon wafer. After a mechanical contact between AFM tip and the surface of the nanoribbon is accomplished in contact mode AFM, we conducted displacement-voltage (D-V) measurements applying 10 millisecond bipolar triangular voltage pulses between the AFM tip (electrical potential) and the metal coating of the substrate (ground). During piezoelectric measurements, we kept AFM control loop off and recorded piezoelectric displacements in a very short time scale compared to that of AFM tip drift. In addition, we used multiple deflection measurements from each local contact surface and calculated the average D-V curve in order to analytically cancel drifting effects and calculate a more accurate piezoelectric coefficient.

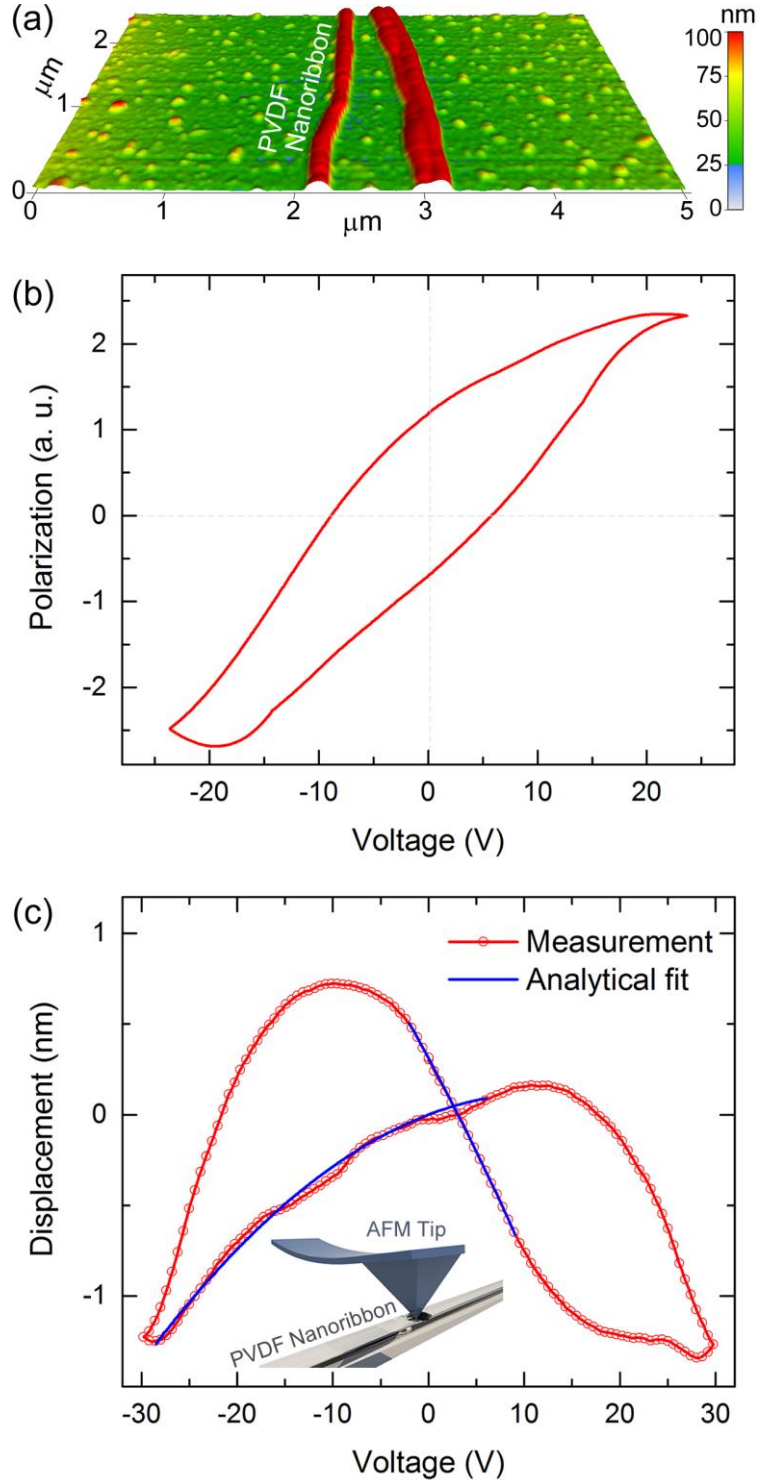


Figure 3.15: (a) AFM topography of 80 nm thick and 180 nm wide single and double nanoribbons on a metal coated substrate. (b) Hysteresis loop of as produced single nanoribbons at 25 V and 100 Hz which represents the spontaneous electric polarization. (c) Displacement-voltage hysteresis loop taken by an AFM and piezoelectric evaluation system from a single PVDF nanoribbon. Inverse butterfly loop is a characteristic result of the negative d_{33} piezoelectric coefficient. Total measured displacement is a function of E and E^2 . Since the applied electric field and displacement are known, d_{33} and Q values can be calculated in least square sense. Data fitting is executed by using 370 data points.

AFM is one of the most precise deflection sensors which can dynamically detect the change in the thickness of PVDF nanoribbons according to alternating electric potential. However, many artifacts can occur related to applied electric field and contact indentation regime during piezoelectric measurements at nanoscales. We used experimental and analytical approaches in order to eliminate such effects and analyzed the origin of the large displacement in PVDF nanoribbons. First, electrostatic forces can dislocate AFM tip in nanoscale distances. This effect can be simply eliminated using a stiffer ($k=40$ N/m and $f=300$ kHz) AFM tip. Measured signal from AFM deflection corresponds to the change in the thickness of PVDF nanoribbon due to, in principle, AFM tip follows the surface motions of the sample. From the mechanics of materials perspective, we can calculate the total strain in PVDF nanoribbons:

$$s = \frac{\Delta t}{t} \quad (3.6)$$

where s is the total strain, t is the thickness of the nanoribbons and Δt is the measured change in the thickness. The measured strain is not a pure piezoelectric deflection, but rather a sum of strain components caused by electrostriction, thermal effects and applied pressure in the direction of the electric field.

$$s = s_{piezoelectric} + s_{electrostriction} + s_{thermal} + s_{pressure} \quad (3.7)$$

$$s = d_{33}E - QE^2 + \lambda\Delta T + e_{33}\sigma_{33} \quad (3.8)$$

where d_{33} is the piezoelectric coefficient, E is the electric field, Q is the electrostriction coefficient, λ is the thermal expansion coefficient, ΔT is the change in the temperature, e_{33} is the elastic coefficient and σ_{33} is the stress.

3.4.2. Numerical Calculations for Indentation Induced Elastic/Ferroelastic Deformation in Piezoelectric Nanoribbons

The pressure induced strain related to indentation regime or AFM tip can trigger ferroelastic motions in PVDF nanoribbons, unless the indentation force is very small

and constant. Since we need to apply a voltage to our conductive tip, it is required to make a mechanical contact with the surface of the nanoribbons. A COMSOL Multiphysics simulation is designed to analyses the linear elastic deflection that deformation of contact region during piezoelectric measurements due to 60 nN indentation force (Figure 3.16).

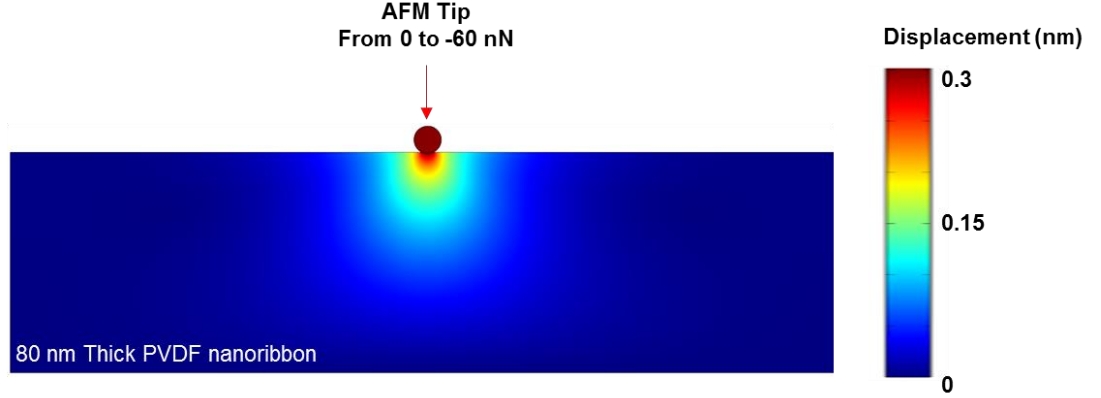


Figure 3.16: COMSOL Multiphysics simulation for understanding the characteristic of the displacement induced via tip indentation. In model design, AFM tip assumed a sphere ($D=10$ nm) and the temperature kept constant at 295 K. In order to make a mechanical contact on the surface of the PVDF nanoribbons, we set the AFM control loon on and apply a -60 nN which generate maximum 0.3 nm elastic deformation on the top of the nanoribbons.

The simulation is conducted at constant room temperature. Tip radius is chosen as 10 nm for all simulations. Hook's law is used in linear elastic model. Governing equation for total strain which is a function of displacement gradient can be expressed as:

$$\varepsilon = \frac{1}{2}(\nabla d + \nabla d^T) \quad (3.8)$$

The equation of motion is:

$$-\nabla \cdot \sigma = F_V \quad (3.9)$$

and the strain – stress relation can be expressed as:

$$\sigma_{ij} = C_{ijkl}\varepsilon_{kl} \quad (3.10)$$

where ε and ε_{kl} are the strain tensors, ∇d is the gradient of the displacement and ∇d^T is the transpose of displacement gradient, σ and σ_{ij} are the Cauchy stress

tensors, F_V is the body force per unit volume and C_{ijkl} is the fourth order stiffness tensor which is a function of Poisson ratio and linear elastic modulus.

The simulation results show that applying a -60 nN indentation force on the 80 nm thick PVDF nanoribbon, which corresponds to 15 nm static deflection in AFM cantilever, triggers maximum 0.3 nm elastic deformation on the surface with an AFM tip diameter of 10 nm. Therefore, AFM tip is guaranteed to be in constant mechanical contact with the nanoribbon surface during measurements, due to AFM tip deflection range is higher than the total piezoelectric displacement measured.

3.4.3. Numerical Calculations for Joule Heating and Induced Thermoelastic Deformation in Piezoelectric Nanoribbons

Dilatation of PVDF nanoribbons and pyroelectric effects can also be ignored, because all measurements are conducted at constant room temperature. In addition, to consider the local temperature changes caused by Joule Heating, we modelled the change in the PVDF nanoribbon temperature as a function of the electric potential (Figure 3.17).

The governing equation in equations 3.3 is also valid for joule heating simulations which is performed using COMSOL 4.3 software. However, heating term is expressed with following equation:

$$Q = j \cdot E \quad (3.11)$$

Because joule heating is heat transfer phenomenon related to current density (j) and electric field (E).

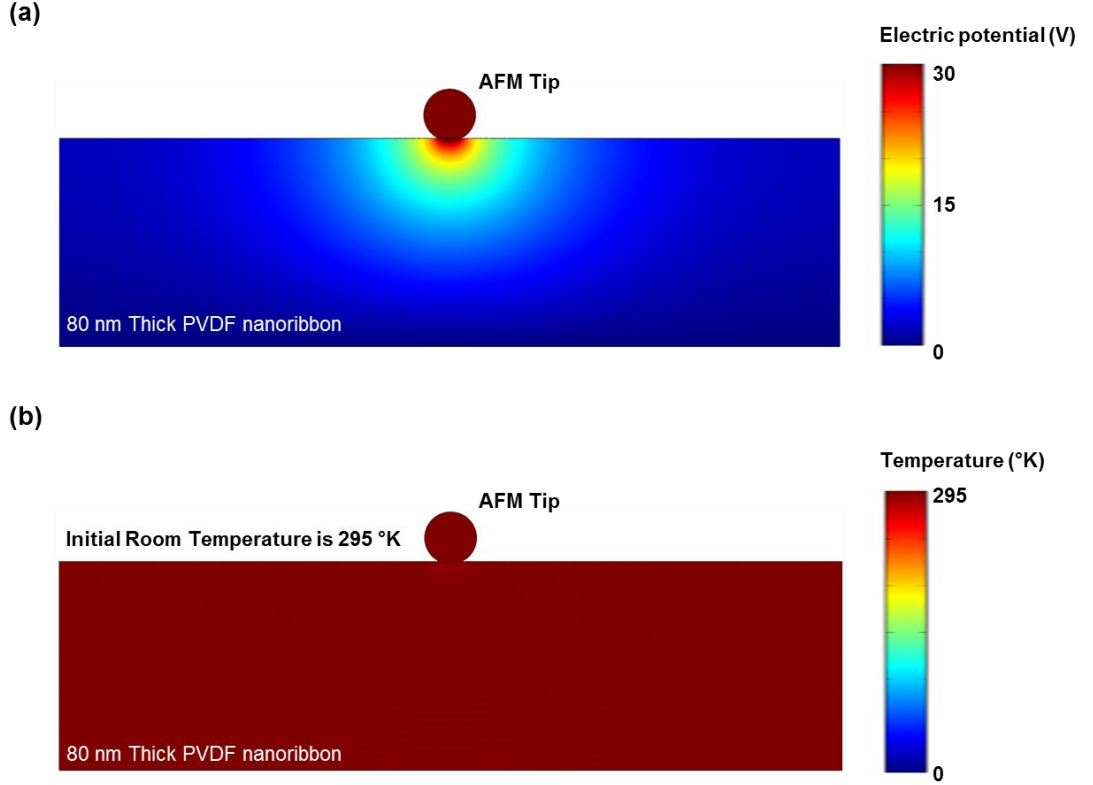


Figure 3.17: COMSOL Multiphysics simulation for understanding Joule Heating phenomena in 80 nm thick PVDF nanoribbons. In model design, AFM tip assumed a sphere ($D=10$ nm) and the temperature kept constant at 295 °K. (a) Electric potential distribution between conductive AFM tip with a 30 V applied voltage and grounded surface. (b) Since Joule Heating proportional to i^2R (i is the current traveling between electrodes, R is the resistance), there is no temperature change observed in nanoribbons as a function of electric field.

Joule heating is proportional to i^2 and R , where i is the traveling current across the PVDF thickness and R is the resistance. Since resulting current is very small, there is no change in the temperature caused by Joule Heating.

3.4.4. Analytical Calculations and Deductions of Piezoelectric and Electrostriction Coefficient

We calculated piezoelectric and electrostriction coefficient of PVDF nanoribbons using equation 3.8 and measured data of displacement versus electric field. After eliminating mechanical and thermal strain components, only sources for the total strain are remaining piezoelectric effect and electrostriction. Using measured total deflection and applied electric field for 370 data points, we can calculate the d_{33} and Q coefficients from the over-determined system of equations as follows:

$$s = d_{33}E - QE^2 \quad (3.12)$$

Inserting the measured data (displacement vs. applied field) in equation 4, an underdetermined system of equations for two unknowns (d_{33} and Q) is obtained, which can be solved in least square.

$$\begin{bmatrix} s_1 \\ \vdots \\ s_n \end{bmatrix} = \begin{bmatrix} E_1 & E_1^2 \\ \vdots & \vdots \\ E_n & E_n^2 \end{bmatrix} \begin{bmatrix} d_{33} \\ Q \end{bmatrix} \quad (3.13)$$

$$\begin{bmatrix} d_{33} \\ Q \end{bmatrix} = \left[\begin{bmatrix} E_1 & E_1^2 \\ \vdots & \vdots \\ E_n & E_n^2 \end{bmatrix}^T \begin{bmatrix} E_1 & E_1^2 \\ \vdots & \vdots \\ E_n & E_n^2 \end{bmatrix} \right]^{-1} \begin{bmatrix} E_1 & E_1^2 \\ \vdots & \vdots \\ E_n & E_n^2 \end{bmatrix}^T \begin{bmatrix} s_1 \\ \vdots \\ s_n \end{bmatrix} \quad (3.14)$$

Results are perfectly fitted to the measured curve (Figure 3.15c). We calculated that electrostriction and piezoelectric coefficient of γ phase PVDF nanoribbons are $Q = -67.8 \times 10^{-9} \text{ pm}^2/\text{V}^2$ and $d_{33}^{eff} = -58.5 \text{ pm/V}$. In the range of a maximum $\pm 10 \text{ V}$ applied electric potential difference, 87.4 % (585.3 pm) and 12.6 % (84.47 pm) of the deflection result from pure piezoelectric effect and electrostriction, respectively. The measured average effective piezoelectric coefficient of γ phase PVDF nanoribbons is higher than the reported values of β phase ($d_{33} = -30 \text{ pm/V}$) and γ phase ($d_{33} = -7 \text{ pm/V}$) PVDF thin films, [26], [29] and on same order of magnitude with β phase ($d_{33} = -57.6 \text{ pm/V}$) PVDF nanowires which are characterized in a similar manner using AFM [28].

Effective d_{33} coefficient for the thin film structure is less than that of 1D structures due to surface clamping conditions. Following equations represent d_{33} coefficient relation for thin films and 1D nanostructures respectively,

$$d_{33}^{eff} = d_{33} - \frac{2S_{13}}{S_{11} + S_{12}} \quad (3.15)$$

$$d_{33}^{eff} \cong d_{33} \quad (3.16)$$

where S_{ij} is an element of compliance matrix. Unlike the nanoribbons, the effective d_{33} coefficient for thin films is expected to be reduced, due to surface clamping boundary conditions [42] The reverse form of D-V hysteresis loop (Butterfly Loop) is

due to the negative value of d_{33} coefficient (Figure 3.15c). The general relation between piezoelectric coefficients of PVDF is $-d_{33} \geq d_{31} > d_{32} > 0$ [160], [171]. In order to confirm the measurement technique, we conducted the same measurement on α phase commercial PVDF thin film with 60 μm thickness, 25 μm^2 surface area and we observed no significant deflection as expected.

3.5. Tapping Sensor and Energy Harvesting Device Fabrication

To utilize the superior performance, we designed two different device structures for the purpose of energy harvesting and tapping sensor. Peak voltage and current outputs of our devices are measured as 60 V and 10 μA .

3.5.1. Device Fabrication Using Microribbons

We developed two devices with different geometries using PVDF micro and nanoribbons produced by thermal size reduction technique. In the first device, a first step fiber is longitudinally divided in two halves without damaging the PVDF microribbon and one face of the microribbon PVDF is uncovered. 50 nm gold is sputtered on the open surface of the microribbon. After mechanically removing the remaining part of PES cladding, the microribbon is cut in smaller pieces and aligned on a silicon substrate, so that the gold deposited faces are on the top. A contact pad is attached to the gold coated surface of 50 μm thick PVDF microribbons and the structure is transferred onto a polydimethylsiloxane (PDMS) layer which avoids the short circuit of the device and maintains the alignment of the microribbons. Subsequently, the other surfaces of the microribbons are also coated with 50 nm thick gold and whole device is embedded in PDMS (Figure 3.18a-g).

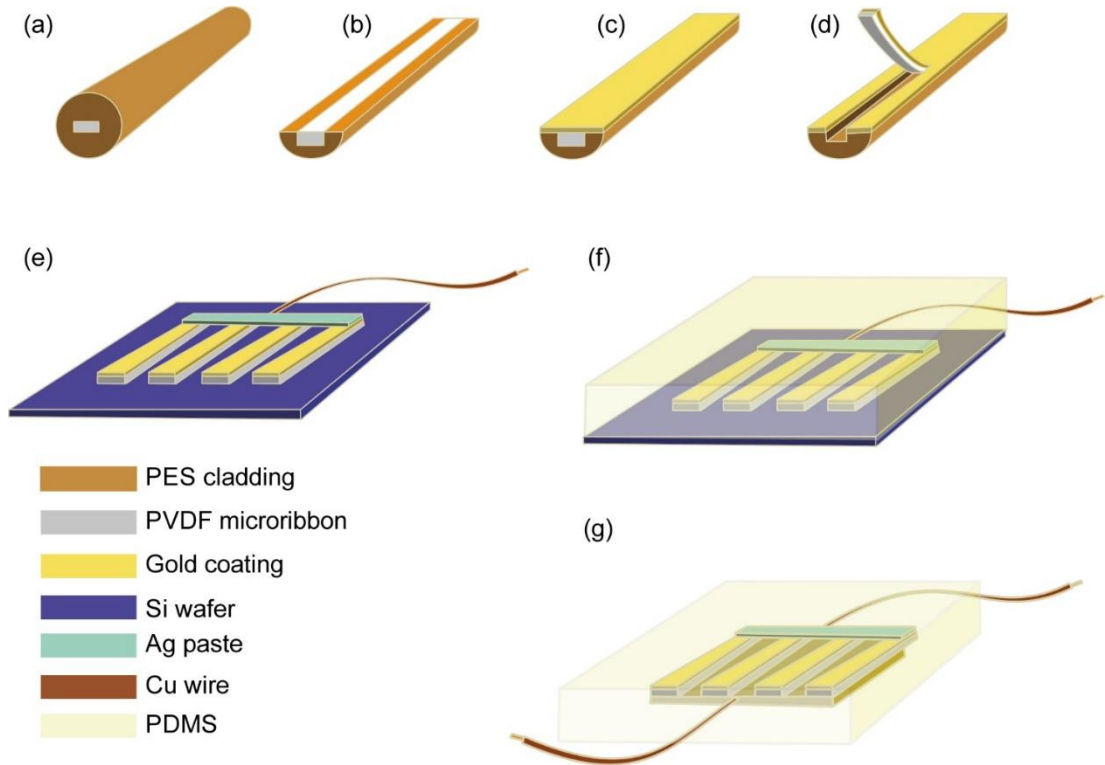


Figure 3.18: Fabrication process for the device produced using first step microribbons. (a) A 50 μm thick microribbon embedded single fiber is selected. (b) The fiber is longitudinally divided in two pieces. (c) The surface of the piece with the ribbon trapped is coated 50 nm gold. (d) After carving the PVDF microribbon out of the cladding, it is cut in equal pieces. (e) One side coated microribbons are aligned on a silicon substrate. Next, Ag paste and Cu wire electrodes are attached on the gold coated surface of the microribbons. (f) The structure is transferred onto a PDMS layer. (g) The back side of the PVDF microribbons are also coated with 50 nm gold and the whole device is embedded in PDMS.

Preparation of PDMS: Structures are embedded in PDMS (Sygard 184 Silicone Elastomer KIT). In the preparation of PDMS, base and curing agent are mixed using 10:1 ratio. The mixture is degassed for 1 hour under 10^{-2} Torr vacuum pressure. After pouring the PDMS on PVDF ribbons devices are held under 10^{-2} Torr vacuum pressure at room temperature for two days.

3.5.2. Device Fabrication Using Nanoribbons

The second device with a different structure convenient for nanoribbons is fabricated using 300 nm PVDF ribbons, which are extracted out of the PES cladding using DCM. The both side of the nanoribbon bundles are coated with sputtering of 50 nm gold film using a shadow mask (Figure 3.19).

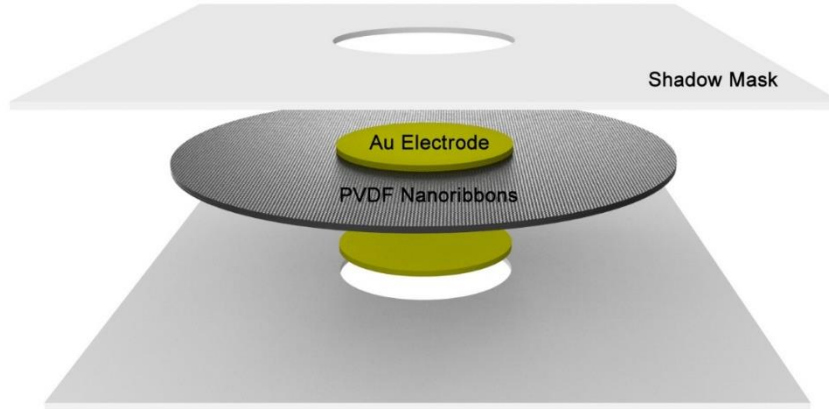


Figure 3.19: Design of the device using PVDF nanoribbons. 50 nm gold is sputtered using a shadow mask on the surface of a PVDF nanoribbon layer which is extracted out of the PES cladding in a DCM solution.

Misalignment of nanoribbons is expected to be reduced output voltage and current of the device. Effective area of the devices fabricated using microribbons and nanoribbons are 100 mm^2 and 20 mm^2 , respectively.

3.6. Electrical Characterization of the Devices

Characterizations of the devices are carried out with an external load capacitance ($C_L = 16 \text{ pF}$) and resistance ($R_L = 10 \text{ M}\Omega$). An equivalent circuit for piezoelectric devices can be represented by a parallel RC circuit containing a charge source (q), a resistor (R_0), capacitor (C_0). From DC and impedance measurements (Figure 3.20), internal resistor (R_0) and capacitor (C_0) for the first and second device are calculated to be $R_0 = 100 \text{ G}\Omega$ and $C_0 = 3.4 \text{ pF}$, $R_0 = 40 \text{ G}\Omega$ and $C_0 = 4.6 \text{ pF}$, respectively.

3.6.1. Device Impedance Measurement

DC resistance of devices are measured by Keithley 2400 Source Meter. Impedance of the devices are measured using Cascade Microtech PM-5 probe station. Magnitude of the impedance versus frequency is given in Figure 3.20.

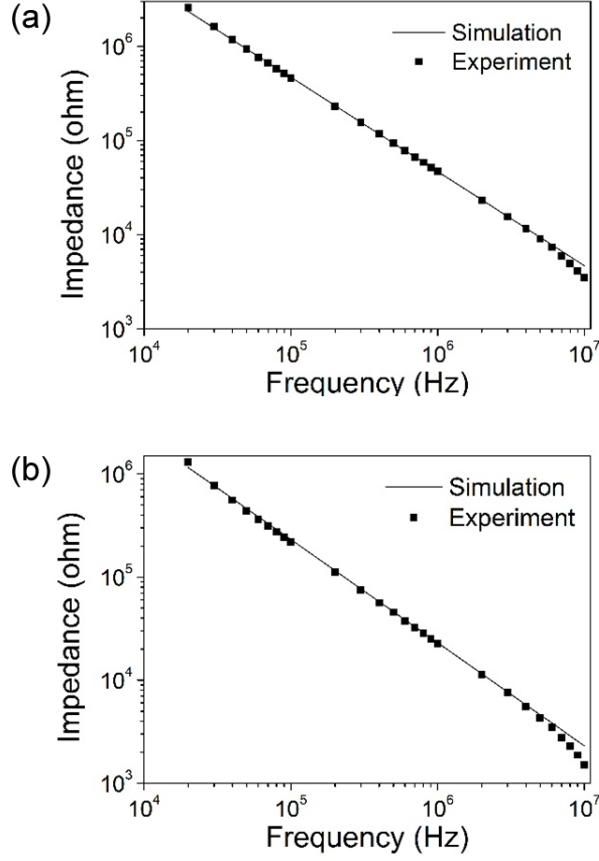


Figure 3.20: Impedance measurement of the piezoelectric devices modeled as a parallel R-C circuit in order to determine internal capacitance and resistance of (a) the device produced using microribbons and (b) the device produced using nanoribbons. Experimental results data are perfectly fitted with simulation.

Theoretical fits to the impedance measurements are done using parallel R-C circuit impedance relation as given in equation 3.16.

$$|Z_{eq}| = \frac{R}{\sqrt{1+(\omega RC)^2}} \quad (3.16)$$

Z_{eq} , R and C represents equivalent impedance, resistance and capacitance of the parallel $R - C$ circuit respectively, and ω is angular frequency.

3.6.2. Open Circuit Voltage and Short Circuit Current Measurements

Owing to PVDF dipoles oriented perpendicular to the fiber axis, when a force is applied vertical to the fiber axis, a positive piezoelectric potential is produced and collected on positive electrode. The same phenomenon occurs vice versa during the releasing. Output voltages and currents of the devices (see Figure 3.21a-b) are recorded

under quasi-periodic tapping forces. Current and voltage output of piezoelectric devices with a load R_L and C_L are measured concurrently with Stanford SR-570 Current Preamplifier and Tetronix TDS-1012B Oscilloscope. The output voltage and current are related to the magnitude and period of tapping force. An equivalent circuit for piezoelectric devices can be represented in Figure 3.21c. The typical output values of the device fabricated using microribbons is 6 V and 3 μA (Figure 3.21d-e) and the typical output values of the device produced using nanoribbons is 40 V and 6 μA (Figure 3.21f-g).

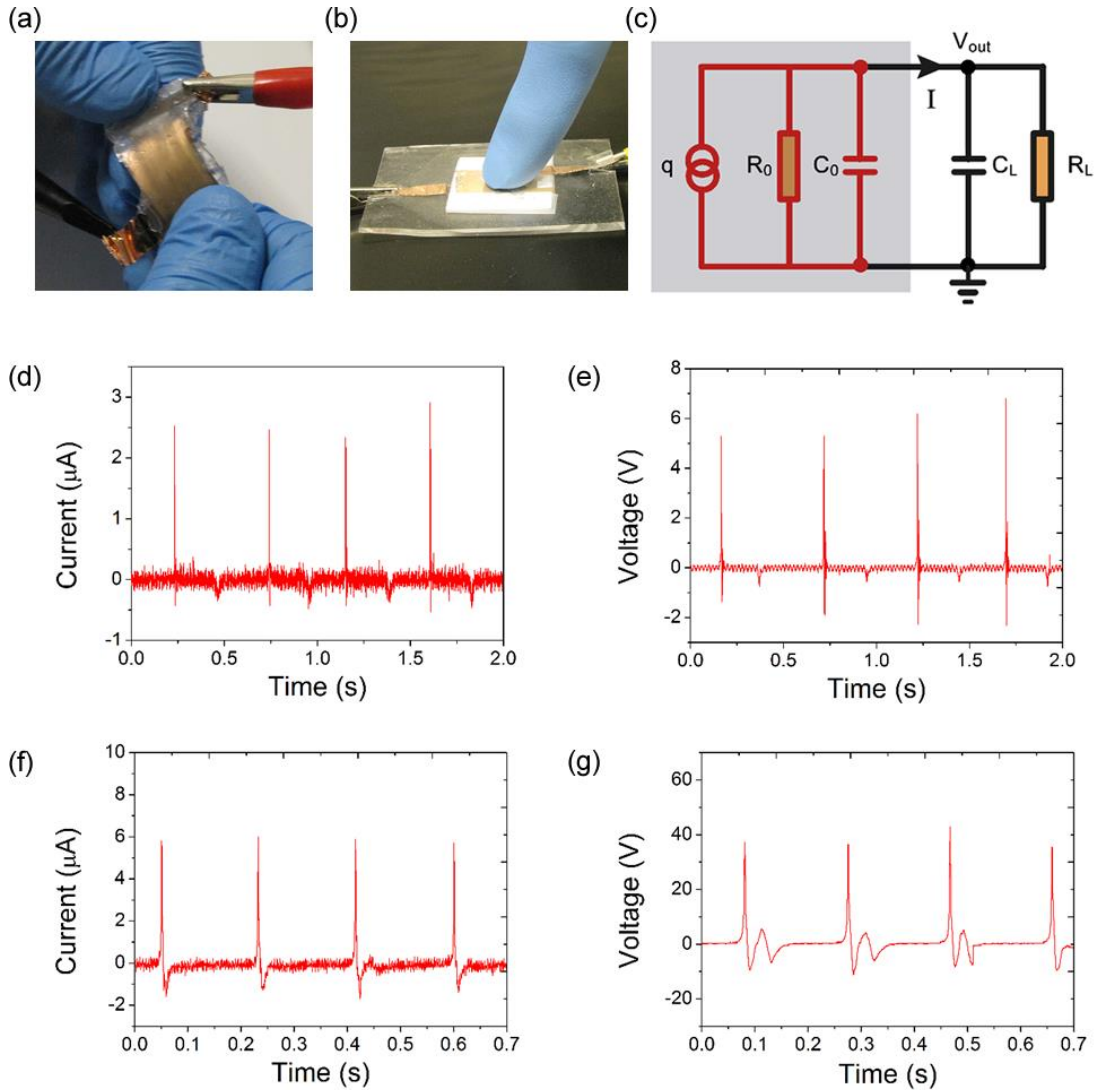


Figure 3.21: Voltage and current outputs of the devices are tested under quasi-periodic tapping forces. Output intensity is related to the applied tapping force magnitude and frequency. (a) The device produced with 50 μm thick microribbons has an output current up to 3 μA and (b) voltage up to 7 V. (c) The device produced with 300 nm thick nanoribbons has an output current up to 10 μA and (d) voltage up to 60 V.

Although, microribbons have 4 % higher amount of polar phase content, charge collected from the device built with nanoribbons is approximately 9 fold higher due to greater contact surface area (two orders of magnitude higher) and better charge collection efficiency of nanoribbons. Maximum output (60 V and 10 μ A for the nanoribbons, 7V and 3 μ A for the microribbons) of the piezoelectric devices can be seen from a broader range of the electrical measurements given in Figure 3.22.

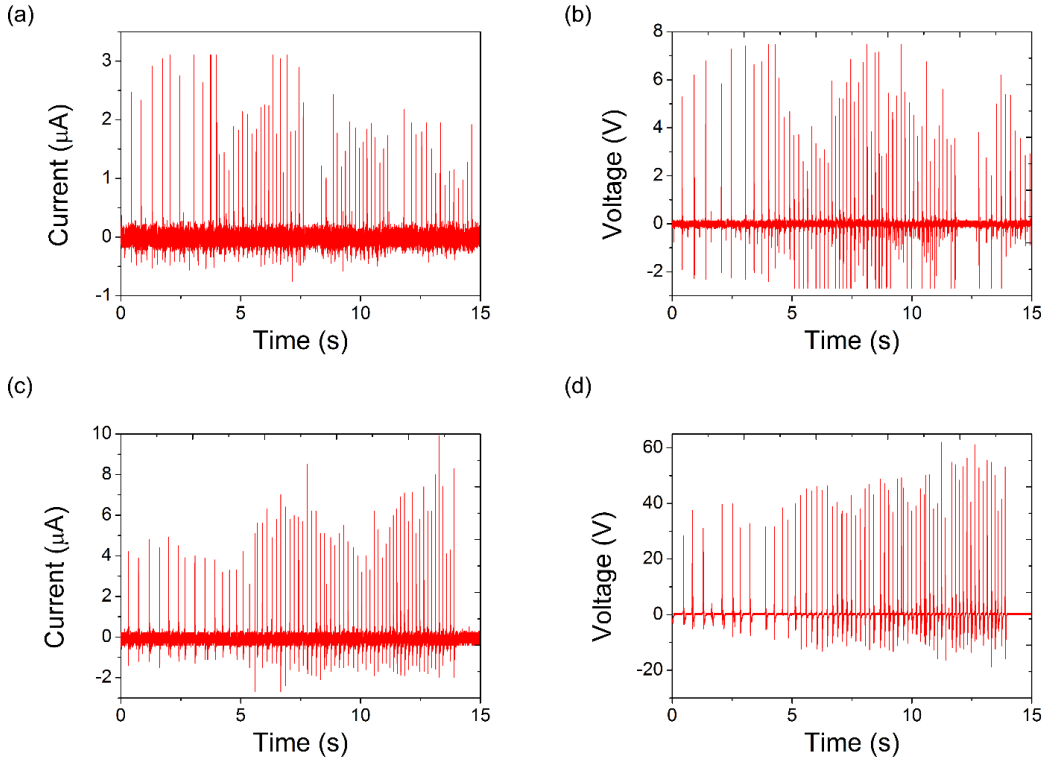


Figure 3.22: Voltage and current outputs of the devices are tested under quasi-periodic tapping forces. Output intensity is related to the applied tapping force magnitude and frequency. (a) The device produced with 50 μ m thick microribbons has an output current up to 3 μ A and (b) voltage up to 7 V. (c) The device produced with 300 nm thick nanoribbons has an output current up to 10 μ A and (d) voltage up to 60 V.

Besides, peak output power densities of first and second devices are 5.25 μ W/cm² and 750 μ W/cm² which prove that efficiency of the nanoribbons is much higher. We built another identical device using non-piezoelectric amorphous As₂Se₃ nanowires (150 nm in diameter) produced by thermal fiber drawing technique in order to confirm piezoelectric effect observed in our devices (Figure 3.23).

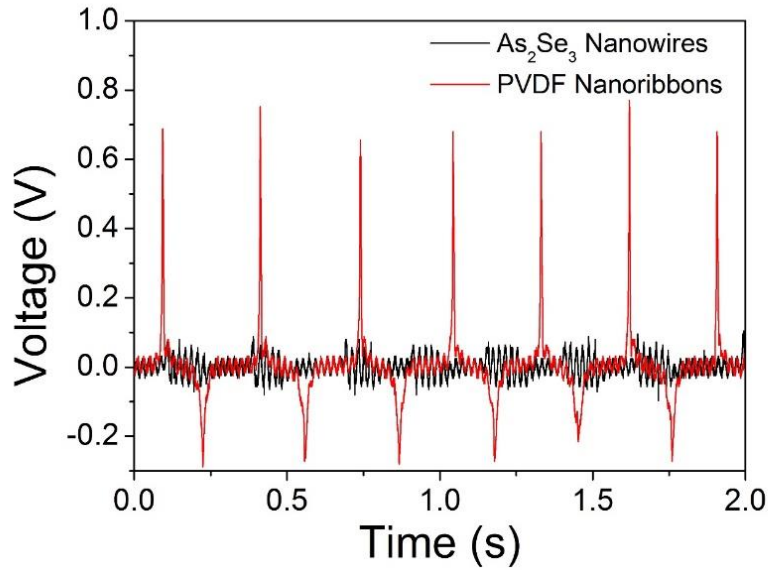


Figure 3.23: We produced a device with identical structure using non-piezoelectric amorphous As_2Se_3 nanowires instead of PVDF nanoribbons in order to confirm that the measured peaks are result of a piezoelectric response.

There is no response observed except noise from the non-piezoelectric device, despite the device produced using PVDF nanoribbons can response even for small tapping forces.

3.7. Summary

We introduced a novel top-down solvent free method for the production of dominantly γ phase one dimensional PVDF nanostructures. PVDF micro and nano ribbons ranging from 100 μm to 5 nanometer in thickness are produced by using iterative fiber drawing technique in three drawing steps. As-produced nanoribbons have an ultra-high aspect ratio (km/nm), good uniformity with cross sectional ribbon geometry, high thermal stability, and high piezoelectric properties. XRD and FTIR results reveal that the γ phase is the dominant phase (72 %) in all nanoribbons. The shear stress and high temperature applied during fiber drawing process favors the polar γ phase transition. Simulating the fiber drawing process using ab initio calculations, we confirmed that transformation into γ phase from other phases at elevated temperature above the melting point of PVDF is favorable. Moreover, PVDF nanoribbons are annealed at several different temperatures up to 175 $^{\circ}\text{C}$ and XRD results show that γ phase is still the exist form. Piezoelectric characterizations of single 80 nm thick nanoribbons are accomplished by exploiting a piezo evaluation system

and an AFM Instrument as a nanoscale probing tool. To our knowledge, we report the highest effective piezoelectric coefficient ($d_{33} = -58.5$ pm/V) measured from a γ phase PVDF single nanoribbon. Results were compared with the literature in Table 3.2

Table 3.2: Comparison of the piezoelectric coefficients of γ -phase PVDF structures.

Material	Phase	$ d_{33} $ (pm/V)	Type	Method	Poling	Reference
PVDF	γ	58.5	Nanoribbon	ISR*	No	Our Study
PVDF	β / γ	16.02	Nanoribbons	Template	Yes	[27]
PVDF	β / γ	10.62	Thin Film	Solution	Yes	[27]
PVDF	γ	7	Nanocomposite	Solution	No	[26]

In addition, we built two proof of principle devices using 50 μm and 300 nm ribbons for the purpose of mechanical energy harvesting and tapping sensor application. Short circuit peak voltage and peak short-circuit current outputs of the devices are measured up to 60 V and 10 μA . Our devices can be used with an energy harvesting circuit (rectifier and storage capacitor with a switching element) in low power requiring applications. Owing to the polymer encapsulation, nanoribbon arrays can be transferred on any substrate and chemically extracted out of their polymer jacket for further device integration such as piezoelectric nanoribbons on interdigitated metal electrodes. Iterative fiber drawing technique holds a huge potential due to the capacity for multimaterial (metal–piezoelectric–dielectric) co-processing in order to produce building blocks for large area, flexible, lightweight, long endurance, cost-effective piezoelectric devices such as artificial muscle and skin, smart textiles, and energy generators.

Chapter 4

High Performance, Organic Piezoelectric Nanofibers

We explained the effect of fiber drawing mechanism on induction of spontaneous polarization in Poly (vinylidene fluoride) (PVDF) in Chapter 3. According to ab initio calculation and X-ray Diffraction (XRD) measurements, only γ phase induced in PVDF due to high stress and temperature in fiber drawing [22]. Ab initio calculations proved that, because of high energy barriers it is practically impossible to obtain β phase in fiber drawing process. Different than the PVDF, its copolymer with Poly(vinylidene fluoride)-tri(fluoroethylene) (PVDF-TrFE) transforms into β phase, which has even higher piezoelectric coefficient than PVDF [83]. To our knowledge, we measured the highest piezoelectric coefficient ever measured from PVDF-TrFE. According to our results, we obtained even higher piezoelectric coefficient than the most used ceramic piezoelectric materials [21], [148]. We proposed several proof of principle devices. Since some of them were still under testing stage, I included them in the future work. We built several proof of principle devices, artificial skin for large area measurements and cardiac measurements. In addition, we developed an anthropometric hand, which mimics the real human hand and can detect even very small pressure changes and angular changes. In the fabrication of the devices many new materials and techniques were developed for flexible electronic applications.

4.1. Introduction

Dielectric materials play an important role in electronics [10], [23], [144], [146], [176]. Almost any conventional electronic device, which facilitates from sensors and actuators and provides energy and data storage possibility, have made with a major amount of dielectric building blocks [1], [3], [9], [24], [76], [127]. Dielectrics used in electronics made of rigid ceramic and rarely polymer materials, which are prior to manufacture robust components that can be assembled on board. Usage of flexible dielectric materials started a new era for electronics. Recent innovations about geometry and mechanical properties of electronic materials push the limits and enabled to transformation of electronic circuits from flat and rigid to the stretchable and flexible form [1], [2], [9], [14], [16], [72]. Light weight, non-toxic chemical composition, high chemical resistance, high dielectric constant, high dipole density and good flexibility and conductivity as observed in some polymers are the key properties that required to manufacture flexible electronic devices [1]. Building organic piezoelectric materials introduces the opportunity of manufacturing flexible, wearable and stretchable self-powering devices, where there is a greater demand for developing high performance, piezoelectric organic materials. PVDF and its copolymer PVDF-TrFE seem to be the best candidate for organic piezoelectric applications [83], [127], [141]. However, only the β crystals of those polymers represent high piezoelectric property out of their basic three different conformations (α , γ and β), because of all-trans stereochemical conformation. Although, the piezoelectric phase can only be obtained using electric field and mechanical deformation, recently developed electrical polarization independent processes are promising for fabricating high performance piezoelectric materials [22], [163], [167]. Enhancement in performance of piezoelectric polymers related to dimensional factors as well as the fabrication method. Piezoelectric polymers in form of 1D structures was known to be presenting better performance in comparison with the form of 2D and 3D structures [62], [74], [75], [146], [177]. Although, they are less efficient in terms of performance and electrical output, 2D and 3D piezoelectric polymers such as thin films and bulk structures are still lead in the market, because of easy handling, good process ability, practical large scale integration and lower cost. The challenging part is the manufacturing macroscopically ergonomic devices perfectly integrated with metal electrodes which can simply interact with surrounding environment using 1D

structures such as nanowires. Table 4.1 shows performance device relation between 1D, 2D and 3D piezoelectric polymers.

Table 4.1: Comparison between key properties of piezoelectric polymer structures

Key Properties for Piezoelectric Polymers	1D	2D	3D
Piezoelectric Coefficient	+	+	+
Flexibility	+	+	+
Large Area Device Integration	+	+	+
Easy Handling	+	+	+
Output / Performance	+	+	+

The current study introduces a technique that will overcome the persisting challenges by building a bridge between nanoscopic and macroscopic worlds and enabling to produce large area, flexible, stretchable and high performance piezoelectric devices meanwhile utilizing the advantages of nanoscale effects. We fabricated kilometer long high performance piezoelectric PVDF-TrFE nanoribbons using thermal size reduction technique, which eliminates post processes such as polarization under high electric field strengths. Piezoelectric β phase was induced due to high stress and temperature during the process. The phase transition phenomenon was theoretically explained using first principle ab initio calculation. The method has two sequential fiber drawing process based on size reduction of a macroscopic slab by redrawing the fibers in an iterative fashion. Although, first size reduction results in micro scale fibers, after the following step fibers yields in encapsulated high performance piezoelectric polymer fibers, nanoscale in cross-section and kilometer long in length. In addition, we show several large area flexible and high performance and self-powered devices. Simply, we represent energy harvesting performance of thermally drawn PVDF-TrFE micro and nanoribbons as proof of superior piezoelectric properties of thermally drawn piezo-fibers.

4.2. Fabrication of High Performance Piezoelectric Nanoribbons Using Iterative Size Reduction Technique

Initially, we produced a slab from PVDF-TrFE powders using an isostatic press in a mold (Figure 4.1). The slab later was inserted in a polyethersulfone (PES) preform, which is produced by rolling PES thin films and consolidated in a vacuum oven above the glass transition temperature. The preform, which is a macroscopic copy of the resulting fibers, was drawn in a custom made fiber tower above the melting point of PVDF-TrFE and glass transition temperature of PES preform. Similarly another preform was prepared for the second step fiber drawing in sequence. Different than the first step process, microfibers produced in the first step was stacked and inserted in the second preform and drawn.

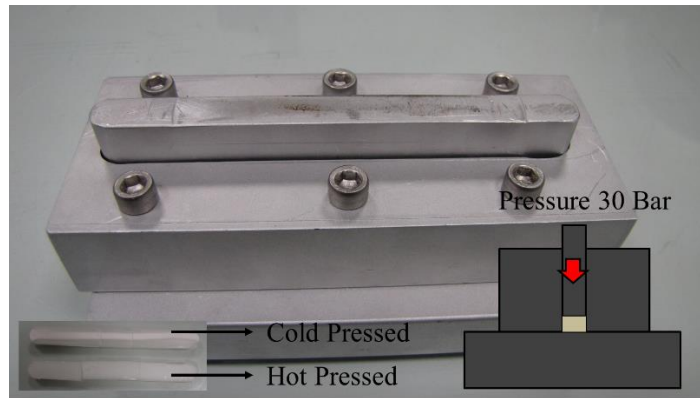


Figure 4.1: Polymer slabs we produced in a directional press under 30 Bar pressures using 3 pieces Al mold. Cold pressing doesn't result in a homogenous consolidation of the polymer powders as shown in inset. Elevating the temperature up 90 °C results in a perfectly homogenized and air bubble free slab.

A schematics presenting the fabrication process and scanning electron microscopy (SEM) images of micro and nanoribbons was shown in Figure 4.2. Number of the ribbons and the total length increases, while the size of each ribbon drastically decreases through step 1 to step 2 drawing process. The thickness of the slab is 3 mm and after first step fiber drawing the thickness reduces to micron sizes (50 – 300 μm). In the following step, feature size of nanoribbons was observed around 50 nm – 800 nm.

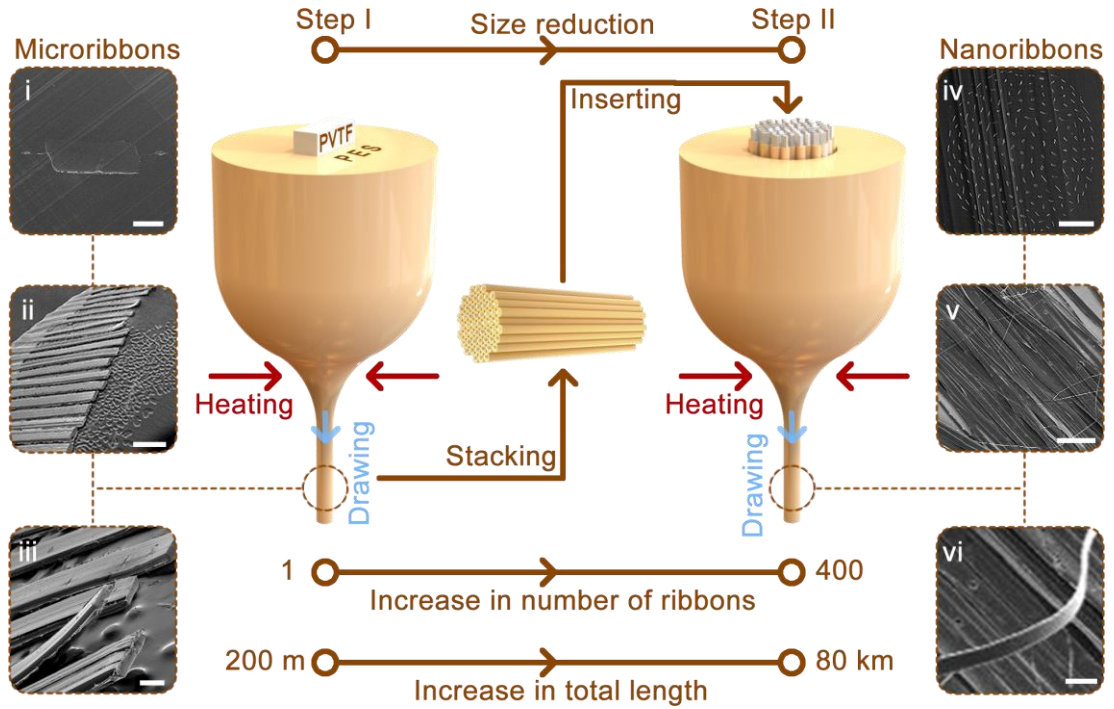


Figure 4.2: A schematics explaining the iterative fiber drawing technique. PVTf corresponds to PVDF-TrFE. In the first step fiber drawing process, a macroscopic slab diminished down to micro scale by the help of applied temperature and stress. Inset SEM pictures were taken from the first step ribbons; i is the cross sectional SEM image of the first step fiber and the scale bar is 50 μm . ii and iii are the SEM pictures of micro ribbons after the cladding was etched. The scale bars for ii and iii are 1 mm and 100 μm , respectively. The first step micro fibers were stacked and inserted in a new PES preform and redrawn. Inset SEM pictures were taken from the second step ribbons; iv is the cross sectional picture of the nanoribbon array and the scale bar is 50 μm . v and vi were taken after the cladding was etched. Inset picture vi was taken from a single ribbon and conservation of the ribbon shape is clear in that picture. Scale bars of inset figure v and iv are 25 μm and 5 μm , respectively. Since there is 3:10 ratio between thickness and the width of the ribbon, a ribbon with 1 μm in width has 300 nm thickness.

The change in the size can be tuned by tuning the reduction factor, which is related to process parameters such as drawing temperature, applied force and deformation speed. In addition, ratios between preform dimensions were inherited to fibers. That brings a significant freedom in fiber and preform design. Fibers were encapsulated by cladding part of the preform. PES cladding and piezoelectric core can be separated by selective etching using dichloromethane (DCM), because PVDF-TrFE chemically resistive against many solvent including DCM as shown in Figure 4.2 inset.

4.3. Phase Transformation Mechanism

Piezoelectric β phase was induced due to applied stress and temperature during fiber drawing process in PVDF-TrFE micro and nanoribbons, which were investigated using XRD, attenuated total reflectance (ATR) – Fourier transform infrared spectroscopy (FTIR) techniques. Techniques used in this section was explained in Chapter 3 with all details.

4.3.1. XRD Phase Characterization

Figure 4.3a explains the phase transformation during the first step fiber drawing process with respect to deformation percentage. XRD pattern from the macroscopic slab, where 0% deformation applied, show no significant peak, but a peak at $2\Theta = 42.49^\circ$, which corresponds to β (111) / (201) / (400) / (220) phase with $d = 2,126 \text{ \AA}$ spacing between its planes. The list of XRD results was given in Table 4.2.

The crystallization in β phase was increased by advancing in the deformation percentage, which corresponds to increase in peak heights. In addition, more deformation ratio shifts peaks to lower diffraction angles. This means d spacing between diffraction planes were increased in accordance with increasing deformation, which contributes piezoelectric properties of PVDF-TrFE positively. We observed the primary β phase peak at $2\Theta = 20.36^\circ$ from (200) / (110) diffraction planes with d space of $4.359 \text{ \AA}$, when 25 % deformation ratio was applied. After the deformation ratio increased up to 50 %, d space was increased to $4.415 \text{ \AA}$ ($2\Theta = 20.08^\circ$), while the peak intensity increases more than two folds. At full stretching point, where the deformation ratio is 100 %, the intensity of the primary peak increases to its double and d spacing increases to $4.448 \text{ \AA}$ ($2\Theta = 19.94^\circ$).

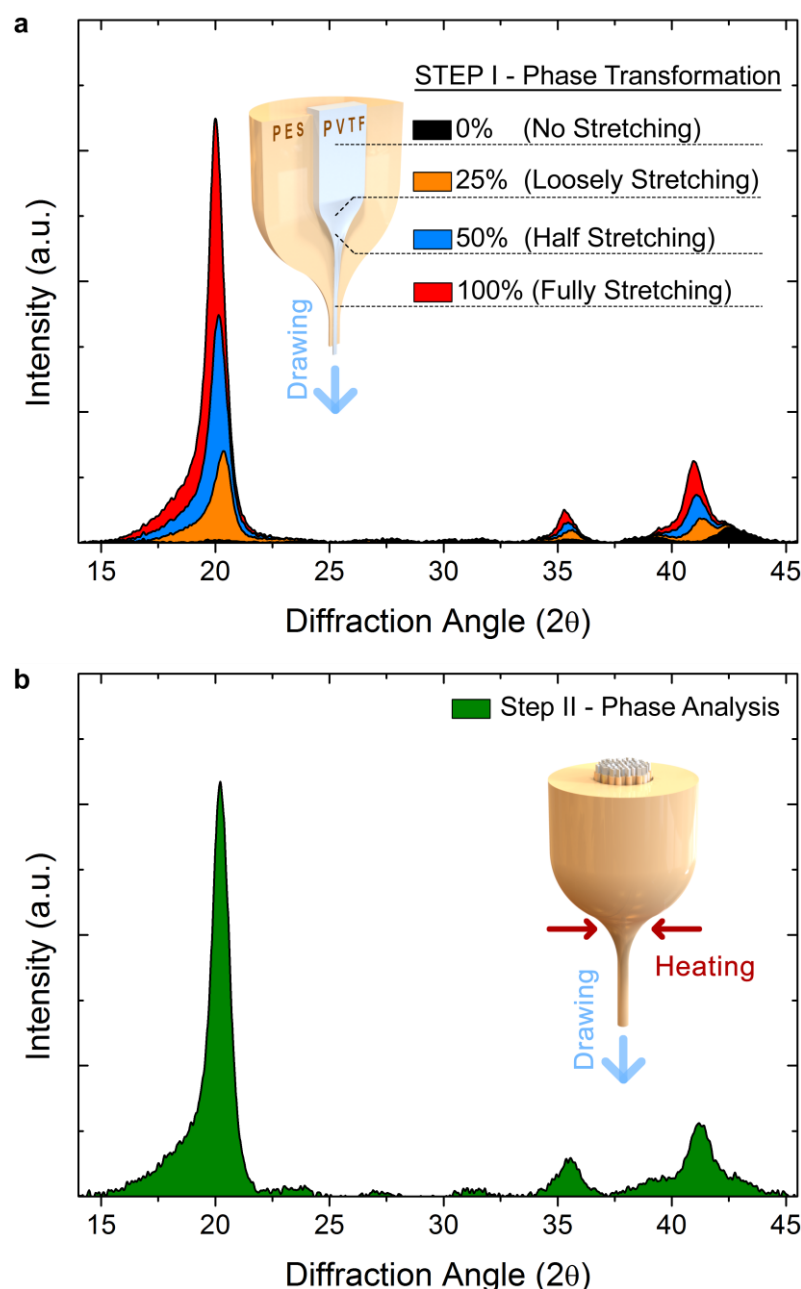


Figure 4.3: XRD measurements from the first and the second step ribbons. a) Phase transformation with respect induced deformation was observed in preform. Increasing deformation also increases the orientation as well as the crystallization in piezoelectric form. Increasing trend in the peak heights showing the ratio of crystallization. Shift in the peaks trough the lower diffraction angels correspond to increase in the d space between planes and enhancement in orientation. b) The first step fibers were already exposed to high deformation and temperature was redrawn in the second following process. Since redrawing can be considered as secondary heat treatments, there is a slight relaxation was observed in molecules. On the other hand, orientation (200) / (110) drastically increased. Nanoribbons discloses better piezoelectric properties because they have higher surface area, less impurities and defect, and better orientation.

Table 4.2 : A detailed list of XRD results from the first and the second step piezoelectric ribbons explaining the relation between relative intensity and change in the d space for explaining the orientation direction.

	Deformation Ratio (%)	Relative Intensity (%)	Diffraction Angle (2θ)	Diffraction Plane	d space ($\text{\AA}$)
Step I	0	100	42.49°	(111) / (201) (400) / (220)	2.126
		100	20.36°	(200) / (110)	4.359
	25	25	41.30°	(111) / (201) (400) / (220)	2.184
		11	35.61°	(001) / (310) (020)	2.519
		100	20.08°	(200) / (110)	4.415
	50	19	40.98°	(111) / (201) (400) / (220)	2.200
		6	35.35°	(001) / (310) (020)	2.537
		100	19.94°	(200) / (110)	4.448
	100	17	40.87°	(111) / (201) (400) / (220)	2.206
		6	35.23°	(001) / (310) (020)	2.545
		100	20.21°	(200) / (110)	4.390
		14	41.22°	(111) / (201) (400) / (220)	2.188
Step II		3	35.52°	(001) / (310) (020)	2.525

Although increasing deformation ratio increases the d space, in the second step we observed that d space was slightly reduced (Figure 4.3b). Changes in the diffraction angle and d space with relative intensity of the peaks were given in Figure 4.4a-i. Relative intensity of peaks was constant for the peak around 20° . On the other hand, relative intensity of the peaks around 41° and 35° were decreased in the second and the first step with respect to deformation ratio. That means polymer chain orientation increased in (200) / (110), whereas a significant decrease occur in other direction.

Increasing in the orientation is an important sign of higher degree of crystallinity. High deformation ratio was elevated the intensity of crystalline peaks in XRD measurement. Expectedly, when amorphous/ crystalline phase distribution was calculated, we observed an increasing trend in crystallinity percentage with increasing deformation ratio. Figure 4.5 reveals that, crystallinity degree was at the lowest value with 13 %, before any stress applied to the slab. Further deformation lead to further crystallization, for instance, crystalline percentage higher up to 67 %, 77 % and 80 % at 25 %, 50 % and 100 % deformation ratio, respectively. 80 % crystallinity was the highest value that we can achieve.

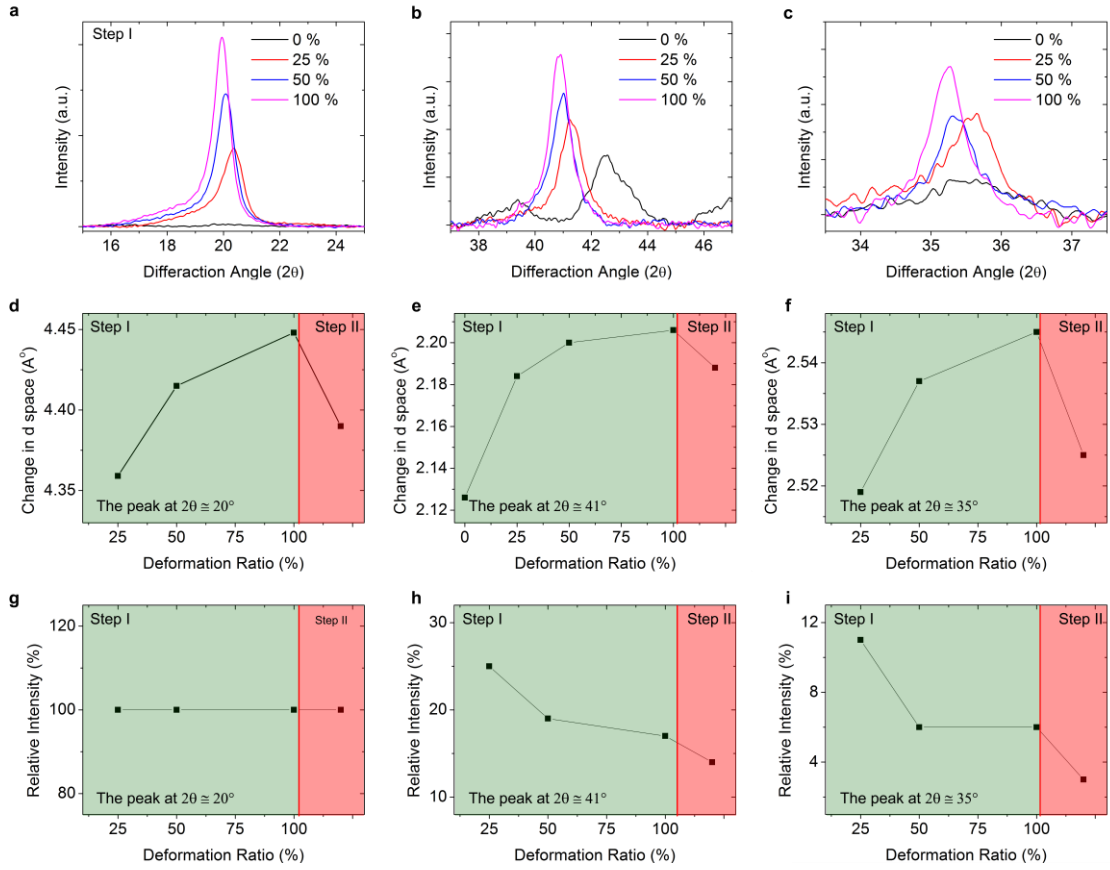


Figure 4.4: Detailed analysis of XRD results. a-c) Peaks at 20° , 41° and 35° shifts to lower diffraction angles with respect to increasing deformation percentage. Besides, increase in the deformation increase in the nucleation in (200) / (110) direction. d-c) This effect also causes a drastic increase in d space between crystal planes, and simply corresponds to better chain orientation and polarization. Although deformation ratio was increased the d space in the first step drawing, chains are relaxed and d space distance slightly decreased in the second step process. g-c) Increase in the orientation can be detected by calculating the relative intensity of the peaks. In XRD characterization technique highest peak always should be taken as the 100 % peak and the relative intensity of the other peaks calculated with respect to the highest peak. We clearly see that, peak for (200) / (110) diffraction planes were constant and the highest in the first and the second step. On the other hand increasing deformation and drawing steps decreases the peak intensity for the other diffraction planes. That means, orientation of the polymer chains and the nucleation of the crystals were increased through (200) / (110) orientation, while the orientation in the other directions were decreased. This effect proves that the dipole orientation and chain orientation became more homogenous with increasing deformation ratio.

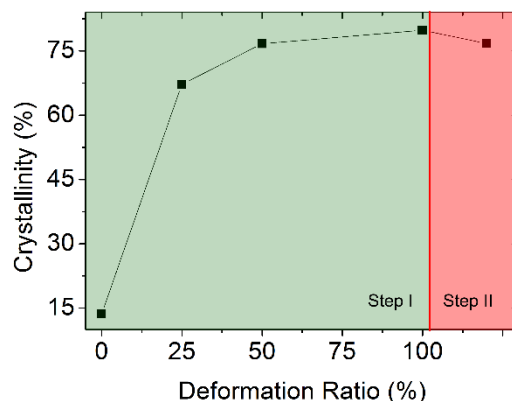


Figure 4.5: Orientation and nucleation were increased in (200) / (110) direction with increasing deformation. Confirming that change in the crystallinity with respect to deformation ratio also shows that there is an increasing trend with respect to increasing deformation ratio. Since, only 13 % of the slab was crystalline, it was increased to 80 % after fiber drawing process. In the second step fiber drawing, crystallinity was decreased to 77 %.

Through the second step, 3 % of crystalline phase transformed into amorphous phase and thus the crystallinity decreased to 77 %. According to relative intensity v.s. deformation ratio curves, polymer chains in step 2 were better aligned in comparison with step 1.

4.3.2. FTIR Phase Characterization

ATR-FTIR results at Figure 4.6a with absorption peaks at 505, 840, 843, 1285, and 1429 cm^{-1} were proving the existence of β phase PVDF-TrFE inside the first and the second step ribbons. Non-polar α phase absorption bands at 532, 612, 765, 796, 854, 870, 970 cm^{-1} were not observed. The peak at 505 cm^{-1} corresponds to C-F bending, which is a very strong indication of the induced piezoelectric phase. One of the strongest peak at 840 and 843 cm^{-1} can be referred to symmetric stretching bands of C-F and C-C bonds. Similarly, the peak at 1285 cm^{-1} defined for symmetric C-F and C-C stretching and symmetric C-C-C bending. The peak at 1429 cm^{-1} referred for symmetric C-H bending.

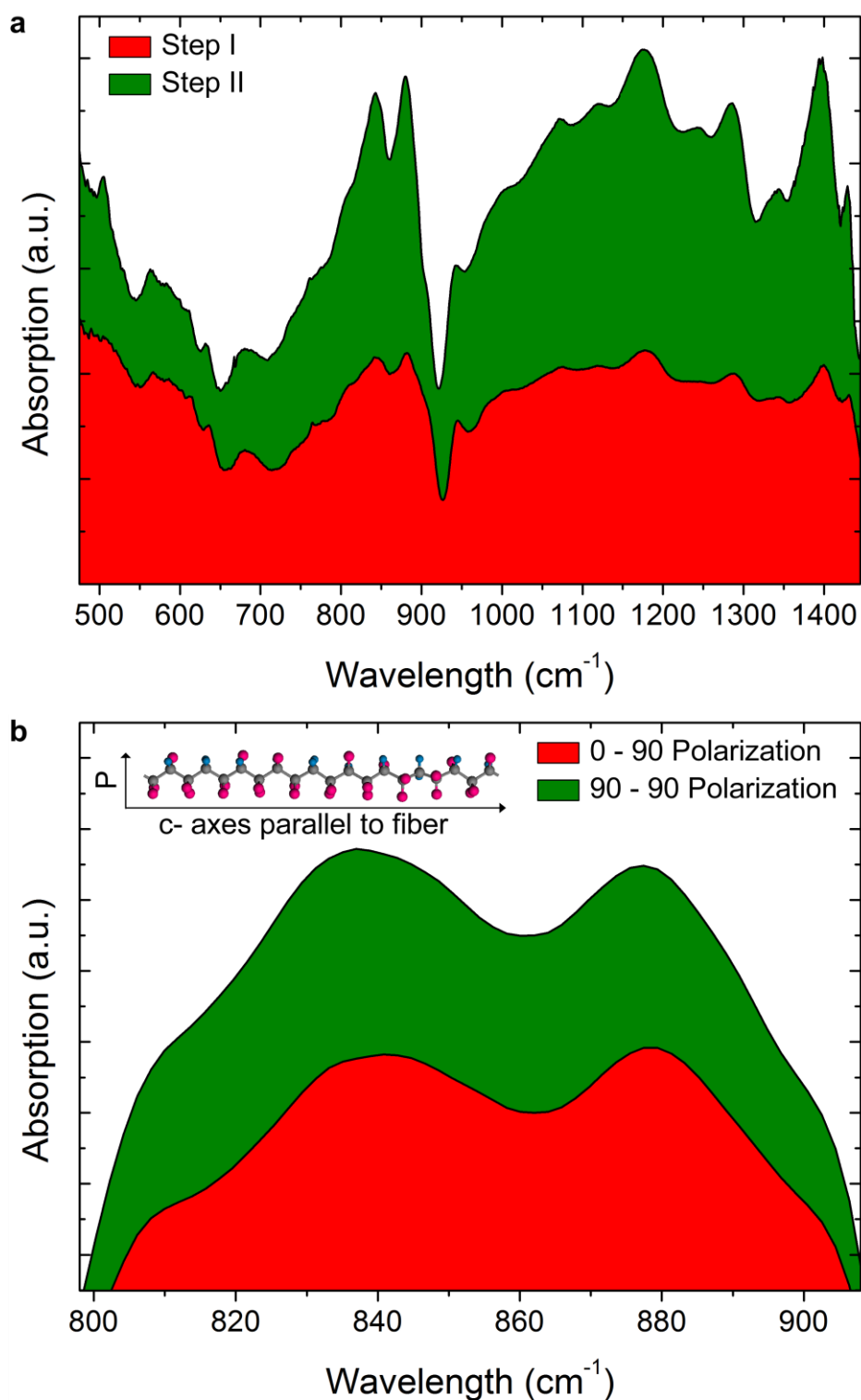


Figure 4.6: a) FTIR measurements from the first and the second step ribbons showing that induced β phase also confirms XRD results. The bands at 505, 840, 843, 1285, and 1429 cm^{-1} corresponds to β phase. b) Alignment of the polymer chains with respect to fiber drawing axis was also investigated using parallel and perpendicularly polarized infrared light. Measurements reveals that, as shown in the inset, polymer chains and dipoles were aligned parallel and perpendicular to fiber drawing axis, respectively.

Alignment of the polymer chains with respect to fiber drawing axis also were investigated using polarized infrared light. As shown in Figure 4.6b, change in the light polarization with respect to alignment of the fiber axis also changes the intensity of the FTIR bands between 800 and 900 cm^{-1} . According to our measurement results, c axis of the polymer chains parallel to fiber drawing axis, whereas dipole of the nanoribbons perpendicular to fiber axis as shown in Figure 4.6b inset. As explained in the Chapter 1, dipole direction of the polymer chains was chosen as the direction 3, and an electric field was applied through the same direction in piezoelectric measurements, which corresponds trough width of the ribbons.

4.3.3. Ab Initio (Density Functional Theory) Calculations

Figure 4.7. In order to understand the dynamics during the iterative fiber drawing process of PVDF-TrFE and investigate the effect of the temperature, we employ ab-initio density functional theory (DFT) calculations. The length of the unit cell primitive vectors along the chain axis were ranging from 23 Å to 27.5 Å containing 60 atoms (20 C, 13 H and 27 F atoms) to have a 65% content of F atoms among F and H in total inside the unit cell. Indeed, PVDF and TrFE block copolymer ratio is 7:3 for PVDF-TrFE that used in fiber drawing.

Computational Results: Before fiber drawing process PVDF-TrFE was processed from the powder form to a slab. In the powder form was in α phase. In addition, α form of PVDF-TrFE known to be more relaxed and stable. Therefore, we first performed some initial calculations to find the most stable configuration for α -PVDF-TrFE. PVDF-TrFE has an asymmetrical geometry with respect to PVDF due to the removal of H for extra F atoms. In order to have %65 content of F atoms, 7 of the H atoms in 10 monomers was replaced with F and 3 monomers were remained unchanged in PVDF molecule.

We performed ground state total energy calculations for several different combinations of the position unchanged monomers and extra F atoms added monomers. We present the most symmetrical ones in Table 4.3. In this table, "FS" stands for "furthest and the same side", which means the unchanged monomers are as far from each other as possible and the extra F atoms are all on the same side of the

chain. Similarly, "CO" stands for "closest and opposite side". From Table 4.3, it is clear that the most stable configuration for α -PVDF-TrFE was the FS configuration. During iterative fiber drawing process, tensile strain was applied in drawing direction, which causes a compressive strain in perpendicular direction.

Table 4.3: Total energy of most symmetrical α -PVDF-TrFE with respect to FS configuration.

	Total Energy (eV)	Lattice Constant (Å)
FS	0.000	23.47
FO	0.138	23.45
CS	0.373	23.36
CO	0.395	23.52

In our simulations, we considered both tensile and compressive strain. Since before the drawing process, orientation of molecules was unknown. Starting from FS configuration, we performed tensile strain both in 0K and 470K. The results were summarized in Figure 4.7 setting the total energy of FS configuration α -PVDF-TrFE to zero shown as the point i in the Figure 4.7. Under tensile strain, the transformation from α to β -PVDF-TrFE was occurred. This transformation has a much lower barrier and appear at a lower strain at 470 K, shown as point ii, with respect to 0 K.

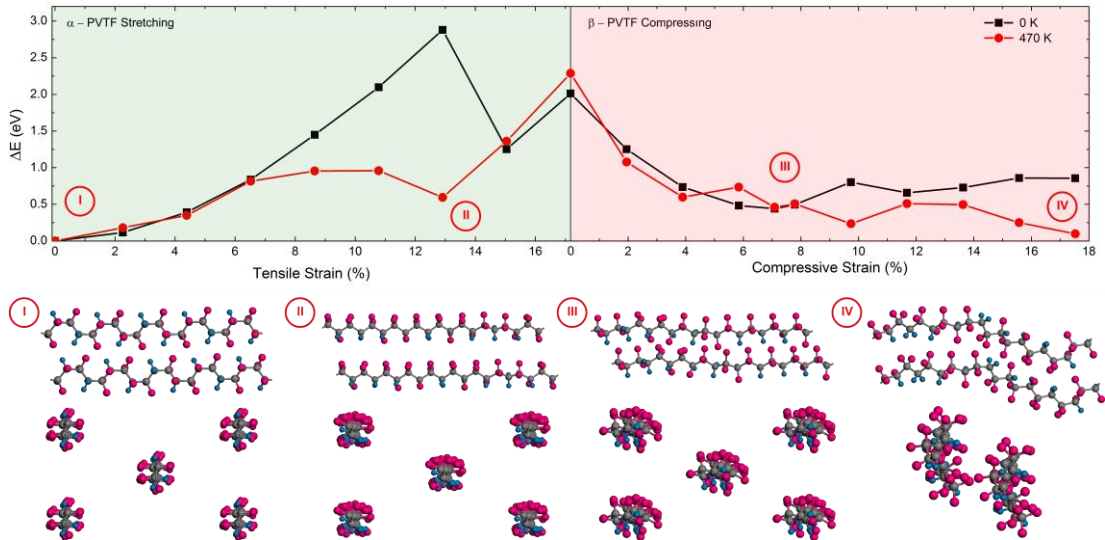


Figure 4.7: Ab initio simulations was conducted to understand phase transformation dynamics in fiber drawing process. Since the orientation of the molecules was unknown before fiber drawing, the both compressive and the tensile strain considered, which take place during fiber drawing in the necking region of the preform. We started by optimizing the α -PVDF-TrFE and we applied tensile strain. 13 % tensile strain was enough to obtain a perfect β -PVDF-TrFE. Compared to ground state calculation, which ignores temperature effect, applied temperature

decreases the energy barrier for phase transformation. Applying compression on β -PVDF-TrFE, relaxes the system with and without temperature. Similarly, α -PVDF-TrFE was destroyed, when a compressive strain was applied.

Although application of higher strain after transformation requires lots of energy for making it practically impossible, from the simulations, we see that PVDF-TrFE still remains in β phase. In the second part of the graph, we apply compressive strain on the β -PVDF-TrFE obtained in the first part. Although the compression decreases the total energy of the system to the optimum β -PVDF-TrFE energy shown as point iii, and then, towards zero, the fiber does not transform back to α -PVDF-TrFE but into some amorphous phase shown as in the point iv. The results indicate that the transformation of α -PVDF-TrFE to β -PVDF-TrFE was possible by applied strain and the temperature in fiber drawing process. On the other hand, compressive strain was the reason for the relaxation of the β -PVDF-TrFE molecules that observed in the second step fiber drawing process as shown in Figure 4.3b. Indeed, 3 % decrease in the crystallization after the second step drawing as shown in Figure 4.5 was related to restructuring of β -PVDF-TrFE into amorphous phase with respect to increasing compressive strain.

4.4. Piezoelectric Characterization

To measure the piezoelectric properties of nanofibers, we have used Asylum MFP3D AFM. Radiant Technologies Premier II precision multiferroic piezoelectric evaluation system was connected to apply high voltage and direct the measurement procedure, such as bias sweeping, strain data collection and rate of bias application and data acquisition. The cantilevers used in the measurement were of 40N/m spring constant and of 300 kHz resonance frequency. The cantilevers were coated with 30 nm of Pt for the application of voltage bias.

We isolated a single 300 nm thick nanoribbon and performed a topography scan in non-contact mode scanning as shown in Figure 4.8. But, piezoelectric measurements were done in contact mode from the single nanoribbon. The topography scan was done to find the nanofibers and a suitable place for measurement on a fiber. After the determination of a suitable measurement point, voltage bias sweep with 10 ms duration was repeated to obtain an average piezoelectric coefficient. The determination of d_{33}

was done on the greatest physically meaningful response. No meaningful results were excluded due to loss of contact or other experimental errors, so they are out of discussion.

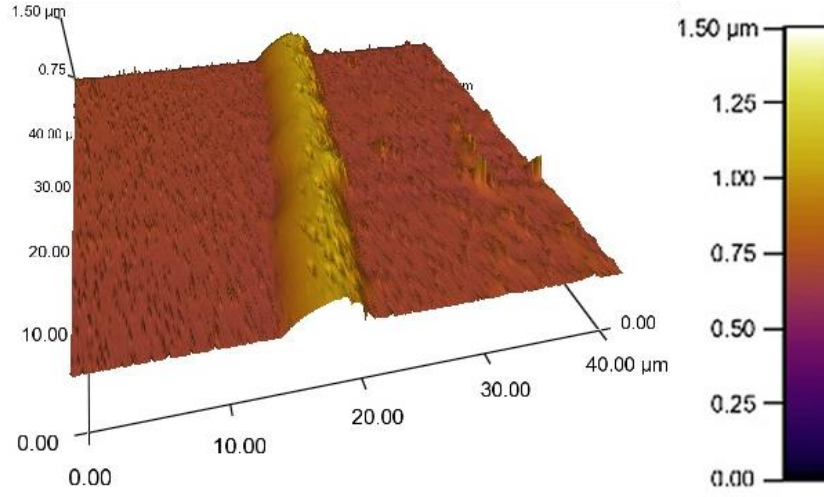


Figure 4.8: Piezoelectric measurements was performed from a 300 nm thick single nanoribbon. Before the measurements, position of the nanoribbon was located using non-contact surface scanning techniques.

We measured the record-high piezoelectric coefficient from as produced PVDF-TrFE nanoribbons as $d_{33}^{eff} = -384$ pm/V. The electrostatic force response has DC, the first and the second time harmonics of and applied sinusoidal electrical signal. Since piezoelectric signal also has DC and the first time harmonics contribution, that effect should be eliminated. Pt coating to cantilever and Au coating to the substrate eliminates that contribution if contact was formed appropriately. Besides, the stiff cantilever eliminates the effect of electrostatic force, since the displacement because of piezoelectricity was almost equal to piezoelectric strain, whereas that of electrostatics is inversely proportional to cantilever stiffness. There was also contribution of electrostriction, which was eliminated by parabolic fitting the displacement vs voltage bias data (Figure 4.9). The piezoelectric effect should affect the displacement linearly, however electrostriction should affect with the square of the voltage bias. As described in a previous Chapter 3, since the conditions make the thermal contribution negligible, the displacement was assumed to consist of piezoelectric and electrostriction terms and no other terms was included. Parabolic curve fittings and the determination of the piezoelectric constants were done using

MATLAB. Data was smoothed with averaging with a window of width of 10 or 20 data points.

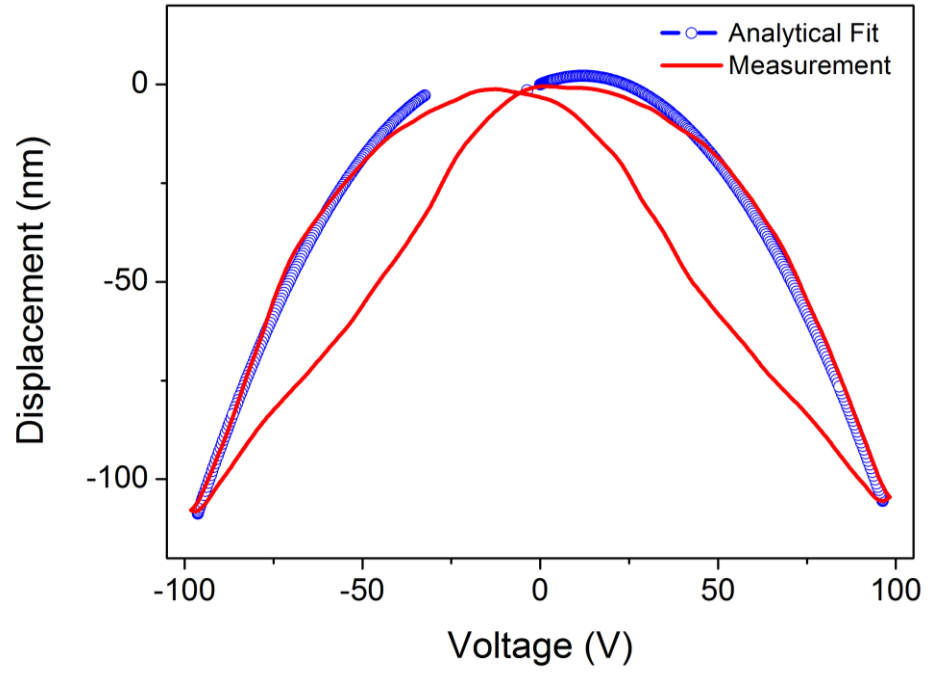


Figure 4.9: Volumetric displacement with respect applied voltage was used to characterize charge constant of as produced PVDF-TrFE nanoribbons.

4.5. Energy Harvesting and Tapping Sensor

Performance of piezoelectric micro and nanoribbons was tested after two devices built as described in Chapter 3, Figure 3.18 and Figure 3.19. In Figure 4.10, we present the power output of nanoribbon device.

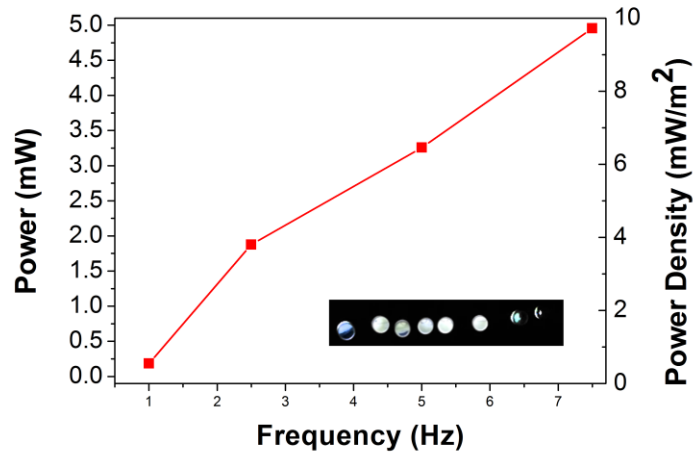


Figure 4.10: Frequency dependent power measurements of the device made by nanoribbons.

Because of increased d space between crystal planes, maximum peak to peak induced potential was measured high as 600 V. On the other hand, induced peak to peak maximum charge is 7 μA . Maximum values were obtained as 7.5 Hz. We also calculated output instantaneous power with respect to frequency. Maximum output power was observed at 7.5 Hz as 4.75 mW and maximum power density calculated as 9.8 mW/m^2 . Finally, devices were able to power 8 commercial LEDs.

4.6. Summary

In conclusion, produced from PVDF and its copolymer PVDF-TrFE, our piezoelectric materials were developed through a technique called iterative size reduction, a low-cost thermal drawing method that allows the fabrication of well-ordered nanofibers in prodigious lengths. Possessing the high piezoelectric capacity ($d_{33}^{eff} = -384 \text{ pm}/\text{V}$), thermal endurance and chemical resistance of ceramic piezoelectric materials with none of the drawbacks, the PVDF fibers are a strong candidate for the design of next-generation piezo-electronics. Table 4.4 represents the comparison of our PVDF-TrFE nanoribbons with other nanostructured PVDF-TrFE polymers reported in the literature.

Table 4.4: Comparison of PVDF-TrFE nanostructures in terms of fabrication methods and the piezoelectric charge coefficient.

Material	Phase	$ d_{33} $ (pm/V)	Type	Method	Poling	Reference
PVDF-TrFE	β	384	Nanoribbon	ISR	No	Our Study
PVDF-TrFE	β	72.7-210.4	Nano-grass	Template	Yes	[32]
PVDF-TrFE	β	48 - 81	Nanoribbons	Template	Yes	[33]
PVDF-TrFE	β	13 – 19	Thin Film	Solution	Yes	[33]
PVDF-TrFE	β	25-45	Nanowire	Template	No	[34]
PVDF-TrFE	β	16-23	Thin Film	Solution	No	[34]
PVDF-TrFE	β	22	Nanowires	Template	No	[30]
PVDF-TrFE	β	8	Nanowires	Template	No	[31]

Using our polymeric materials, we have already designed a high-sensitivity tapping device and an energy-harvesting mechanism with enough power-generation capacity to run small devices such as pacemakers.

Chapter 5

A Motion and Sound Activated, 3D Printed, Chalcogenide-Based Triboelectric Nanogenerator

A multilayered triboelectric nanogenerator (MULTENG) that can be actuated by acoustic waves, vibration of a moving car, and tapping motion is built using a 3D-printing technique. The MULTENG can generate an open-circuit voltage of up to 396 V and a short-circuit current of up to 1.62 mA, and can power 38 LEDs. The layers of the triboelectric generator are made of polyetherimide nanopillars and chalcogenide core-shell nanofibers.

5.1. Introduction

Scavenging the waste energy is an alternative prominent solution which may play an important role for the world energy problem. Nowadays, many electronic devices are produced as portable and they require very low power for functioning [178], [179]. A compact mobile device design assumed to be light weight with long-lasting battery life [3], [72]. However, end of the battery life is inevitable. Besides, a mobile device should be plugged into an energy distribution source in order to charge its battery, which limits the mobility of the user. A portable energy harvesting system is a considerable energy source which never depletes. There are many piezoelectric nanogenerators proposed for this purpose [22], [62], [146], [160], [177]. Drawbacks

of piezoelectric materials are the requirement of complex and high cost manufacturing processes such as electric polarization using high electric field strengths to obtain high efficient piezoelectric materials, high brittleness and toxic elemental composition [73]. In order to overcome these drawbacks, very sophisticated processing conditions and techniques are required [22], [24].

5.1.1. Triboelectric Nanogenerators and Materials

In the last few years, many researchers reported that nanogenerators based on the triboelectric effect are promising energy sources which can harvest mechanical energy from human motions, sound, hydraulic pressure and wind using nanostructured surfaces of the dielectric materials [49], [53]–[56], [102], [180], [181], [48], [182]. Triboelectric effect has been known for a couple of centuries, but it has not been clearly understood yet. However, there are a few significant attempts based on charged atom transfer, [94], [99] ion transfer [183] and bonding of radicals [91], [100] to explain the mystery behind triboelectric effect. When micro and nanostructured dielectric surfaces are contacted each other or separated, there are positive and negative charges are generated on coated electrodes depending on the triboelectric polarity of those dielectric materials. Therefore, a perfect design for a triboelectric nanogenerator (TENG) can be achieved by choosing the most distinct materials in terms of triboelectric polarity as well as the diminishing the feature sizes of those materials down to nanometer scale for obtaining maximum contact area [102]. A list of the triboelectric materials in accordance with their polarity is presented in Table 5.1.

Working mechanisms of TENG devices are based on two mechanical motion modes, contact and sliding mode [102]. Recent studies reveal that the sliding mode has a better voltage output [54]. However, it requires more complicated device design. Output voltage of TENGs is enhanced above 1 kV by using different material combinations and device geometries [180].

Table 5.1: Triboelectric materials are listed according to their triboelectric polarity

Triboelectric Polarity		
	Silicone elastomer with silica filler	Wood
	Borosilicate Glass	Hard Rubber
	Aniline – formol resin	Acetate, Rayon
	Polyformaldehyde 1.3-1.4	Polyvinil alcohol
	Polymethylmethacrylate	Polyester (Dacron)
	Ethycellulose	Polyisobutylene
	Polyamide 11	Polyurethane flexible sponge
	Polyamide 6-6	Polyethylene glycol terephthalate
	Rock Salt	Polyvinyl butyral
	Melamine formol	Formo-phenelique
	Wool, knitted	Epoxide resin
	Silk, woven	Natural Rubber
	Poly-ethylene glycol succinate	Polystyrene
	Cellulose - Cellulose acetate	Polyethylene
	Polyethylene glycol adipate	Polypropylene
	Cotton, woven	Polyimide (Kapton)
	Polyurethane elastomer	Polyethylene terephthalate
	Styrene – acrylonitrile copolymer	Polyvinyl Chloride (PVC)
	Styrene – butadiene copolymer	Polytrifluoroethylene – Silicon
	Steel (Neutral)	Polytetrafluoroethylene (Teflon) – Flourinated PEI
		

5.1.2. Multi-layered Triboelectric Nanogenerator

In this study, we constructed a multi-layered triboelectric nanogenerator (MULTENG) by 3D (Figure 5.1a and Figure 5.1a-4) printing technique which consists of 6 alternating layers made of Polyetherimide (PEI) nanopillars (Figure 5.1a-2 and Figure 5.1a-3), and fluorinated core-shell nanostructures Polyethersulfone (PES) is in the core and As_2Se_3 in the shell) (Figure 5.1a-6 and Figure 5.1a-7). Aluminum tape is used as a substrate and contact electrode for both PEI nanopillars and As_2Se_3 core-shell nanostructures (Figure 5.1a-1 and Figure 5.1a-5). The detailed information about fabrication of As_2Se_3 core-shell nanostructures and PEI nanopillars is given in chapter 5.4.

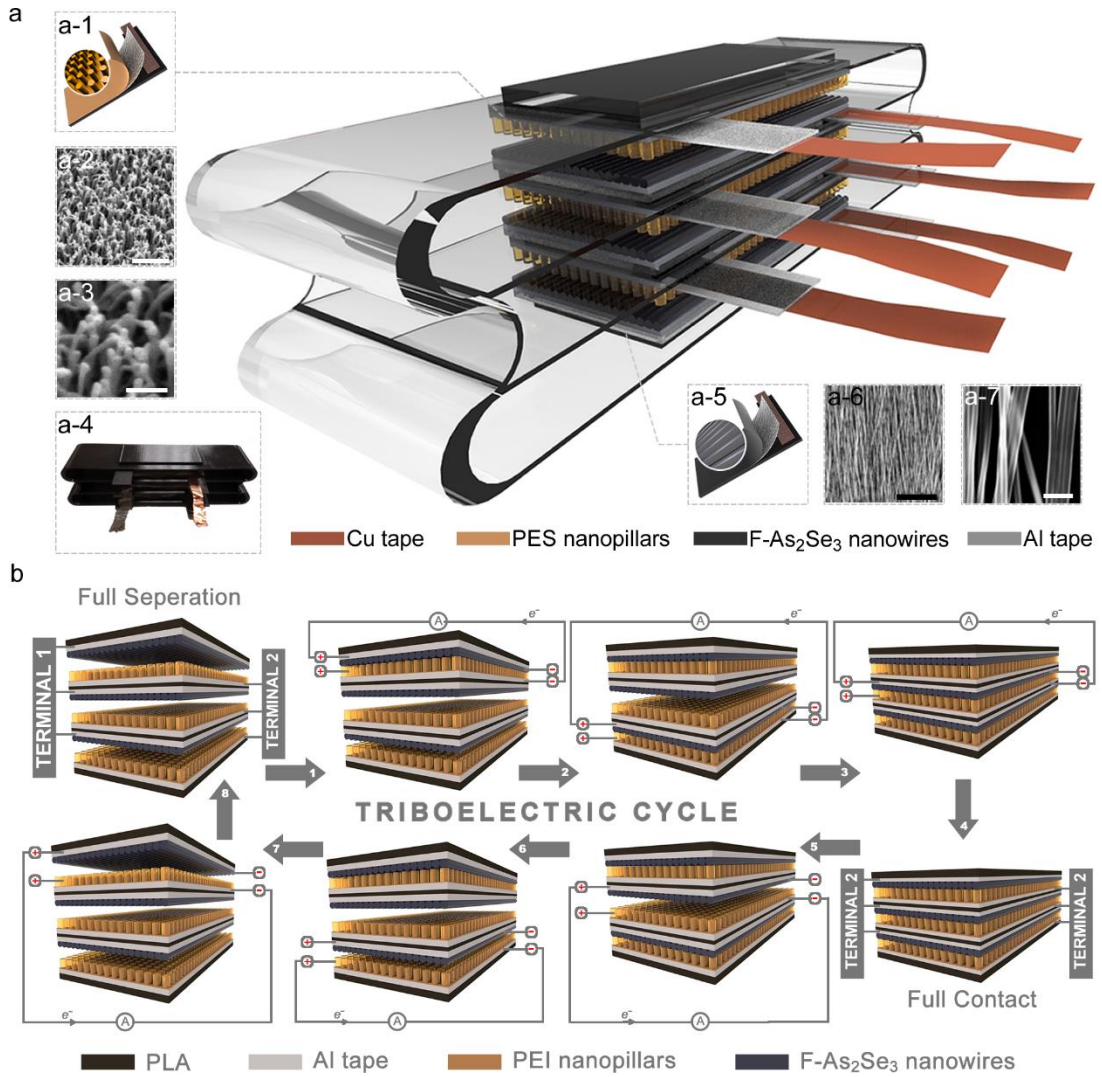


Figure 5.1: Detailed images of chalcogenide based 3D printed MULTENG energy harvesting device and its layers. a) An illustration of 3D printed MULTENG energy harvesting device which consists of 6 alternating polymer and chalcogenide layers. a-1) Representation of layers which consist of PEI nanopillars. a-2) SEM image of PEI nanopillars. Scale bar is 1 μm . a-3) Higher magnification SEM image of PES nanopillars. Scale bar is 250 nm. a-4) Photograph of MULTENG device fabricated with 3D printing method. a-5) Representation of layers, which consist of F-As₂Se₃ core-shell nanostructure. a-6) SEM image of F-As₂Se₃ core-shell nanostructures. Scale bar is 25 μm . a-7) Higher magnification SEM image of F-As₂Se₃ core-shell nanostructures. Scale bar is 500 nm. b) Working mechanism of the MULTENG that utilizes the contact mode triboelectrification with external electronic flow in short circuit condition. 1. Motion of MULTENG from original state to charge generation state. Sharing charges & Positive peak current generation (current flow) in unit 1 of MULTENG. 2. Sharing charges & Positive peak current generation (current flow) in unit 3 of MULTENG. 3. Sharing charges & Positive peak current generation (current flow) in unit 2 of MULTENG. 4. Full Contact position. 5. Separation of layers and sharing charges & Positive peak current generation (current flow) in unit 2 of MULTENG. 6. Separation of layers and sharing charges & Positive peak current generation (current flow) in unit 3 of MULTENG. 7. Separation of layers and sharing charges & Positive peak current generation (current flow) in unit 1 of MULTENG. 8. Full separation position.

Our device can be stimulated by both motion and acoustic waves at different frequencies. Combination of fluorinated As_2Se_3 kilometer long core-shell nanostructures, which are produced using iterative fiber drawing technique, with PEI nanopillars, which are produced by template based method, for contact mode TENG in a multi-layer fashion resulted in maximum 1.23 mW DC and 0.51 W peak power output which can power parallel connected 38 LEDs simultaneously. Our chalcogenide based triboelectric generator has maximum 396 V and 1.6 mA peak to peak output voltage and current, respectively. In addition, a finite element model is developed to explain contact electrification between core-shell nanostructures and nanopillars using COMSOL Multiphysics. A perfect match between analytically calculated open circuit voltage and open circuit voltage measurement for a single layer generator was presented.

5.2. Triboelectric Materials and Charge Measurement

To enhance the performance of triboelectric devices, there are two important parameters which play a major role to select material combinations; surface properties and triboelectric polarity [102]. Since surface properties can be modified using various techniques, triboelectric polarity is the most important inherent parameter that need to be considered.

5.2.1. Initial Measurement Setup for Material Selection

We analyzed the triboelectric response of many materials by measuring open circuit voltage (OCV) and short circuit currents (SCC) from 1 cm x 2 cm samples. Measurement setup and samples are illustrated in Figure 5.2a-c. Measurements were conducted under same conditions (3 gr load and at 20 Hz tapping frequency) for all samples.

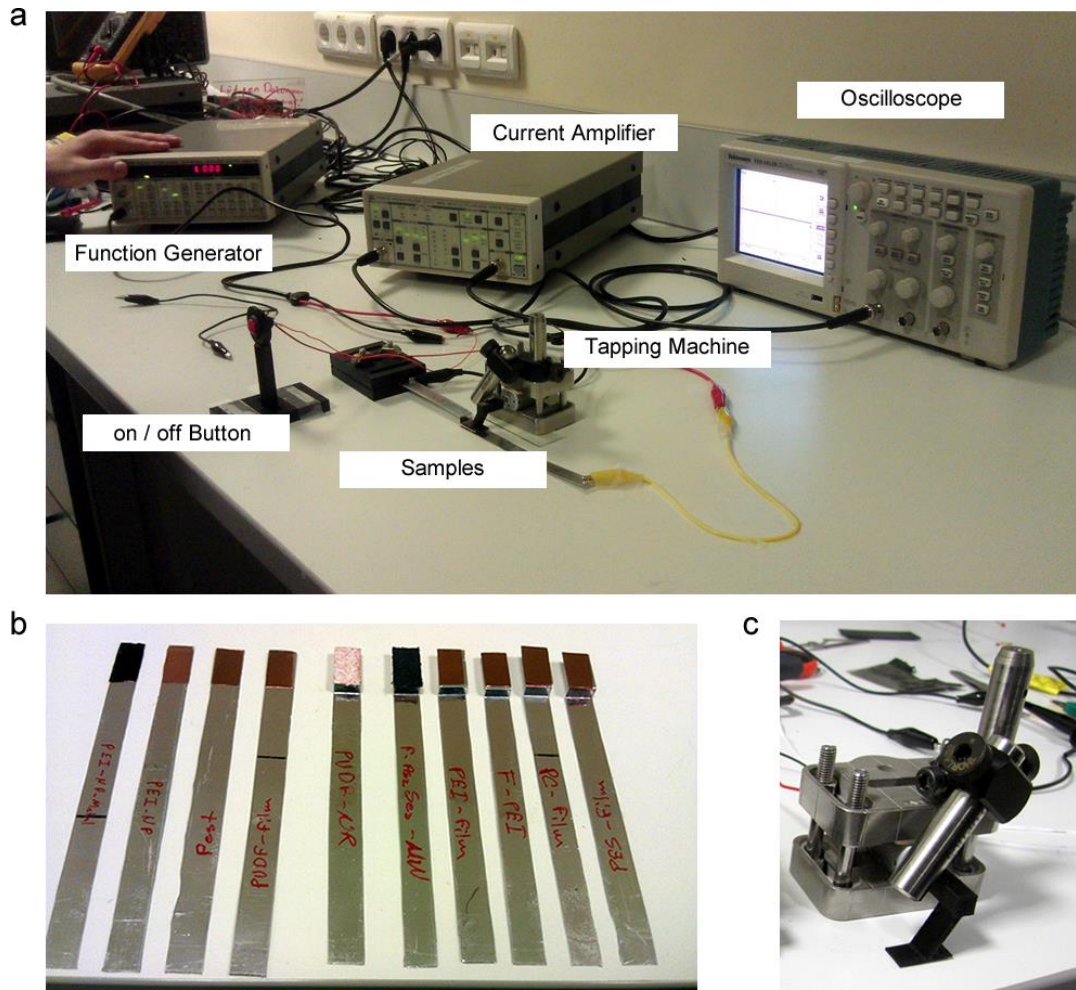


Figure 5.2: Initial measurement setup in order to obtain the best material couple to obtain highest output values. b) Image of the samples that were investigated for material selection measurements. c) Tapping device with a 5V DC motor, which gives the mechanical power in order to achieve voltage and current characteristics.

Since the triboelectric effect is not well known and the triboelectric series are not perfectly and fully characterized, we combined different material sets, which are promising for energy harvesting applications. Following materials were combined : Carbon loaded polyethylene (CPE), polycarbonate (PC), polyester (PEST), polyetherimide (PEI), polydimethylsiloxane (PDMS), polyethersulfone (PES), poly(vinylidene fluoride) PVDF, fluorinated polyetherimide (F-PEI), fluorinated arsenic selenide (F-As₂Se₃), TEFLON (Table 5.2).

Table 5.2: List of dielectric materials in accordance with their triboelectric response as we tested in pairs.

Triboelectric Polarity	
	Carbon Loaded Polyethene (CPE)
	Polycarbonate (PC)
	Polyester (PEST)
	Polyetherimide (PEI)
	Polydimethylsiloxane (PDMS)
	Polyether Sulphone (PES)
	Polyvinylidene Fluoride (PVDF)
	Flourinated Polyetherimide (F-PEI)
	Flourinated Arsenic-Selenide (F-As ₂ Se ₃)
	Polytetrafluoroethylene (TEFLON)
	

5.2.2. Charge Measurements

We measured the surface charge of dielectric samples by Keithley Electrometer 6514 and custom made Faraday cage using the following protocol. We prepared 2x1 cm² equal size samples and grounded them at least for 5 minutes. We also grounded all equipment that needed to be used including tweezers, gloves, cables and etc. We made sure that samples were in constant conditions with no contact to any other substances. Next, we left samples on wooden (neutral) table for 1 minute. Therefore, samples regained their natural charges without touching any other charged material. Finally, we measured their surface charges 3 times to make sure if the results were reliable and we averaged the results. The averages for materials that have positive triboelectric series as follows: PEI has 4210 pC, PC has 3380 pC, CPE has 550 pC and As₂Se₃ has 100 pC. For materials that have negative triboelectric series, Teflon gives the maximum with -5300 pC charge, PDMS has -4770 pC, F-As₂Se₃ has -2820 pC. That drastic incensement in surface charge of As₂Se₃ nanostructures proves the effect of the fluorination. Polyester has -2700 pC and PVDF has -1670 pC charge.

5.2.3. Fluorine Content Dependence of Triboelectric Performance and Materials Selection

TEFLON present superior properties in terms of triboelectric properties. Unfortunately, it is not compatible with iterative fiber drawing process which is an exciting fabrication technique [24] that enables to produce kilometer-long, parallel oriented and polymer encapsulated nano-structures from variety of materials including As_2Se_3 [127] and some fluorine rich polymers such as PVDF [22]. In the fabrication, there are at least two materials with compatible properties take place, guard polymer jacket and core material.

Materials used in iterative fiber drawing process represent unique properties, e.g. low thermal expansion, low melting point (for core material), low glass transition temperature and no crystallinity. In case of that the core material is crystalline, the glass transition temperature of the covering polymer preform should be higher than the melting point of the core material. So that, the core material can melt in the preform and liquefied material takes shape of the fiber (nanowire) during the process [22], [24]. Unfortunately, TEFLON is a highly crystalline polymer with high melting temperature, which makes it incompatible with iterative fiber drawing process.

Unlike TEFLON, As_2Se_3 is perfectly compatible with iterative fiber drawing process because of its low glass transition temperature, easy process-ability and amorphous structure [127]. In addition, although arsenic is a toxic element, As_2Se_3 is an inert intermetallic material with no toxicity, which doesn't reflect any hazardous characteristics of arsenic and used in open cancer surgeries in fiber shape [121], [184]. Although, the voltage peaks obtained from bare As_2Se_3 core-shell nanostructures were insignificant, the performance of the core-shell nanostructures were enhanced close that of TEFLON's after core-shell nanostructures were coated with fluorine monolayer. As a result of our experiments, we concluded that the materials with higher fluorine content tend to generate more triboelectric charges.

5.3. Working Principle of Multi-layered Triboelectric Nanogenerator

Triboelectric effect is a surface contact and separation phenomenon and increasing surface area also increases the device performance. In addition to increase total surface area by using nano-scale materials, using multi-layers is also important to multiple the total converted energy. Working principle of MULTENG device which consists of 6 alternating layers was illustrated in Figure 5.1b. We investigated the synchronism of the three units of MULTENG and voltage response of MULTENG at different frequencies (Figure 5.3). To explain the working mechanism of MULTENG, we recorded video of a spare MULTENG during operation (tapping) using a high frame rate (HFR) camera. In addition, we designed a finite element simulation of MULTENG to confirm HFR video results. Before examination of the working mechanism of MULTENG, we should recall that MULTENG has three units which consists of six layers making contact and separation in pairs (Unit 1 consists of layer 1 and 2, Unit 2 consists of layer 3 and 4, unit 2 consists of layer 5 and 6). The force for making contact between layers of the MULTENG was applied through the top and the MULTENG was fixed from the bottom. MULTENG was started to squeeze when triggering force was applied. In the early stage of its motion, distances between layers were started to decrease in unit 1 and 3 and slightly increase in unit 2. This is because of the shape of the side connections of three units were designed different. The curvatures in convex connections of unit 1 and 3 contracted and the curvature in concave connection of unit 2 expanded by applied force. Therefore, layers of unit 1 and 3 approaches each other whereas layers of unit 2 move apart from each other.

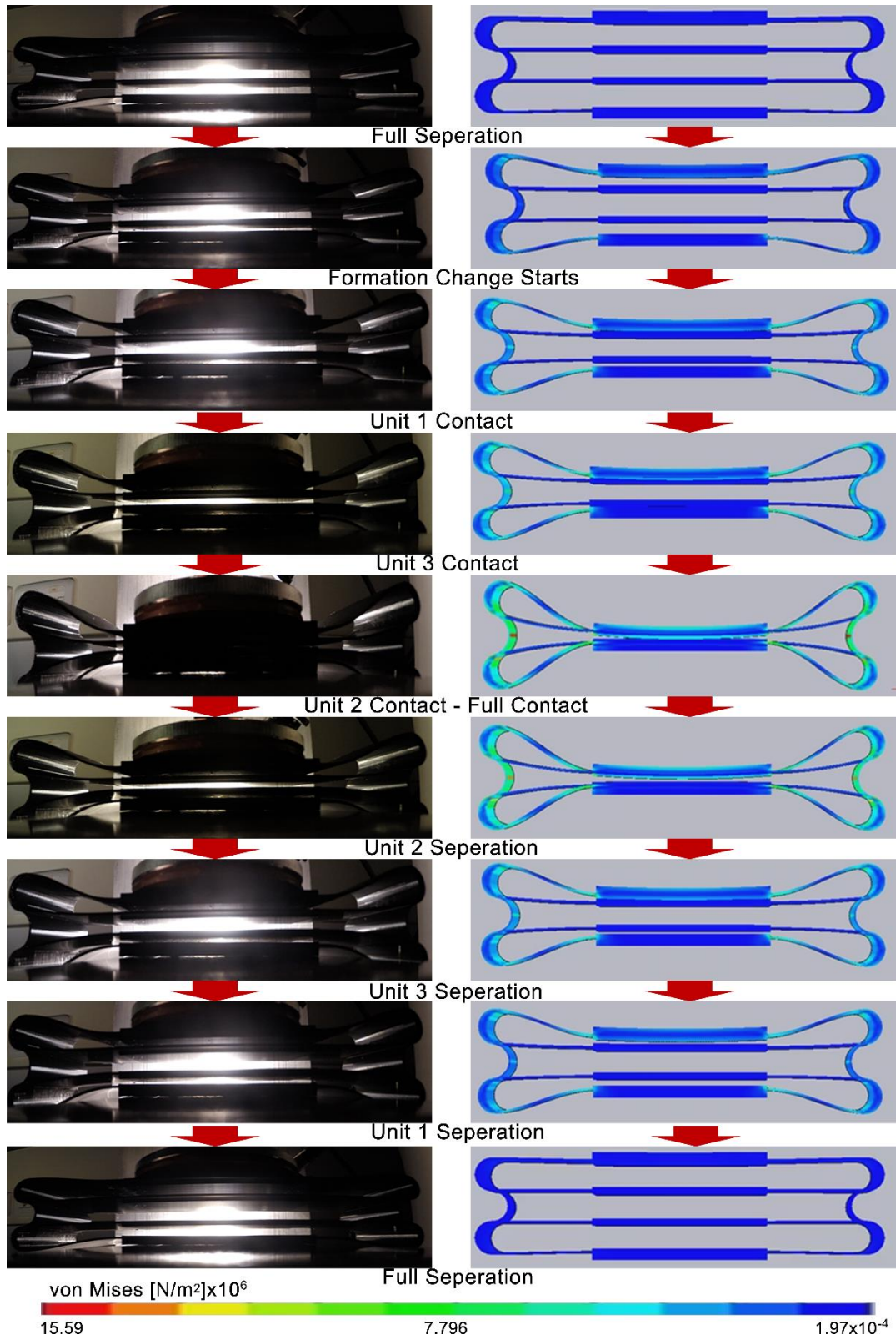


Figure 5.3: Left column: Contact and separation of MULTENG under tapping force. Right column: finite element model of mechanical response of MULTENG which perfectly matches with real behavior of MULTENG.

According to simulation and HFR recordings, motion of three units were at different speeds and this was observed as unit 1 to make contact firstly while unit 3 was slightly apart and unit 2 was completely separated. Following to unit 1, layers of unit 3 was brought in contact position by further pressing on top of the MULTENG. In the last stage, after layers of unit 1 and 3 was made contact, they transmit to force to unit 2 and thus, layers of unit 2 becomes in contact position. When applied force was released, layers of units were separated vice versa with making contact sequence. Firstly, layers of unit 2 separated, secondly, layers of unit 3 separated and lastly, layers of unit 1 separated.

5.4. Device Fabrication

Several techniques was used such as, 3D printing technique, fiber drawing, wet chemistry techniques and template infiltration technique for the fabrication of different layers and units of MULTENG.

5.4.1. 3D Printing

Considering the fact that a MULTENG should be durable against high cyclic motions and each layer should perform perfect contact and separation, we design a MULTENG with 175 mm in length, 50 mm in width and 49 mm in thickness as shown in Figure 5.1a. A detailed technical drawing of our device is given in Figure 5.4a-f. Polylacticacid (PLA) were used as 3D printing material because it has low density, high flexibility and low melting temperature. As shown in Figure 5.4a and Figure 5.4d, there are 1 mm thick four PLA layers connected to each other with three half circular loops which provide a good restore mechanism and flexibility. There are thicker rectangular (75 mm in length and 35 mm in width) rigid regions in the middle of these layers which facilitate to make a better contact between layers during triboelectric cycle. In addition to main body, 6 PLA thick layers (80 mm in length and 40 mm in width) were printed (Figure 5.4e) as a holder for Al electrodes, As₂Se₃ core-shell nanostructures and PEI nanopillars. 27 mm long and 500 μ m thick tails were extended on PLA holders which render the Cu tape contacts to be durable under high cyclic motions.

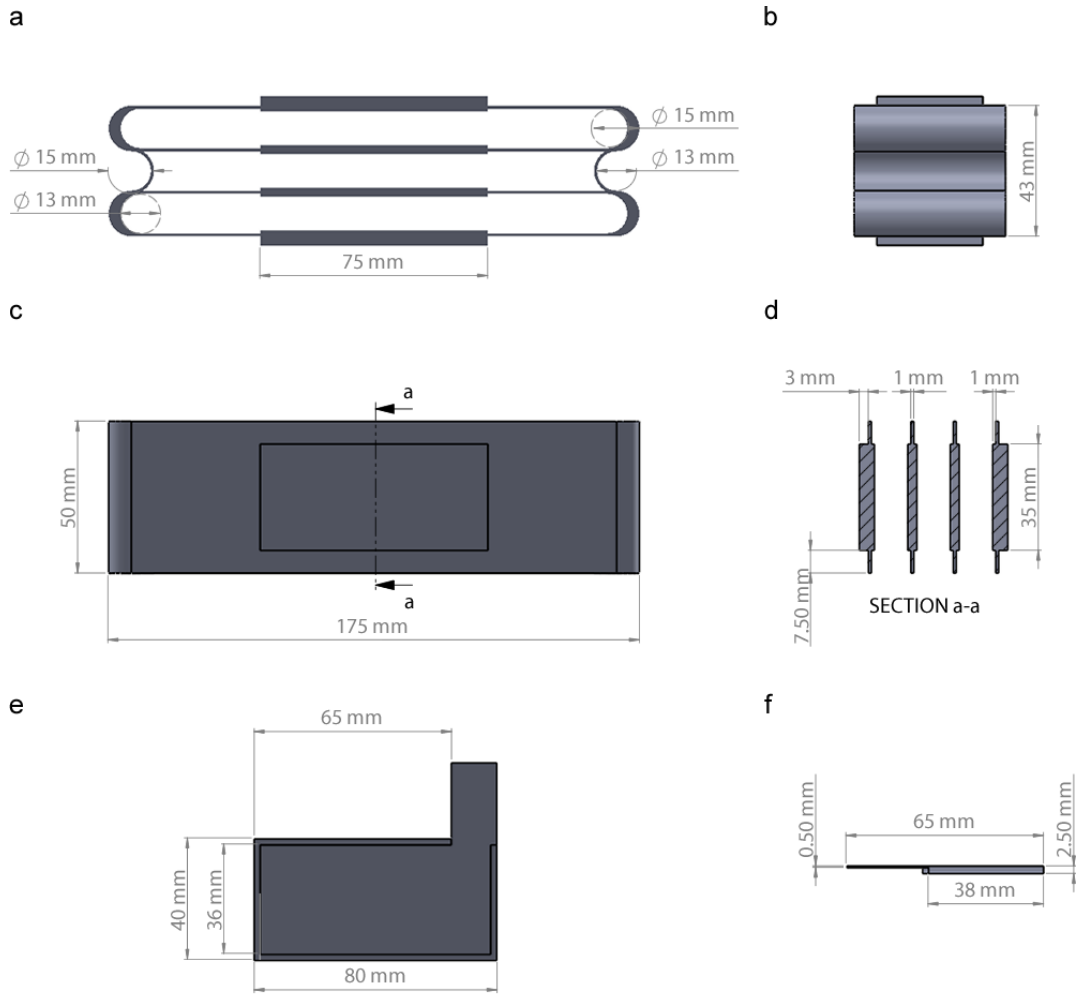


Figure 5.4: Detailed sketches and dimensions of MULTENG. a) Cross section of multi layered structure. b) Side view, c) and top view of the MULTENG. d) Cross section of layers of MULTENG. e) Bottom view, f) and side view of layers of MULTENG.

In the assembling process, Cu tapes (10 mm in width, 50 μ m in thickness) were attached on PLA holder surface along the width of holders and extended through flexible tails, 50 μ m thick double sided Al conductive tapes (40 mm by 80 mm) were located on holders in contact with Cu tapes in all 6 holders. Three of the holders with Al electrodes were covered with PEI nanopillars (100 nm in diameter) (Figure 5.5a). F-As₂Se₃ core-shell nanostructures (180 nm in diameter) were dispersed on the last 3 of the holders with Al electrodes (Figure 5.5b).

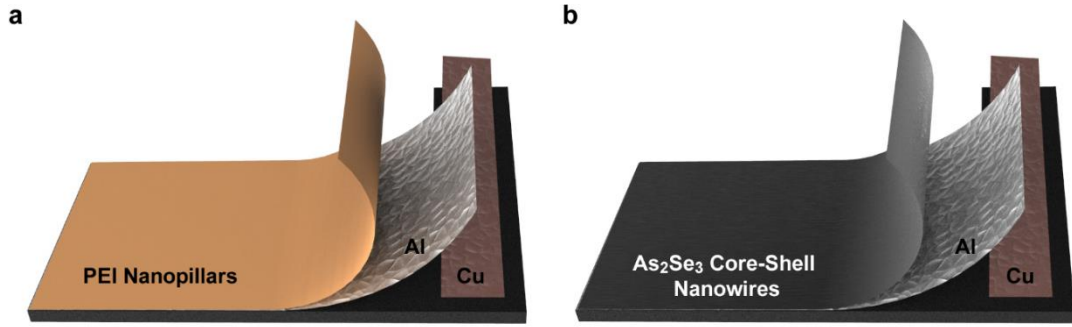


Figure 5.5: Detailed representation of a) PEI nanopillar decorated and b) As_2Se_3 nanostructure transferred films. Bottom of the PEI film was coated with Aluminum (Al) using thermal evaporation while As_2Se_3 nanostructures were directly deposited on the Al tape. Copper (Cu) tapes were attached to both of the film in order to provide conductivity.

Finally, PLA holders with nanostructures on top of them were attached to the main body. To our knowledge, this is the first study showing that a chalcogenide material was used for constructing a triboelectric device.

5.4.2. Nanopillar Fabrication using Melt-infiltration Method

In the fabrication process of nanopillar decorated PEI films, melt-infiltration method [185], [186] was used (Figure 5.6a-c). Here, dissolved PEI behaves as an infiltration phase and anodized aluminum oxide (AAO) membrane behaves as a template under the base of melt-infiltration.

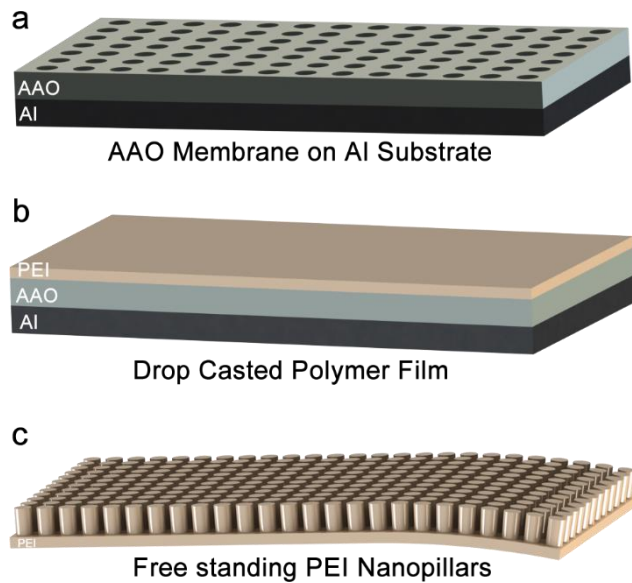


Figure 5.6: Fabrication process of PEI nanopillars. a) AAO membrane is used as supported on its aluminum (Al) substrate. b) Dissolved PEI film is drop casted on the AAO template. c) Polymeric film is peeled off from the template after solvent evaporation process.

AAO template was coated with 1% (v/v) 1H,1H,2H,2H-perfluorodecyl-trichloro silane (FOTS) in n-heptane solution prior to use [185]. Fluorination prevents the polymer adherence into the membrane pores. In this process, AAO membrane, which was grown on the aluminum sheet, was directly used as supported on its aluminum substrate. Template has 5 x 10 cm dimensions with 100 nm pore diameter and 2 μm pore depth. PEI was dissolved in dichloromethane (DCM) at a concentration of 0.3 % (w/v). PEI solution was drop casted on the AAO template and left for solvent evaporation. After the evaporation step, PEI film was peeled off from the surface. Therefore, 4 cm by 8 cm PEI nanopillar films were obtained for the fabrication of MULTENG.

5.4.3. Fabrication of Fluorinated Chalcogenide Core-Shell Structures

F-As₂Se₃ core-shell nanostructures were produced using iterative thermal size reduction technique based on fiber drawing. Initially, we produced a 10 cm in length and 10 mm in diameter As₂Se₃ tube using sealed ampule method (Figure 5.7).

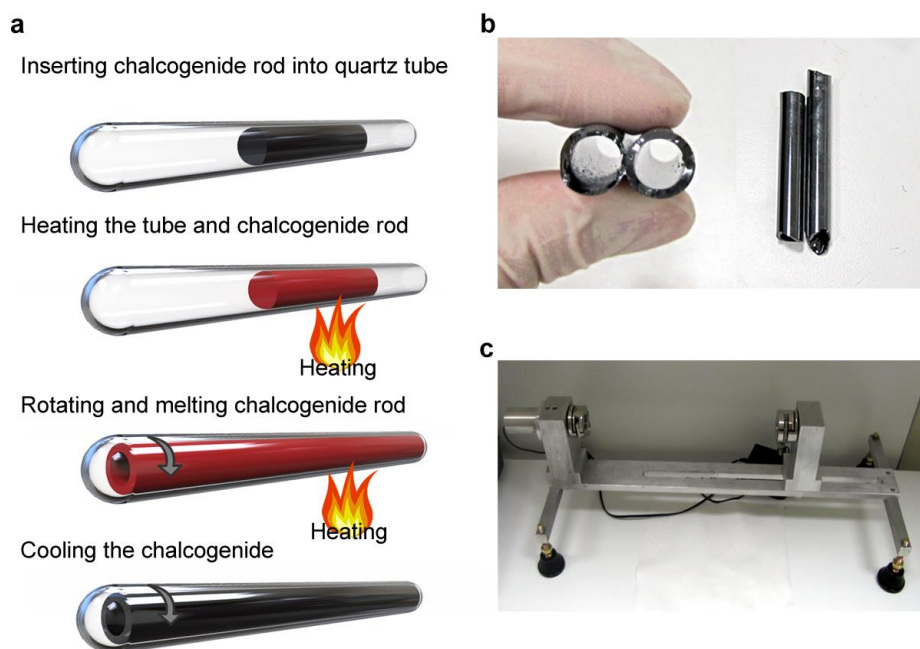


Figure 5.7: a) As₂Se₃ rod was synthesized by sealed quartz ampoule method and then the material is inserted in a rotating machine. It transformed from rod to the tube shape by using centrifugal force. b) As₂Se₃ tubes after extracting from quartz ampoule by cracking and uniformly etching the quartz ampoule. c) The photograph of rotating machine.

In this method, elements were inserted in a quartz tube and vacuum sealed at elevated temperatures to remove all impurities and oxygen as well as the moisture. The mixture in the tube was melted in a rocking oven (Figure 5.8) at 750 °C. After overnight rocking of the samples, the molten material was quenched in tap water for increasing the glass formation by over-cooling the material. Before quenching, molten As_2Se_3 was centrifuged for the formation of a 10 cm long hollow core structure with 10 mm outer diameter and 6 mm inner diameter. To absorb the impact during the tapping on the MULTENG, we filled inside of the tube with a PES rod which is mechanically extracted out from a PES preform.

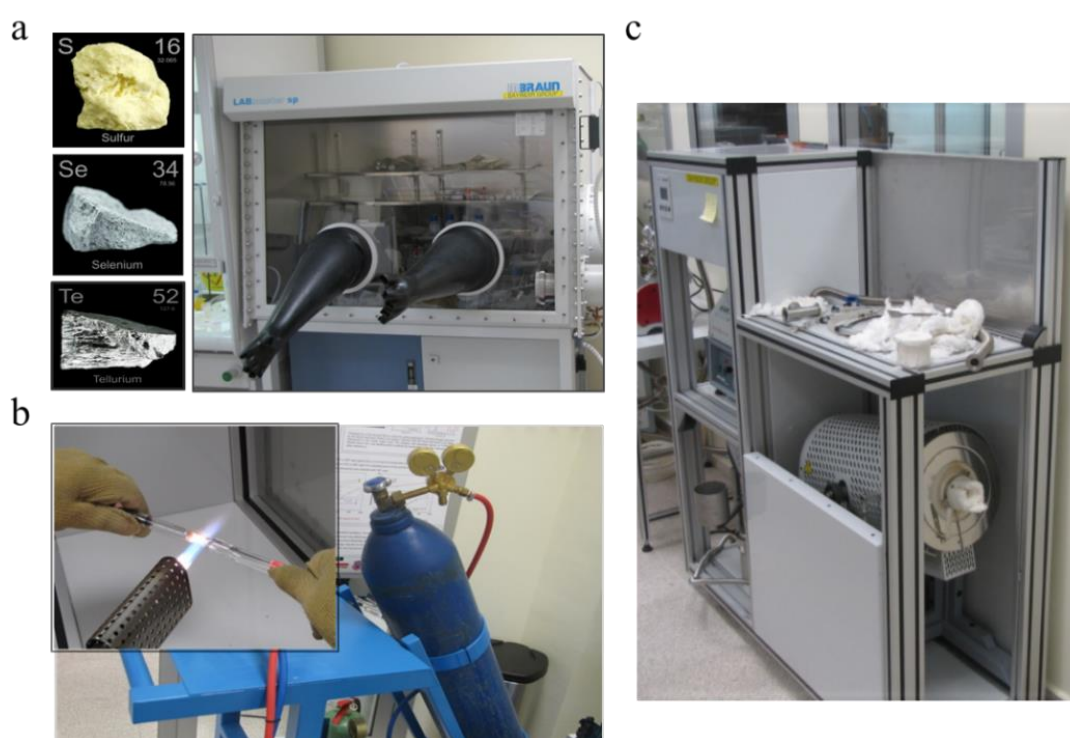


Figure 5.8: Synthesis of chalcogenide glass tubes. Three steps process (a) collection of materials, (b) material purification and sealing, (c) rocking and homogenization.

After three steps of iterative fiber drawing (Figure 5.9), we obtained 100 nm to 1 μm thick core-shell nanostructures. Detailed SEM images of the nanowires were shown in Figure 5.10. Finally, nanostructures were coated with self-assembled fluorine monolayer. Fluorination process was repeated as performed in the template coating step. Then, nanostructures were washed with n-heptane and dried at 100 °C in a vacuum oven.

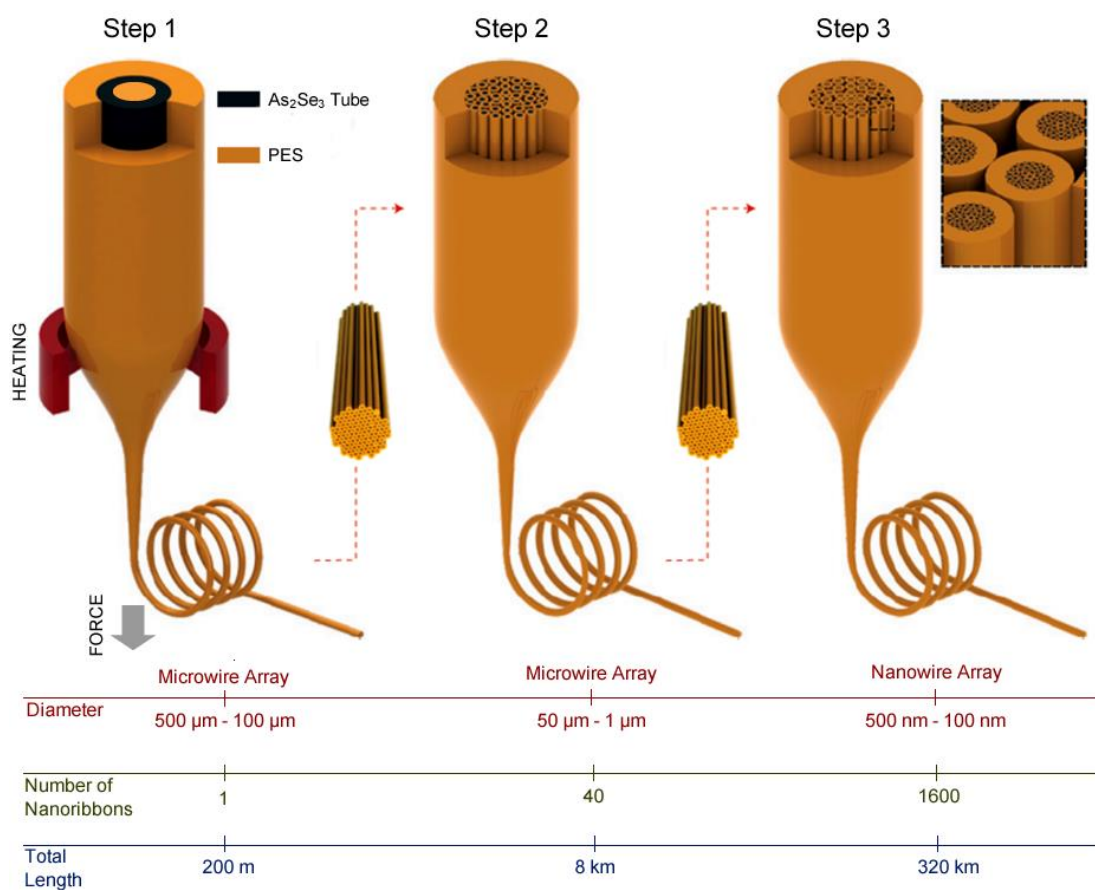


Figure 5.9: A model shows iterative size reduction technique. Macroscopic core of the preform shrinks into microscopic fibers in the first step size reduction process. In the following size reduction steps, size of the cores decreases down to nanoscale and the total length increases up to kilometer range. Iterative drawing occurs by putting first step fibers into the core of the second step preform, putting second step fibers into third step and drawing consecutively.

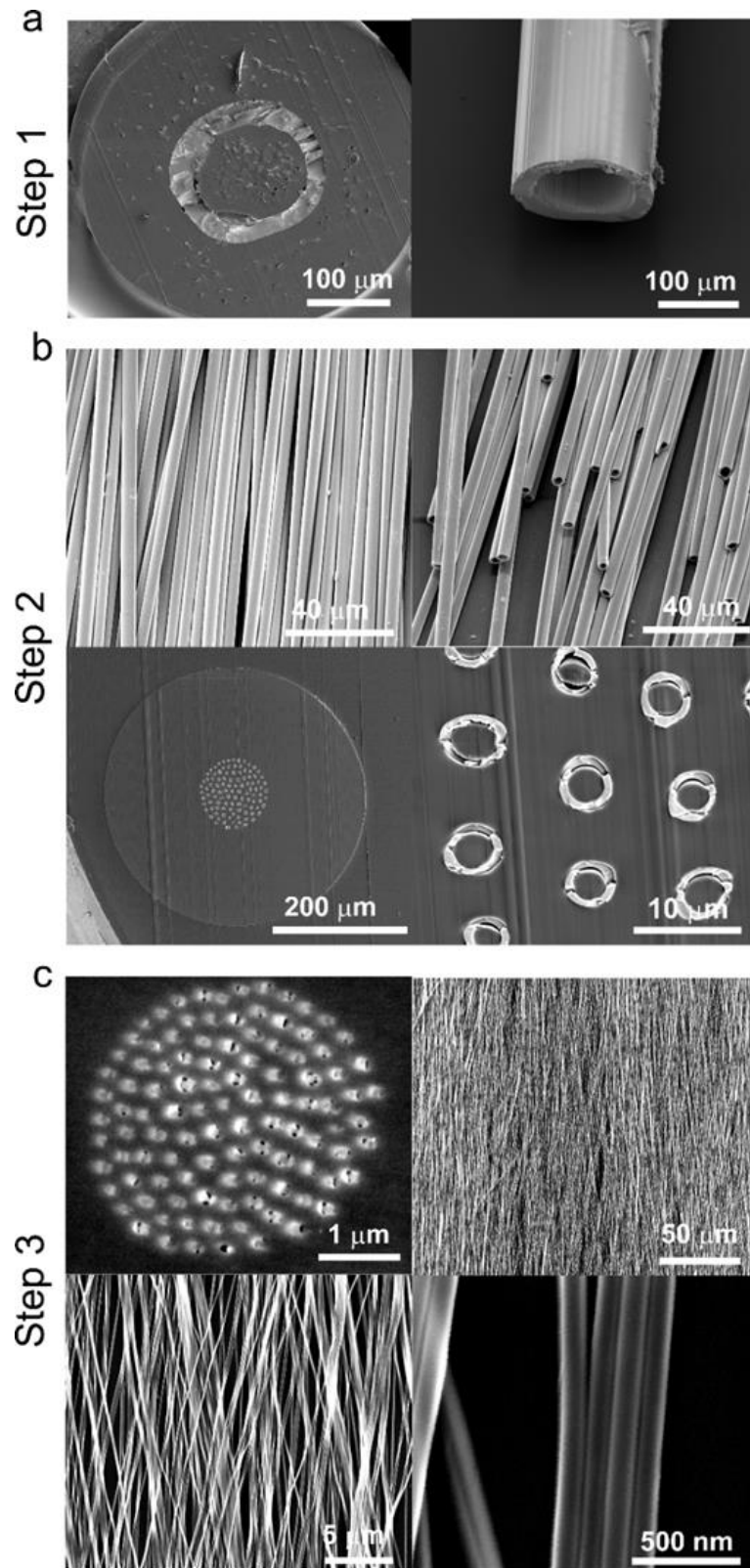


Figure 5.10: Cross-sectional and longitudinal SEM images a) first step, b) second step, c) third step PES-As₂Se₃ core-shell structures.

5.4.4. Surface Modification by Fluorine Ligands

As_2Se_3 nanostructures were immersed into the 1% (v/v) 1H,1H,2H,2H-perfluorodecyl-trichloro silane (FDTS) in n-heptane solution for 3 minute after etching their polymer cladding using dichloromethane (DCM). Then, the nanostructures were washed with n-heptane solvent to remove unbounded ligands and vacuumed at 100 °C for 1 h (Figure 5.11).

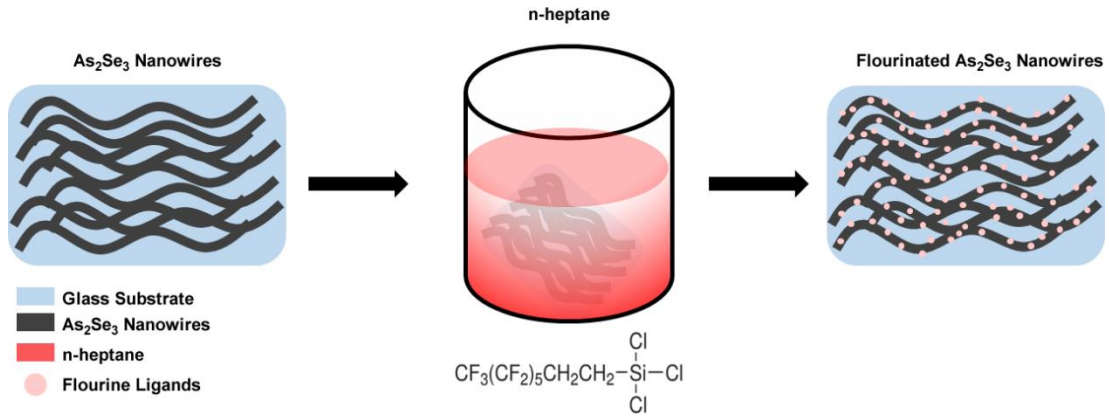


Figure 5.11: Fluorination process of the As_2Se_3 nanostructures. As_2Se_3 nanostructures are immersed into the FDTS solution. Finally, nanostructures are washed to remove free FDTS ligands and are produced as monolayer protected.

5.5. Device Testing Under Versatile Conditions and Theoretical Device Modelling

MULTENG can be operated using a single hand. Performance of MULTENG was characterized under different conditions. OCV and SCC of the device were recorded using various activation sources such as mechanical tapping, car vibration and sound. Peak power, power density and device efficiency were calculated. In addition, DC power was also calculated which represent the constant power supply capacity of MULTENG as a function of triboelectric device performance and triboelectric cycle frequency.

Working mechanism of MULTENG isn't similar for mechanical tapping, sound and car vibration. In mechanical tapping measurements, units of MULTENG has an exact sequence of making contact and separation. In tapping measurements, MULTENG was fixed from the bottom and the force applied from the top. In first stage, unit 1 collapsed and made contact and then unit 3 at the bottom made contact in

stage 2. Finally, unit 2 in the middle made contact in stage 3. This sequence was reserved in reverse manner in separation phenomenon. In case of sound measurements, a static force applied from the sides of the MULTENG and layers took a close position to each other. However, MULTENG wasn't fixed from the bottom or top. It was suspended on sound source by fixtures from the sides. Thus, we were able to measure response of MULTENG by obtaining freely moving suspended layers. Finally, in case of car vibration measurements, MULTENG was fixed from the bottom and a weight located on the top of the MULTENG. The applied weight collapsed the units of MULTENG and initial position set as contact. Since the weight was positioned perpendicular in length to MULTENG in width, vibrations and jumps have made angular motions in layers of MULTENG. Thus, MULTENG can make angular contact and separation simultaneously in different layers of units.

5.5.1. Energy Harvesting by Tapping

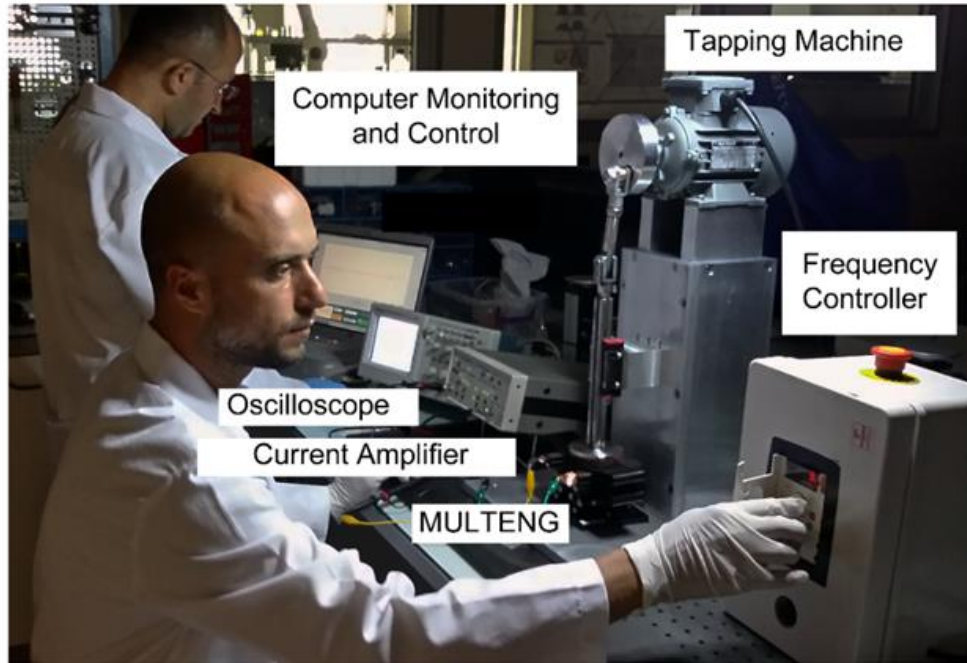
OCV and SCC of MULTENG were measured under constant force and tapping frequencies at 1 Hz, 2.5 Hz, 5 Hz and 7.5 Hz using a custom made tapping machine with a measurement setup as shown in Figure 5.12a-c. The tapping machine consists of a 10 N.m motor with a maximum speed of 1360 rpm. The base part of the device is stable and the height of the base is manually adjustable. Top part is movable and its frequency and applied load can be adjusted. The power of the motor was calculated using following formula:

$$P_w = T \cdot f \cdot \eta \cdot 6.28 \quad (5.1)$$

where P_w is the output power (W), T is the torque (N.m), f is the frequency (Hz) and η is the efficiency. As seen in Figure 5.13a, the OCV increases with increasing frequency. Variations in OCV with respect to frequency were basically because of that input power which triggers to MULTENG increases with increasing frequency in our system (Figure 5.14). However, same increasing trend with respect to increasing tapping frequency was not conserved for SCC values in Figure 5.13b. Maximum peak to peak OCV was measured as 396 V at 7.5 Hz and maximum peak to peak SCC was measured as 1.62 mA at 2.5 Hz. As seen in Figure 5.1a and Figure 5.4, layers of

MULTENG is connected with half circular loops and each layer is long enough to preserve mechanical flexibility. The design resembling a spring in appearance. Actually, MULTENG base structure functions as a spring to separate layers after contact.

a



b

Voltage Measurement Setup



c

Current Measurement Setup

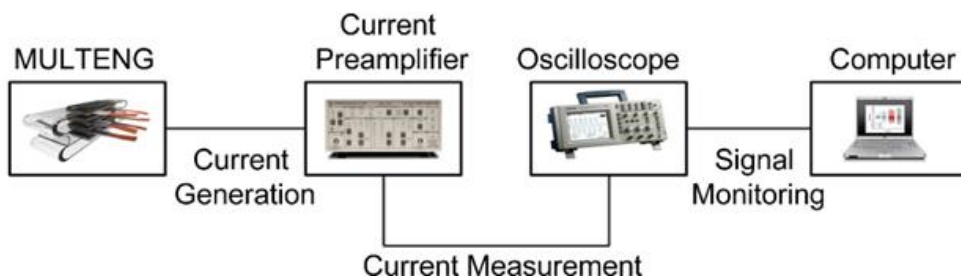


Figure 5.12: Measurement setup for tapping frequency dependent characterization of MULTENG. a) Experimental setup. b) Detailed representation of open circuit voltage measurement tools. c) Detailed representation of short circuit current measurement tools.

Following actions sequentially took place during the measurement: a force was applied from the top of MULTENG as tapping while MULTENG was fixed from the

bottom, layers were bended until they become in full contact position, and the force was released and layers regain the initial position. There was a certain time required for regaining position. Maximum efficiency was obtained when tapping frequency was close or same with the resonance of MULTENG. In the case of tapping frequency was higher than the resonance frequency of MULTENG, which means time delay between two sequential tapping was less than the required time for regaining the initial position of layers, there was no full separation between layers. This causes in decrease and fluctuation at higher frequencies.

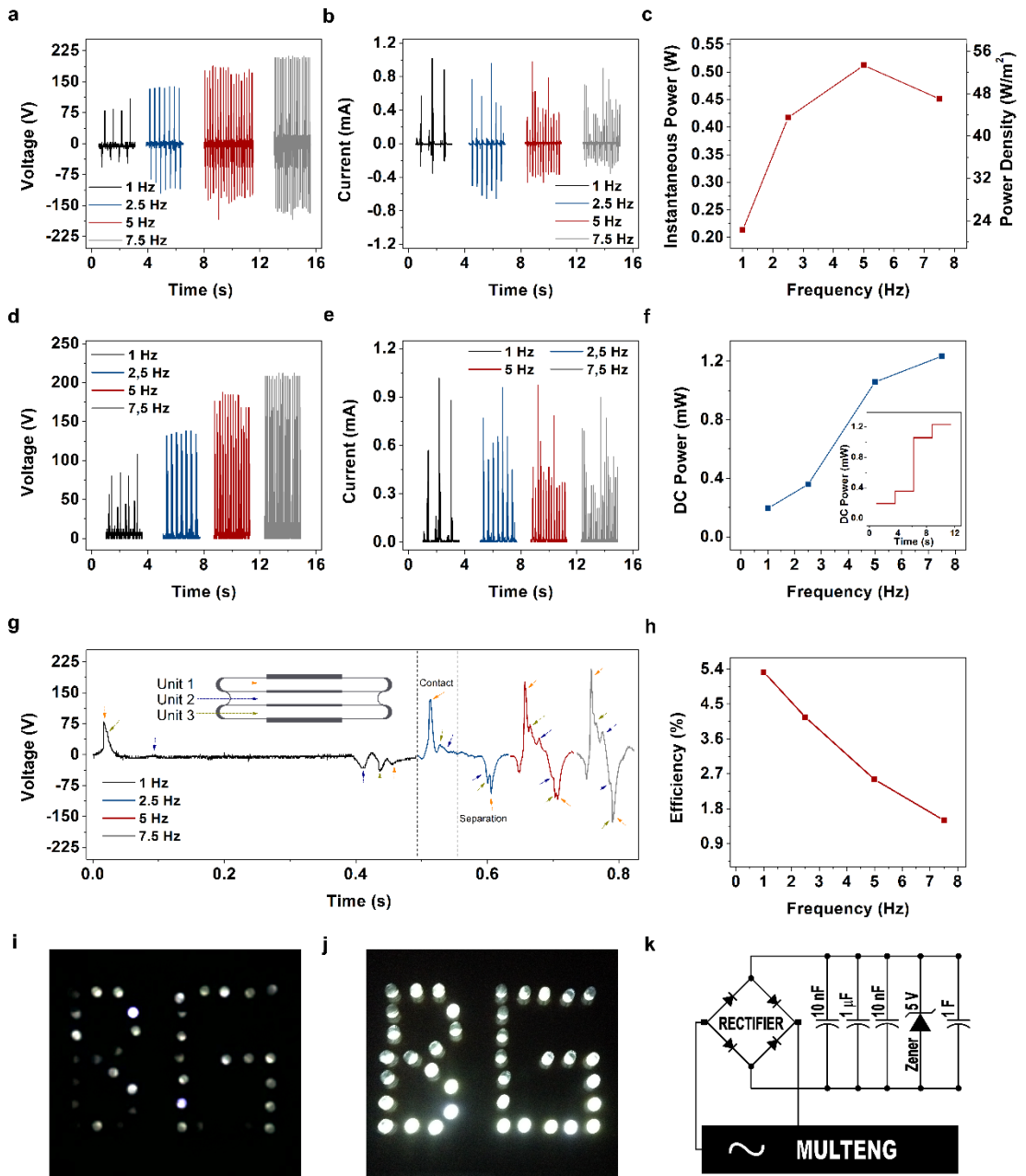


Figure 5.13: Open circuit characteristics and real-time performance of the MULTENG based on the tapping frequency. a) Frequency dependent open circuit voltage and b) short circuit current measurements. c) Frequency dependent instantaneous power and power density

measurements. Rectified d) open circuit voltage and e) short circuit current measurements. f) Frequency dependent DC power analysis. Inset shows the time dependent behavior. g) Detailed plot of single OCV peaks in different frequencies which shows obtained outputs with respect to contact and separation sequence of different units of MULTENG. Orange, blue and green arrows correspond to motion in unit 1, unit 2 and unit 3 respectively. h) Frequency dependent efficiency that was obtained from open and short circuit measurements. i) Captured image of 38 flashing LEDs powered by MULTENG. j) Image of 38 enlightened LEDs by the stored energy in the harvesting circuit. k) Schematic representation of the energy harvesting circuit.

Triboelectric effect is not a well understood, but some parts of the effect is perfectly proven in recent studies [91], [99]. Basically, when two dielectrics with different triboelectric polarity brought together, negatively charged surface becomes more negative and positively charged surface become more positive. At the end, the both negative and positive charges can be localized on the surface simultaneously and the surfaces become inhomogeneous. Discharging of these charges after separation of the surfaces is not in the same rate and homogeneity. This phenomenon was perfectly proven using state-of-the-art techniques including Kelvin Force Microscopy surface charge scanning technique [91], [99].

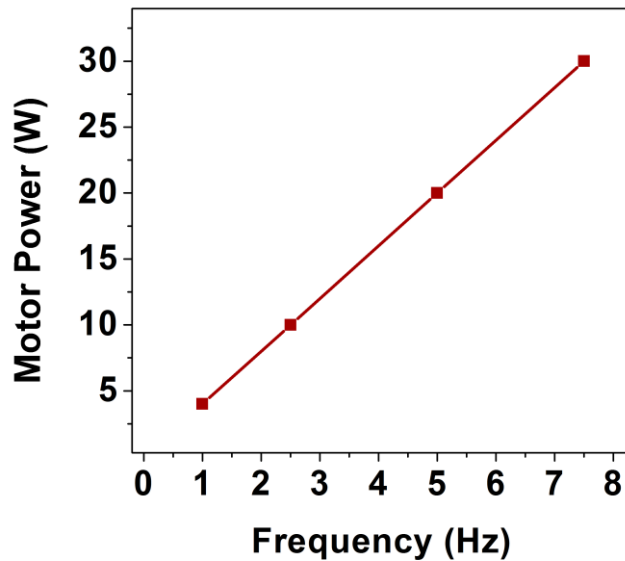


Figure 5.14: Linear relation between tapping frequency and tapping power of tapping machine.

Same phenomenon naturally occurs in our MULTENG layers and this causes fluctuations. As_2Se_3 layers were randomly dispersed on Al tape electrode, which means charging characteristics of different surface scopes can be much different due

to inhomogeneous distribution of nanostructures. Therefore, layers gain inhomogeneous charge distribution as a natural effect in each tapping. In addition, each tapping on MULTENG may move positions of As_2Se_3 nanostructures. This can also slightly effect the charge distribution, especially at high frequency experiments. Besides, Al tape electrodes become sticky at higher tapping frequencies because of some part of the mechanical motion was converted in heat and thus the Al tape electrodes were avoided the proper separation of layers. Therefore, highest instantaneous power and power density were obtained at 5 Hz as 0.51 W and 53.4 W/m^2 , respectively (Figure 5.13c). In addition, sticky part of the tape dramatically decreases the conductivity of the electrode and this influences SCC more than the OCV value. Indeed, we obtained higher conversion efficiency at lower frequency. MULTENG design is more suitable to operate at lower frequencies. Direct current (DC) power is highly used in electronics because billions of low power requiring devices are charged using DC power such as cell phones, music players, portable devices and etc. In power electronics, DC power is the constantly supplied power without any opposite sing polarity (fixed polarity). Output of MULTENG is similar to alternative current (AC) power with two polarity (negative and positive output) and at certain frequency which can be converted in DC power using transformers, rectifier bridges, and stabilizer capacitors. To calculate the DC power capacity of MULTENG, we firstly calculated rectified current and voltage as shown in Figure 5.13d-e and we characterized the change in the DC power with respect to frequency. Figure 5.13f represents DC power that was obtained from MULTENG as a function of tapping frequency. Maximum DC power of 1.23 mW can be supplied *via* our MULTENG, when a constant excitation applied at 7.5 Hz frequency. Non-uniform appearance was observed in many output peaks. One of the reason was that three units of the MULTENG do not touch and separate simultaneously and that causes overlap of multiple output peaks and thus a non-uniform appearance. Contact and separation sequence of MULTENG units were observed in wider plots of OCV outputs in Figure 5.13g. Color coded arrows correspond to measured peaks from motion of different units of MULTENG. Electrical characterization results, HFR video results and simulation were perfectly matched. We represented detailed OCV and SCC single peak plots in Figure 5.15a-c, which clearly shows contact and separation period. As shown in Figure 5.1b, there are two terminals set by connecting the three electrodes for As_2Se_3 layer and the other three electrodes for nanopillar layers. Therefore, generated

charges from all layers pass through external circuit which was also connected to all electrodes in all units of MULTENG. This configuration of electrodes effects device performance in terms of output peak width and height. DC power, which shows the practicability of MULTENG in real applications, was increased because sequential contact and separation of multilayers increases the width of peaks. Heights of peaks corresponding different units of MULTENG weren't homogeneous. Apparently, height of the peaks were related to contact and separation sequences. Maximum peak always observed from unit 1 in contact and separation period. This because, induced charges on electrodes of unit 1 were distributed to external circuit and the electrodes of unit 2 and 3. That was decreased the charge induction performance of unit 2 and 3, which were came in contact before fully discharge of unit 1.

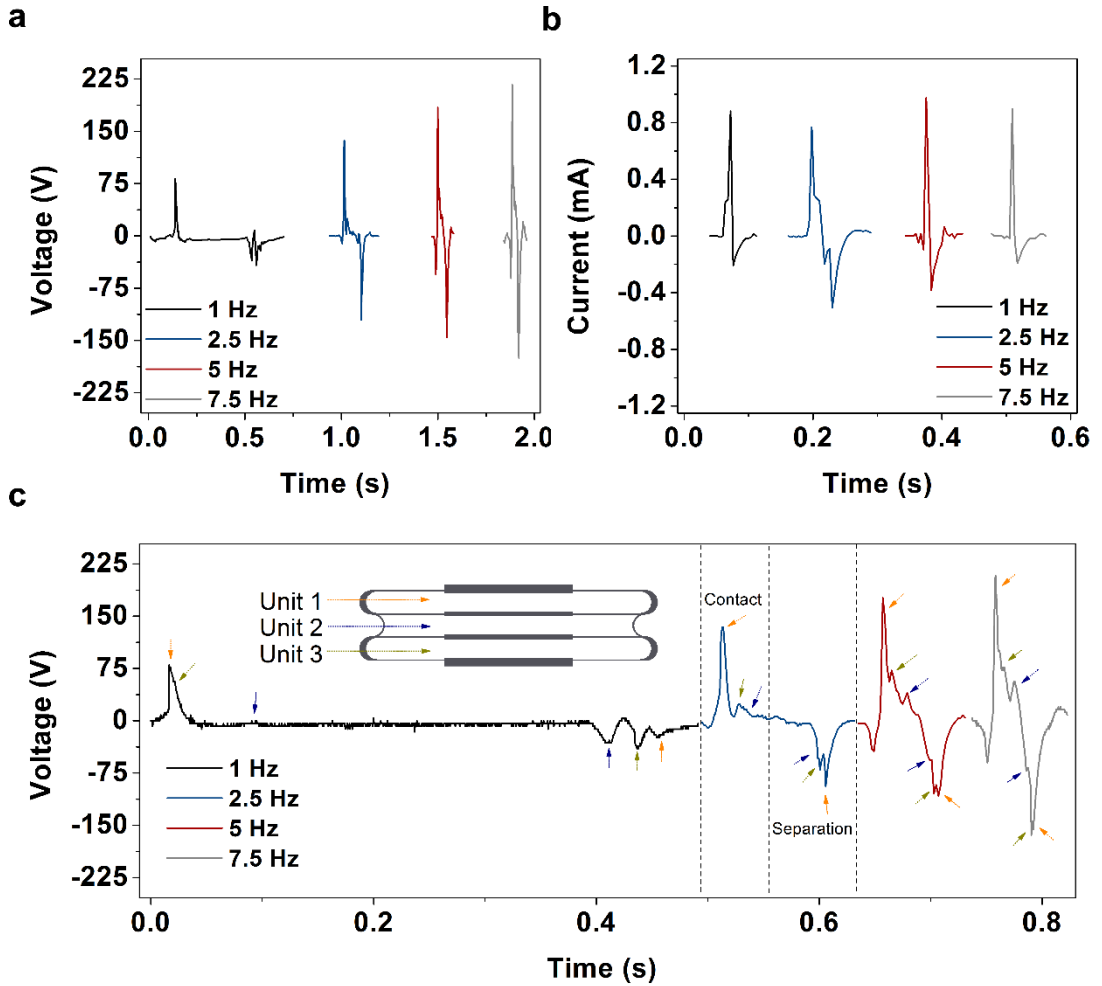


Figure 5.15: Single peak a) OCV and c) SCC plots at different frequencies. c) Expanded OCV representations which show the contact and separation of different units of MULTENG.

Obtaining high output peaks from all units of MULTENG with same peak height could be possible separately and instantaneously discharging all units of MULTENG

[187]. However MULTENG has many conflict with such a discharging geometry. Considering the motor power as an input energy, the highest energy conversion efficiency was obtained at 1 Hz tapping frequency with 5.3 % and efficiency was decreased with increasing tapping frequencies (Figure 5.13h). MULTENG can directly power up 38 LEDs connected in parallel (Figure 5.13i and Video 4). Longer time scale SCC plots were given in Figure 5.16 to show the stability of our device.

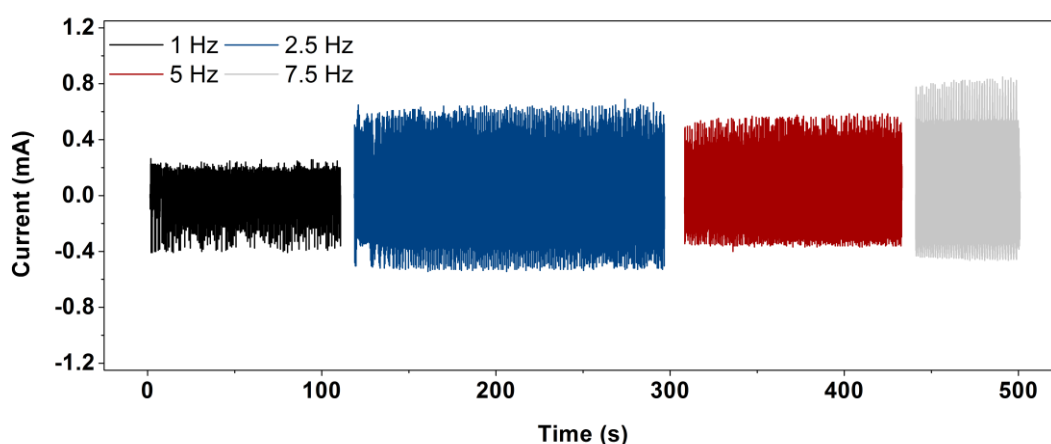


Figure 5.16: Stability test for current response of MULTENG with random time scales and various frequency.

MULTENG was connected to a custom built energy harvesting circuit to facilitate it as a DC power source and a higher intensity was observed from the same LEDs (Figure 5.13j) using the energy harvesting circuit. Instantaneously powered LEDs were observed with lower intensities when compared the intensities of LEDs powered *via* energy harvesting circuit. As long as the energy harvesting circuit supplies a DC power to LEDs, it was expected that LEDs to light constantly without any blinking. Energy harvesting circuit was shown in Figure 5.13k.

5.5.2. Numerical and Analytical Calculations

The mechanism of the charge generation in MULTENG can be explained as follows: once the surfaces of two layers come into contact, surface charge accumulation occurs. This leads to current flow between the two electrodes to compensate for the extra charges injected into them. At the full contact position, the negative charges on the surface of F-As₂Se₃ core-shell nanostructures were fully

compensated by the positive counterparts on the surface of PEI nanopillars. Here, the surface roughness on the two surfaces play a major role in maximizing the triboelectric charge generation. Once the separation of the two surfaces takes place, charge redistribution occurs as a result of charge imbalance inside the layers, this leads to electric current flow between the two terminals of the device opposite in polarity.

To develop a theoretical model and describe the electric characteristics of the device, we assume that the tribocharges were homogeneously distributed on the two surfaces with negligible decay. This assumption is based on the fact of very short time of contact/separate period during the operation of the device being smaller than typical charge decay time for dielectrics. Therefore, induced potential difference (V) generated between two layers is:

$$V = E \cdot d \quad (5.2)$$

We developed a finite element simulation model to visualize the change in the induced potential difference in MULTENG structure (Figure 5.17a-h). In the simulation, each layer of PEI and F-As₂Se₃ was defined as thin films and surface potential values are chosen according to their position in triboelectric series. Initially, outer layers were in contact with each other and they neutralize each other (Figure 5.17b-e). The middle layers become in contact when layers were pushed further (Figure 5.17f-h) as it is illustrated in Figure 5.1b. Finally, all layers were neutralized as they come in full contact position. Releasing the layers starts the same cycle.

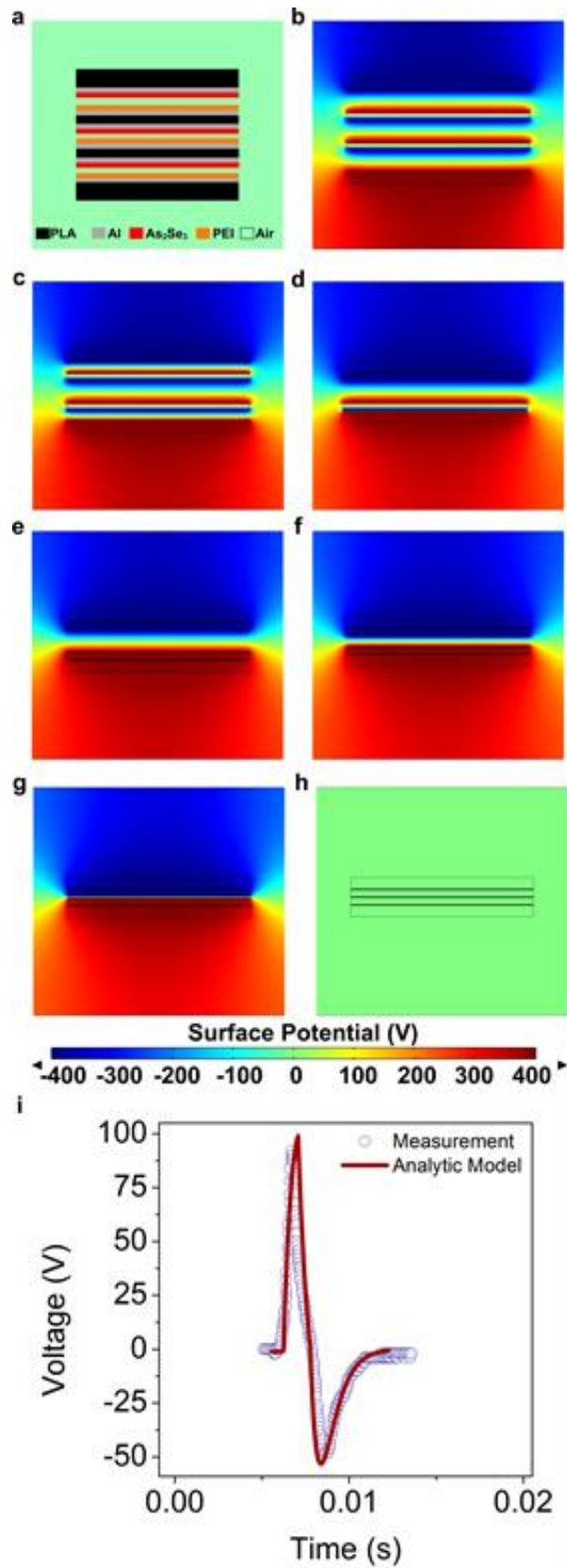


Figure 5.17: Finite element simulation results to understand the change in the induced potential in accordance with the motion of the layers. a) Representation of simulation setup. b-e) Initially, outer layers come in contact (first unit 1 and then unit 3) and surface potential of outer layers are balanced. f-h) All layers are neutralized when MULTENG is in full contact

by applying further pressure to make the inner layers come in contact as well. i) Comparison of between measurement from a single layer generator and our analytical model which simulates the open circuit voltage generation.

Potential difference for a two layer TENG can be calculated using the following formula:

$$V = E_{FAS}d_{FAS} + E_{PEI}d_{PEI} + E_{air}d_{air} \quad (5.3)$$

where E_{FAS} , E_{PEI} and E_{air} are electric field induced in F-As₂Se₃, PEI and air respectively. d_{FAS} , d_{PEI} and d_{air} are the thicknesses of the respective layers. Recently developed theoretical models assume that the amount of the charge (Q) with opposite signs on the electrodes and generated potential with relative displacement ($z(t)$) of the surfaces are related [188]. Considering our device design, potential difference will only evolve in the direction perpendicular to the surfaces as follows:

$$V = -\frac{Q \cdot d_{FAS}}{A \varepsilon_0 \varepsilon_{FAS}} - \frac{Q \cdot d_{PEI}}{A \varepsilon_0 \varepsilon_{PEI}} - \frac{Q \cdot z(t)}{A \varepsilon_0} + \frac{\sigma \cdot z(t)}{\varepsilon_0} \quad (5.4)$$

where ε_{FAS} and ε_{PEI} are the relative permittivity of F-As₂Se₃ and PEI, respectively. ε_0 is the electrical permittivity of vacuum. A is the surface area of the device and σ is the charge density. We should note that charge transfer is considered zero ($Q = 0$) in the case of open circuit voltage. Time derivative of the transferred charge gives the short circuit current when the voltage is considered zero ($V = 0$).

We modeled open circuit voltage peak of two layer generator fabricated using F-As₂Se₃ nanostructures and PEI nanopillars and compared our model with experimental results. The model and the experiment perfectly matched as seen in Figure 5.17i. List of variables used in the model was given in Table 5.3 and detailed information about theoretical model was given in Figure 5.18.

Table 5.3: List of parameters used in our model to calculate open circuit voltage.

Layer thickness	
$d\text{-As}_2\text{Se}_3$	110 μm
$d\text{-PEI}$	70 μm
Relative dielectric constant	
$\varepsilon\text{-As}_2\text{Se}_3$	8.1
$\varepsilon\text{-PEI}$	3.1
Other variables	
σ_0	10^{-6} C/m^2
Frequency	20 Hz
Velocity	0.32 m/s

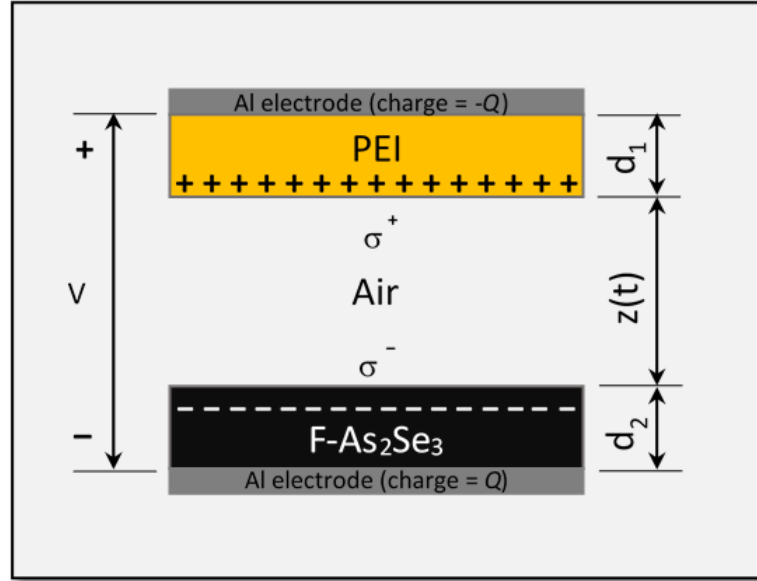


Figure 5.18: Schematics of single layer triboelectric device.

Above all, it should be remembered that induced potential difference is $V = E \cdot d$ and charge density is $\sigma = q/A$. Consider d_{PEI} , d_{FAS} , ε_{PEI} , ε_{FAS} are the thicknesses and the dielectric constants of PEI nanopillars and fluorinated As_2Se_3 nanowires (F- As_2Se_3) triboelectric layers respectively. σ is the charge density, A is the surface area of the surface. For large surface dimensions (i.e. several orders of magnitude larger

than the total separation distance ($d_{PEI} + d_{FAS} + z(t)$) the assumption that the two electrodes are infinitely large is acceptable. Considering our device design, the electric field will only evolve in the direction perpendicular to the surface as follows:

$$E_{PEI} = -\frac{Q}{A\epsilon_0\epsilon_{PEI}} \quad (5.5)$$

$$E_{FAS} = -\frac{Q}{A\epsilon_0\epsilon_{FAS}} \quad (5.6)$$

$$E_{Air} = -\frac{Q}{A\epsilon_0} + \frac{\sigma(t)}{\epsilon_0} \quad (5.7)$$

The potential between the two electrodes can be estimated as in equation 5.3 and 5.4.

$$V = -\frac{Q}{A\epsilon_0} \left(\frac{d_{PEI}}{\epsilon_{PEI}} + \frac{d_{FAS}}{\epsilon_{FAS}} + z(t) \right) + \frac{\sigma \cdot z(t)}{\epsilon_0} \quad (5.8)$$

Effective thickness is:

$$d_0 = \frac{d_{PEI}}{\epsilon_{PEI}} + \frac{d_{FAS}}{\epsilon_{FAS}} \quad (5.9)$$

Potential between electrodes can be defined as:

$$V = -\frac{Q}{A\epsilon_0} (d_0 + z(t)) + \frac{\sigma \cdot z(t)}{\epsilon_0} \quad (5.10)$$

In the case of open circuit voltage, (no charge transfer, $Q = 0$)

$$V_{OC} = \frac{\sigma \cdot z(t)}{\epsilon_0} \quad (5.11)$$

In the case of short circuit current, ($V = 0$)

$$Q_{SC} = \frac{A \cdot \sigma \cdot z(t)}{d_0 + z(t)} \quad (5.12)$$

$$I_{sc} = \frac{dQ_{sc}}{dt} \quad (5.13)$$

$$I_{sc} = \frac{d}{dz} \left[\frac{A \cdot \sigma \cdot z(t)}{d_0 + z(t)} \right] \cdot \frac{dz}{dt} \quad (5.14)$$

$$I_{sc} = \frac{A \cdot \sigma \cdot d_0 \cdot v(t)}{(d_0 + z(t))^2} \quad (5.15)$$

Where $v(t)$ is the average relative velocity of separation / reunification. Here surface charge density is time and materials dependent,

$$\sigma = \sigma_0 \cdot e^{-\frac{t}{\tau}} \quad (5.16)$$

Where σ_0 is the initial surface charge density, when the two surfaces are in contact, and τ is the delay time for charge dissipation, i.e. time required for charge redistribution inside the polymer (time required for charges to equilibrate overall charge of the material after the two surfaces are separated).

5.5.3. Energy Harvesting in a Moving Car

Voltage and current responses of MULTENG in a moving car (2010 Model Ford Fiesta) were characterized during transportation in Bilkent University Campus with various speeds (15 km/h, 30 km/h, 40 km/h). MULTENG was positioned on the front panel of the car. An Al block 1.3 kg in weight, 60 mm in height, 25 mm in width and 280 mm in length was located perpendicularly on top of MULTENG as the centers of the device and the metal block coincide (Figure 5.19a). Because the Al block pushes on top of the device, the initial position of MULTENG was set as full contact with no response and reaction as shown in the fourth stage of triboelectric cycle in Figure 5.1b. As the car was moved forward at various speeds, Al block on the top was tilted the layers of MULTENG backward and forward which causes partially separation and contact of layers. Therefore, small jumps cause quick and weak separations between layers while the car moves in a routine way. So, the input mechanical energy here can be low and output signal can be very complex because response of MULTENG to car

vibration depends on many parameters such as roughness of the road, car model, skills of driver and geometry of MULTENG.

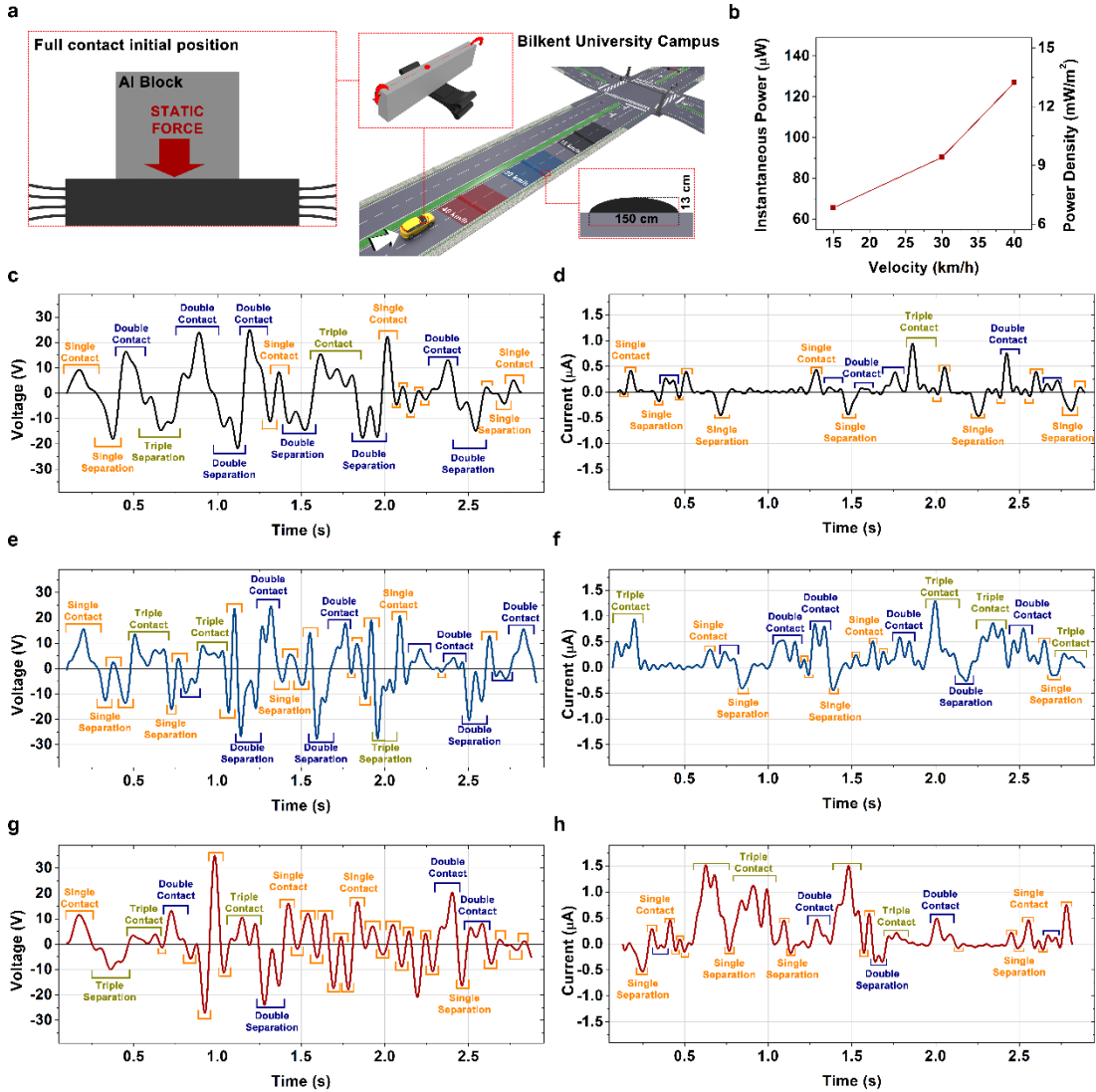


Figure 5.19: Electrical characterizations of MULTENG, activated from the motions of a moving car. a) Schematic representation of driving route in the university campus. Inset shows the squeezed MULTENG in full contact position. Inset shows the bump dimensions on the route. b) Instantaneous power and power density measurements as a function of car velocity. c-h) Open circuit voltage and short circuit current measurements with respect to car velocity. Orange, blue and green colors corresponds to single, double and triple contact and separation in different units of MULTENG, respectively.

The highest instantaneous power and power density were obtained at 40 km/h speed as 127 μW and 13.23 mW/m^2 , respectively as seen in the Figure 5.19b. Instantaneous power and power density were increased with increasing car speed. OCV and SCC values were measured during the car passing through speed bumps (maximum 13 cm in height and 150 cm in width) at 15 km/h , 30 km/h and 45 km/h speeds. Driver of the car was slightly pushed to break just before passing through the speed bumps. This

action causes MULTENG to be tilted backward and separate its layers. As the car was moved further on the speed bump, the vibration and separation were also increased due to greater incline. MULTENG was tilted forward while the car leap over the top of the speed bump to access on the flat asphalt. OCV and SCC graphs with respect to car speed while passing over a speed bump were showed in Figure 5.19c-h. Maximum peak to peak OCV was measured as 61.96 V at 40 km/h speed as shown in Figure 5.19g. The maximum peak to peak SCC was measured as 2.05 μ A at 40 km/h speed as shown in Figure 5.19h.

Since, response of MULTENG to car vibration was complicated because of multiple contact and separation sequences, we pointed single, double and triple contacts and separations in different units of MULTENG during the measurements. Our observations about the motion of MULTENG in car measurements were represented in Figure 5.20 and Figure 5.21. We observed two type of motions (linear and angular) in MULTENG units. Linear motions were caused strong response in OCV and SCC and angular motions were caused weak responses.

Since MULTENG works perfectly at low frequency, we used low pass filter in car measurement to eliminate fluctuations due to high frequency motions. A car is complicated system and many high frequency vibrations produced by the engine and wheels. Besides, we obtained reasonable change in output power, OCV and SCC with respect to car speed. Required acceleration to increase the speed up to 15 and 30 km/h were close to each other. But, higher acceleration rate was required to increase the speed up to 40 km/h since same tracks were used in all measurements. In the measurements, MULTENG was fixed from the bottom and a weight located on the top of the MULTENG. The applied weight was caused to collapse the units of MULTENG and initial position was set as contact. Since the weight was positioned perpendicular in length to MULTENG in width, vibrations and jumps have made angular motions in layers of MULTENG. Thus, MULTENG could make angular contact and separation simultaneously in different layers of units. This causes overlap in peaks and broadening.

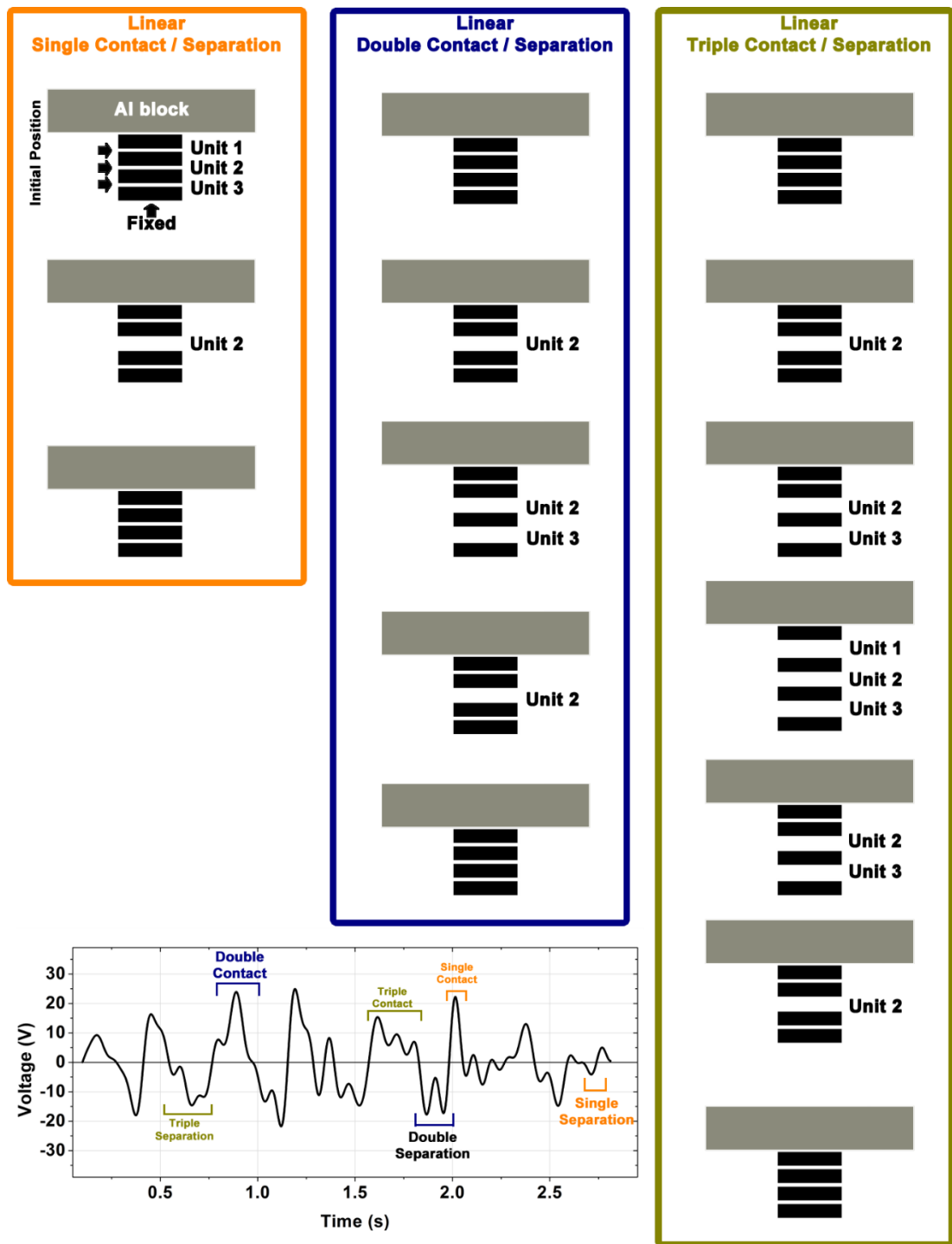


Figure 5.20: Single, double and triple peaks in a sequence were correspond to successive linear contact and separation of different units of MULTENG as a response to car vibration.

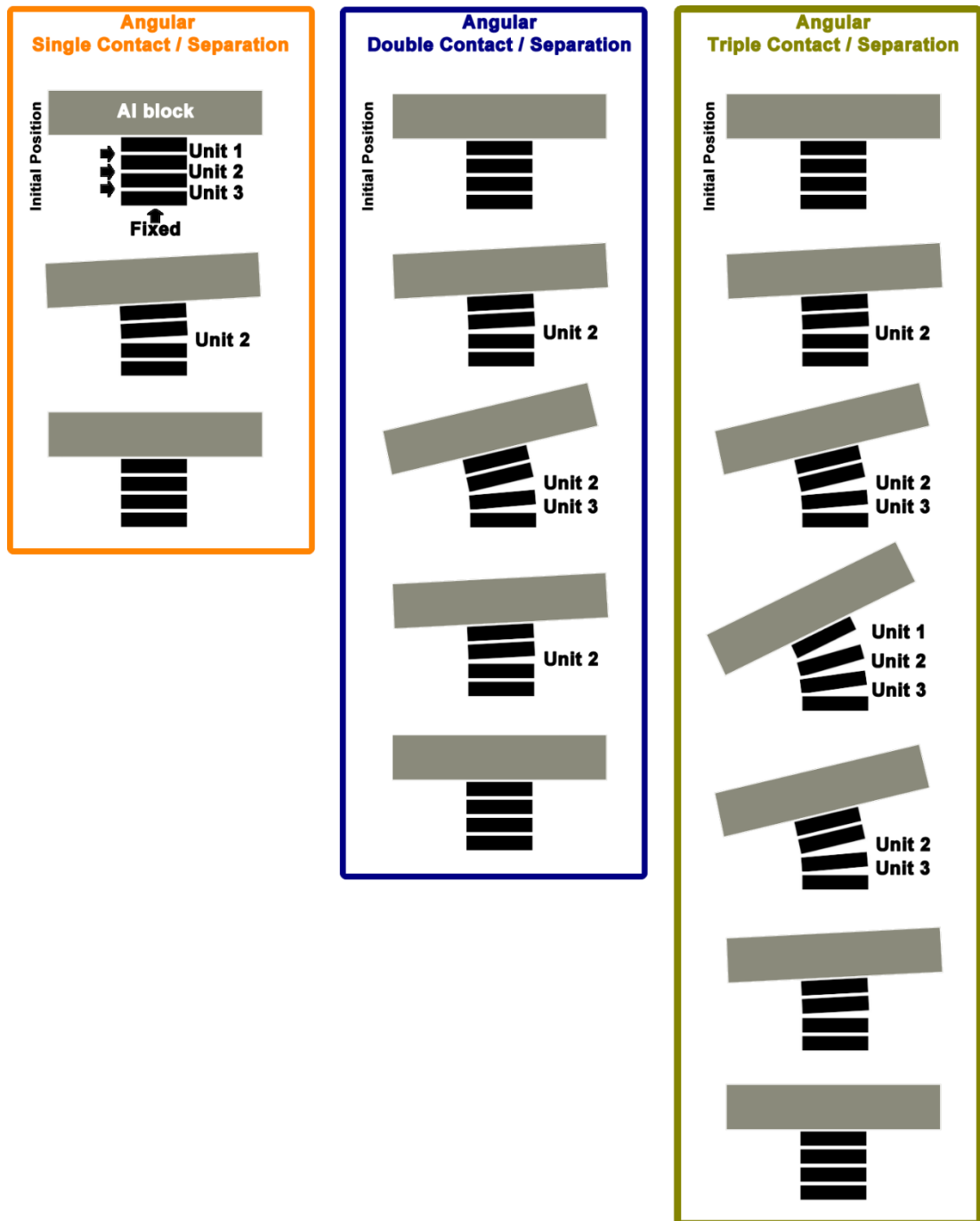


Figure 5.21: Single, double and triple peaks in a sequence were correspond to successive angular contact and separation of different units of MULTENG as a response to car vibration.

5.5.4. Sound Detection and Acoustic Energy Harvesting

Reaction of MULTENG to sound at different frequencies was also measured. Before tests, a constant initial stress was applied to the MULTENG from the sides for closing the gaps between layers to around 1 mm as seen in Figure 5.22a. Squeezed

MULTENG was located 10 cm above from the sound source which has an acoustic power (P_{ac}) of 1.9 W corresponding to 100 dB sound power level (L_W).

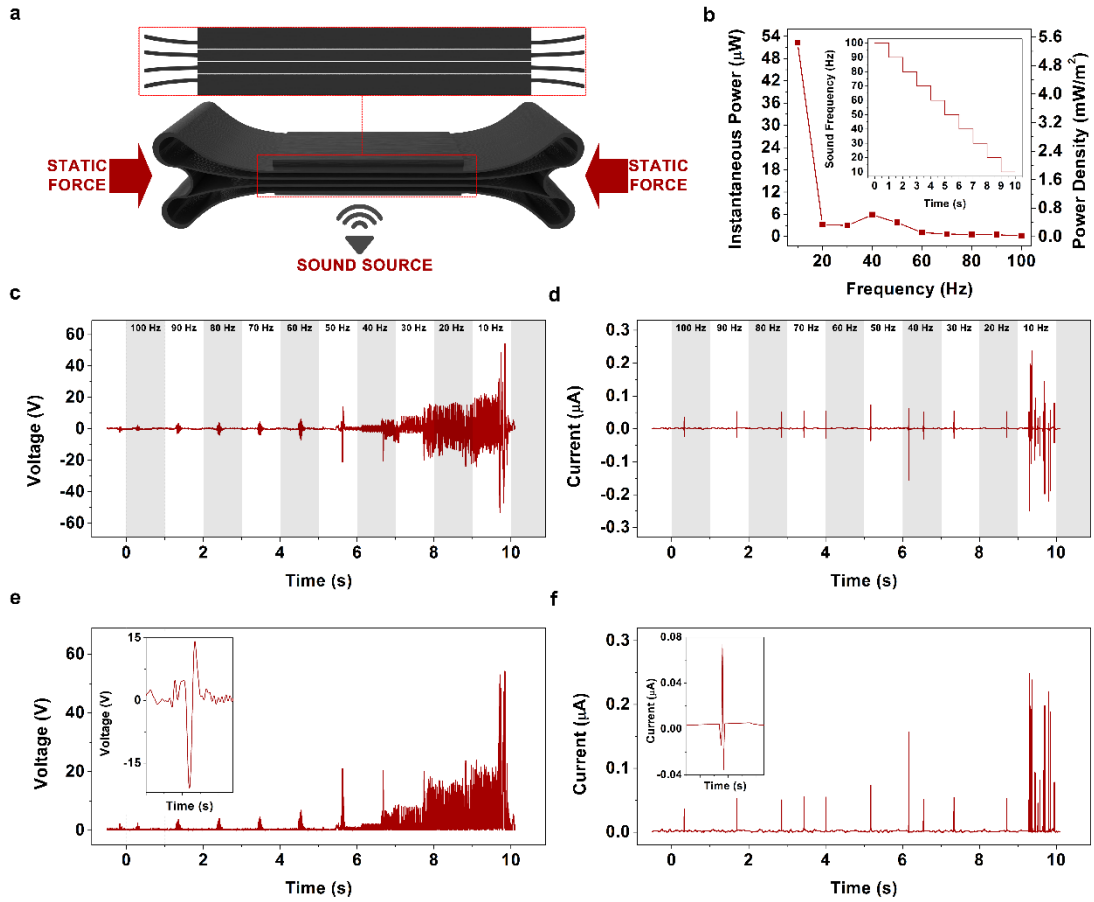


Figure 5.22: Electrical characterization of acoustically excited MULTENG. a) Schematic representation of sound excitation. b) Sound frequency dependent instantaneous power and power density measurements. Inset: Change input sound frequency (Hz) over time. Sound frequency dependent c) open circuit voltage and d) short circuit current measurements. e) Rectified open circuit voltage and single peak open circuit voltage. f) Rectified short circuit current and single peak short circuit current.

Acoustic power and sound power level were calculated using following formulas:

$$P_{ac} = I \cdot S \quad (5.12)$$

$$L_W = 10 \cdot \log_{10} \left(\frac{P_{ac}}{P_0} \right) \quad (5.13)$$

where I is the sound intensity, S is the area of the source, P_0 is the reference sound power in air as the threshold of hearing (10^{-12} W). Acoustic power and sound power level are the characteristics of the sound source. In order to understand the effect of

sound pressure on MULTENG, we calculated sound pressure level (L_p) and sound pressure (p) which is related to distance between source and the MULTENG (r) and sound propagation characteristics (q) using following formulas:

$$L_p = L_W - 10 \cdot \left| \log_{10} \left(\frac{q}{4\pi r^2} \right) \right| \quad (5.14)$$

$$p = \sqrt{\frac{q\rho c P_{ac}}{4\pi r^2}} \quad (5.15)$$

where ρ is the density of air (1.2041 kg/m³) at room temperature, c is the speed of sound in air (343.22 m/s) at room temperature. In our case, $r = 0.1$ m and propagation characteristics is half sphere ($q = 2$). Using the given formula and parameters, we calculated sound pressure level as 87.98 dB and sound pressure as 111.8 N/m² which cause separation and contact between layers of MULTENG. OCV and SCC values were measured and instantaneous power output of MULTENG was calculated as the sound frequency decrease from 100 Hz to 10 Hz with 10 Hz steps and 1 second duration as shown in Figure 5.22b. The highest instantaneous power and power density were also obtained at 10 Hz as 52.5 μ W and 5.47 mW/m², respectively (Figure 5.22b). Peaks with an increasing fashion were obtained with decreasing sound frequency at each 1 second frame. A significant increase in the voltage signal was observed when the sound frequency was reduced to 50 Hz which proves that our MULTENG design is more suitable to operate at lower frequencies. Indeed, OCV value was reached the maximum peak to peak 107.3 V at 10 Hz (Figure 5.22c). Validating these findings, there was no significant SCC signal occurred beyond 10 Hz sound frequency. Maximum peak to peak SCC value was measured as 0.49 μ A at 10 Hz (Figure 5.22d). Rectified OCV and SCC peaks were given in Figure 5.22e-f. Besides, single peak OCV and SCC were given in Figure 5.22e-f insets for a better view of peaks.

5.6. Summary

In conclusion, we developed a multi-layered triboelectric generator based on As₂Se₃ core-shell nanostructures and PEI nanopillars which were produced by iterative size reduction and melt infiltration techniques, respectively. Triboelectric response of a

new materials set was characterized and we deduced that increasing fluorine content in materials increases triboelectric response. MULTENG was activated using mechanical tapping, car vibration and sound with different frequencies and forces. Mechanical tapping force was the most powerful input among these three condition and we obtained the highest signals in mechanical tapping condition, since it made a stronger contact between layers. Results were summarized in Table 5.4.

Table 5.4: Summary of experimental results. Obtained maximum outputs from tapping, automobile motion and sound excitation applications, respectively.

Tapping Maximum Outputs	
Voltage	396 V (7.5 Hz)
Current	1.616 mA (2.5 Hz)
Instantaneous Power	0.512 W (5 Hz)
Power Density	53.4 W/m ² (5 Hz)
DC Power	1.233 mW (7.5 Hz)
Efficiency	5.32 % (1 Hz)
Moving Car Maximum Outputs	
Voltage	61.96 V (40 km/h)
Current	2.05 μ A (40 km/h)
Instantaneous Power	127 μ W (40 km/h)
Power Density	13.23 mW/m ² (40 km/h)
DC Power	1.84 μ W (40 km/h)
Acoustic Signal Frequency Maximum Outputs	
Voltage	107.3 V (10 Hz)
Current	0.49 μ A (10 Hz)
Instantaneous Power	52.5 μ W (10 Hz)
Power Density	5.47 mW/m ² (10 Hz)
DC Power	17.4 μ W (10 Hz)

Maximum peak to peak OCV and SCC were obtained as 396 V at 7.5 Hz and 1.62 mA at 2.5 Hz. Energy conversion efficiency of the device was calculated as 5.3 % at 1 Hz tapping frequency and it was decreased with increasing tapping frequency. MULTENG can supply 1.23 mW constant DC power and directly illuminate 38 LEDs

as well as charge a capacitor *via* an energy harvesting circuit. Our device represent a very high performance compared to the recently reported contact-mode triboelectric devices, as shown in Table 5.5

Table 5.5: Comparison of the triboelectric contact-mode device performances.

Material Set	Working Mode	Voltage (V)	Current (mA)	Power (W)	Working Frequency	Reference
PEI / F- As ₂ Se ₃	Contact	396	1.600	0.51000	Low	Our Study
TEFLON/Al	Contact	215	0.66	0,14190	Low	[48]
PDMS/Al	Contact	232	0,0165	0.00382	Low	[49]
TEFLON/Al	Contact	100	0.0016	0.00016	Low	[50]
TEFLON/SiO ₂	Contact	88.0	0.0610	0.00530	Low	[51]
TEFLON/Cu	Contact	72.0	0.0320	0.00230	High	[52]
TEFLON/TiO ₂	Contact	21.3	0.032	0.00068	Low	[53]

Voltage and current signals were recorded in a car during transportation on campus road and leaping trough speed bumps at various speeds. Signal intensities and output power density (13.23 mW /m² at 40 km/h speed) were increased with increasing car speed. Measurements at sound frequencies between 10 and 100 Hz were revealed that our device has a better response at 10 Hz with peak to peak 107.3 V OCV and peak to peak 0.49 μ A SCC. Output power density (max. 5.47 mW/m²) of MULTENG was decreased with increasing sound frequency. New material and processes proposed in this study such as monolayer fluorine deposition, which enhance the triboelectric properties of materials, will be instigating new theoretical studies to explain the underlying mechanism of triboelectric effect. Demonstration of MULTENG was aimed for charging portable electronic devices such as cell phones and music players with an energy harvesting circuit.

Chapter 6

Summary and Future Work

In this work, we proposed and demonstrated a novel top-down fabrication technique based on thermal fiber drawing for producing piezoelectric nanoribbon structures. Since the new fabrication method can produce extended-length nanowires, we also engineered nanowires for triboelectric nanogenerator materials using the same fabrication technique, where large area nanostructures surfaces are required.

The new fabrication technique can be used to fabricate kilometer-long, polymer-encapsulated, parallel-oriented micro and nanostructures, including square and cylindrical cross sectional core-shell nanostructures, nanoribbons, nanotubes and nanowires. In fact, fabrication requires to fabricate a preform structure in macroscopic scales at least made of two thermally and mechanically compatible materials. The core materials that fills the center of the polymer hollow preform can be semiconducting chalcogenide materials (As-Se, Ge-As-Se-Te), polymer smart and conductive materials (PVDF and copolymers, carbon loaded polycarbonate or polyethylene), low melting point metals (Sn, In, Pb) or chalcogenide phase change glasses (Ge-Sb-Te-Ga-Sn). The filling materials can be expanded with respect to properties of the cladding materials, which generally made of polycarbonate, polyethersulfone, polyetherimide. The compatibility between filling and the cladding materials in terms of thermal and mechanical properties is crucial. On the other hand, material properties such as low glass transition temperature, low melting temperature and no crystallinity vitally expected from filling and cladding materials. Different than the essential fiber drawing process, iterative size reduction technique requires sequential multiple drawing steps.

The initiator process start by a regular fiber drawing to obtain microstructure fibers. The successor processes, different than the first step, has the previous fibers as the filling bundle. Iteratively drawing the fibers leads to iterative size reduction of the first filling materials with preserved cross-sectional shape. The governing parameters in the process can be summarized as the applied stress and temperature, dimensions of the microscopic preforms, reduction factor in each step, numbers of the filling fibers in successive drawing steps.

We produced, proof of principle, high output energy harvesting and tapping sensor devices durable even at high temperature conditions by spontaneously very high piezoelectric (without requiring any electrical polarization), extremely high aspect ratio PVDF micro and nanoribbons. A multimaterial preform structure (polyethersulfone (PES) cladding and PVDF slab as the core material) was used in the initial stage of the fiber drawing. The process was executed in a custom made fiber tower above melting temperature of PVDF and glass transition temperature of PES. In order to produce PVDF nanoribbons, we used three sequential fiber drawing steps. Using that method, we produced millions of 20 nm thin, globally oriented kilometer long, and high piezoelectric PVDF nanoribbon arrays in fiber. PVDF nanoribbons can be separated from PES cladding by selective etching using organic solvents. We discovered a new phase transition mechanism for PVDF, in which PVDF directly nucleate in piezoelectric phases. Although, obtaining piezoelectric phase transformation requires costly post processes, such as electric polarization and stretching under high electric fields, we eliminated such complex and expensive processes. High stress and temperature that used in fiber drawing process induce γ phase and that makes it possible to manufacture kilometer long, large area and flexible devices using as produced PVDF micro and nanoribbons. XRD results demonstrate that we have produced PVDF nanoribbons between 70 - 75 % γ phase content. The Curie temperature of piezoelectric PVDF is normally around 90 °C. We also improved this temperature above the melting temperature of the material by tuning the fabrication process parameters. γ phase content was conserved even after annealing nanoribbons around the melting point of PVDF. Phase transition mechanism during the fiber drawing process was investigated and very well explained using ab-initio calculations. Owing to unique fabrication process and nanoscale effects, we observed

very high piezoelectric coefficient ($d_{33}^{eff} = -58.5 \text{ pm/V}$) from 80 nm thick as produced nanoribbons. This is the highest measured piezoelectric constant from γ -phase PVDF. It is 8 times higher than the reported piezoelectric constant of γ -phase PVDF in the literature. Electrostriction coefficient of the nanoribbons are calculated as $Q = -67.8 \times 10^{-9} \text{ pm}^2/\text{V}^2$. We built two devices using 50 μm thick microribbons and 300 nm thick nanoribbons. Peak voltage and current of first and second devices on an external load were measured as 7 V, 3 μA and 60 V, 10 μA , which shows that performance of nanoribbons were far beyond the performance of the microribbons. We also characterized our devices under random tapping forces and even the weakest tapping forces can be detected using our devices. As a result, our devices can be used with an energy harvesting circuit for low power requiring applications. Using iterative fiber drawing technique, it is possible to produce in fiber ferroelectric and piezoelectric devices such as artificial muscle, artificial skin, energy generator, and metal interdigitated memory.

Inspired from the previous work on PVDF, we also developed a nanoribbon array using its co-polymer PVDF-TrFE using exactly the same fabrication principle. Piezoelectric characterizations show that, we developed PVDF-TrFE nanoribbons with record-high piezoelectric measurements ($d_{33}^{eff} = -384 \text{ pm/V}$). To our knowledge, the maximum piezoelectric coefficient can only reach to - 210 pm/V, which was measured from an electrically polarized very low aspect ratio (20nm in diameter, 305 nm in length) nano pillars. However, our ribbons were kilometers long in length and nanometers in cross-section and were representing higher piezoelectric coefficient without requiring electrical polarization process. Similar to previous work, we built two proof of principle devices as tapping sensor and energy harvesting device. Devices can generate voltage and current up to 600 V and 7 μA respectively and it can power 8 commercial LEDs.

Piezoelectric materials demonstrate superior properties for sensing applications because of that they have a well-understood electric displacements property. On the other hand, they are insufficient for energy harvesting. Therefore, we developed a pocket size multi-layered triboelectric nanogenerator, which has incomparably high performance with piezoelectric nanogenerators. We used state of the art 3D printing

technique for constructing body parts of our device, which is made of 6 alternating layers. Each couple of the layers were covered with nanostructures polymers and core-shell chalcogenide nanowires produced by iterative fiber drawing techniques. Although, chalcogenides known as triboelectrically inactive, we proposed and successfully demonstrated to activate the surfaces of nanostructures by depositing monolayer fluorine ligands. Here, we introduced that fluorine coatings can transform any material into triboelectrically-active and high performance materials, for the first time. We paved the way for potential applications of this technique, and new research groups started to develop new dielectric sets for manufacturing triboelectric generators. The device was tested under versatile conditions including tapping at different frequencies, sensing acoustic waves and harvesting energy from vibrations of a moving car. The device represent very high performance 396 V and 1.62 mA open circuit voltage and short circuit current, respectively. It can power 38 commercial LEDs, detect low frequency acoustic signal (10 - 100 Hz) and it can be excited with small vibrations in a moving car. To our knowledge, we reported the highest output current and power from a triboelectric nanogenerator.

Some of the ongoing studies and device fabrications can be addressed as future work in this study.

- **Artificial Skin and Anthropometric Hand**

We continue to develop high performance large area devices. We developed a new generation, transparent, passive matrix artificial skin with 100 pixels and an anthropometric human hand with 22 pressure nodes and 5 angular motion sensitive points. In addition, we develop a flexible, human skin compatible device for monitoring electrocardiographic of human heart from different measurement points. Cardiac measurements directly performed from arterials at the neck, wrist, arm, fingers, behind of the ears, and besides we measured heart beats direct from the chest. The devices requires no external power sources and generates the self-energy. Similar to the human skin, the artificial skin can detect temperature changes, shear force, high and low frequency pressure stimulations with different intensities. The artificial palm and electronic skin is promising for developing human-like shape and temperature sensing robots.

- **Polymer Matrix Composite Electrodes**

Our further target is developing in fiber electromechanical devices by integrating conductive polymer wires with piezoelectric devices. Nanocomposite materials composed of carbon nanotubes (CNTs) and carbon loaded polymers expected to bring solutions to most fundamental problems in flexible and stretchable electronics related to electrical conductivity, elastic modulus and thermal durability. Especially, when those nanocomposites formed in functional nanowires, they potentially find wide range of electronic and electro-mechanic applications such as capacitors, sensors, actuators and energy harvesting. Although fabrication techniques such as mold template method, liquid – gaseous phase growth, lithography have been used widely in fabrication of composite nanowires for flexible electronics, they are still insufficient to bring on required building block. Therefore, a fabrication technique, which is capable to produce extreme high aspect ratio, well-ordered, high conductive, flexible, stretchable and high elastic modulus nanowires was demanded. We developed a promising CNTs / Polymer nanocomposite material for flexible electronics based on thermal size reduction method. Initially, we optimized composition of Conductive Polyethylene (CPE) and metallic CNTs by dissolving in Xylene and prepared a thin film nanocomposite with a uniform $\sim 10^3$ S/m conductivity. Further, we fabricated a bulk rod using our conductive films for processing it through three steps of size reduction process, which is based on thermal fiber drawing technique. We obtained kilometer long, conductive, ordered, flexible, stretchable micro and nanowires with 300 – 800 μm , 2 – 8 μm and 50 – 300 nm in diameters in step 1, step 2 and step 3 fiber drawing processes, respectively. According to Raman Spectroscopy, SEM, and TEM investigations, carbon nanotubes embedded in polymer has exchange the mixed orientation with end to end alignment parallel to fiber drawing direction. The main reason of maintaining the conductivity in micro and nanocomposite wires was the aligned carbon nanotubes along the fiber and carbon particles through the fiber width. The nanostructures and nanocomposite films can be used to fabricate conductive substrates, ionic capacitors and flexible electrodes.

- **Large Area Triboelectric Floor Tiles**

We continue on further studies on exploiting the applications of triboelectricity. Currently, we are developing new surface modification for triboelectric generators to enhance their performance and reduce the cost. We have been working on an

interesting fabrication technique, which is applicable to wide range of materials, using Ar plasma etching for manufacturing very high performance, low cost and large area triboelectric nanogenerators. Plasma processing basically requires a vacuum chamber, a plasma source (e. g. microwave) and ionizing gas such as Ar. We optimized plasma surface nano-structuring mechanism for many different polymers, which play a key role in nanogenerators. Based on the optimized fabrication parameters, we developed a proof of principle high performance, large area floor tiles for biomechanical energy harvesting with 55 Watt /m² power density using nanostructures 100 μm TEFLON and carbon loaded polyethylene films. The device can power 1500 commercial LED's and can generate peak to peak 2500 V open circuit volt and 0.9 mA short circuit current. The device performance was investigated also according to weight of the people who step on it. We observed that increasing the operator weight helps to scavenge more energy. We also considered the possibility of using TENG floor tiles on car roads and investigated to performance of our nanogenerators while a car passes over it at different speeds.

- **Triboelectric Sensors Based on Microfluidics**

Since triboelectric effect also can be observed in liquid – solid interfaces, I can address and additional ongoing project as a future work in triboelectricity. We confirmed that water waves can be a good source of energy when freely move on a dielectric substrate. The mechanism is related to chemical polarity of the liquid as well as the surface and triboelectric properties of the dielectric substrate. The current ongoing study represents a smart energy harvesting and chemical sensing microfluidic systems that converts mechanical motion of chemicals droplets in a tubular poly (vinylidene fluoride) microfluidic channel to the electrical signals. The system consist of a single microfluidic channel with a PVDF micro-tubular attachment, which is produced using thermal fiber drawing technique. Channel lengths and the diameters can vary, but what effects the output voltage and current signal is the change in the speed or air - deionized water droplet size. We observed that increasing droplet speed increases the induced charge. When there was a continuous flow through the channel, system was generated enough energy to power 6 LEDs. Finally, the system can detect the change in the ratio of water – ethanol mixture down to 5 %. Although output voltage signal was at the maximum 1 V, when plane deionized water flushed, increasing ethanol percentage decreases the output voltage. Our system can be used

for understanding chemical concentrations of liquid chemicals, when accurate and detailed calibration was applied for versatile solution.

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