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

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Table 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. Figure S1 describes the possible phase transformation phenomena among the PVDF forms under versatile conditions. Fiber drawing can be considered as a new method which produces γ phase PVDF nanostructures. We can produce PVDF nanostructures not only with a rectangular but also any arbitrary cross sectional geometry such as square cross sectional core shell nanowires (Figure S2). 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 S3 and Video S1). Fiber drawing processes are conducted in a custom-made fiber tower which is shown in Figure S4. SEM micrographs of the produced PVDF nanoribbons are taken by using a FEI Quanta 200 FEG Electron Microscopy. Shape of the nanoribbons can be observed clearly from the SEM images (Figure S5 and Video S2) of a sample prepared by breaking the nanoribbon embedded fiber after a liquid nitrogen treatment. Size distribution of the second step nanoribbons in width is presented in Figure S6. 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. 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. In order to simulate the phase transformation in iterative fiber drawing process and investigate the effect of temperature, ab initio density functional theory calculations are carried out using VASP program (Kresse, G.; Hafner, J.; Phys. Rev. B, 1993, 47, 558-561 and Kresse, G.; Hafner, J.; Phys. Rev. B,
in which compressive strain of $\alpha$ and $\beta$ PVDF and tensile strain of $\alpha$ PVDF with 6 monomer chains in the unit cell is considered at a temperature higher than drawing temperature ($470 \, ^{\circ}\text{K}$) and compared with 0 $^\circ$K results as shown in figure S7. These calculations are performed with Generalized Gradient Approximation (GGA) (Perdew J.P.; Burke K.; and Ernzerhof M.; Phys. Rev. Lett. 1996, 77, 3865-3868 and Perdew J.P.; Chevary, J.A.; Vosko, S.H.; Jackson, K.A.; Pederson M.R.; Singh, B.J. and Fiolhais, C.; Phys. Rev. B, 1992, 46, 6671-6687) as exchange-correlation, and Projector Augmented Wave (PAW) (Blochl, P.E.; Phys. Rev. B, 1994, 50, 17953-17979 and Kresse, G.; Joubert, D.; Phys. Rev. B, 1999, 59, 1758-1775) as pseudo-potential. Cut-off energy is chosen to be 500 eV and the energy convergence was within $10^{-4}$ eV. For the ground state calculations at 0 $^\circ$K, the forces on the ions and the energy are minimized within the energy convergence and for the calculations at 470 $^\circ$K molecular dynamics simulation is enabled. In order to simulate the effect of temperature and shear stress simultaneously, the lattice constant in axial direction is kept constant for 1 ps at 470 $^\circ$K before it is increased or decreased depending on tensile or compression for the next step. Transformations $\alpha$ phase and $\beta$ phase to $\gamma$ phase PVDF under lattice compression and $\alpha$ to $\gamma$ and $\beta$ phase PVDF under lattice tensile at 470 $^\circ$K given in video S3. At 0 $^\circ$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 $^\circ$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 $^\circ$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 $^\circ$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 S8). 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 S9).

Figure S10 represents the experimental setup that we used to measure effective $d_{33}$ constant of a single 80 nm thick PVDF nanoribbon. We used Radiant Technologies precision multiferroic piezoelectric evaluation system along with Asylum Research MFP-3D AFM System for piezoelectric characterizations of the single PVDF nanoribbons. Effective $d_{33}$ coefficient for the thin film structure is less than that of 1D structures due to surface clamping conditions. Equation 1 and equation 2 represents $d_{33}$ coefficient relation for thin films and 1D nanostructures respectively,

$$d_{33}^{\text{eff}} = d_{33} - \frac{2S_{13}}{S_{11} + S_{12}}$$  \hspace{1cm} (Eq. 1)

$$d_{33}^{\text{eff}} \approx d_{33}$$  \hspace{1cm} (Eq. 2)

where $S_{ij}$ is an element of compliance matrix. Since we can't overlook the geometry of the AFM tip, polarization axis is given in arbitrary units. The strain which can be induced by the indentation of AFM tip is simulated using COMSOL Multiphysics (Figure S11). A -60 nN indentation force causes 0.3 nm elastic deformation on the surface of 80 nm thick PVDF nanoribbons. In addition, we simulated local temperature changes that can occur due to Joule Heating (Figure S12). We calculated piezoelectric and electrostriction coefficient of PVDF nanoribbons using following formulations and measured data of displacement versus electric field (El Hami, K.; Yamada, H.; Matsushige, K.; Appl. Phys. 2001, 72, 347-350):

$$s = \frac{dE}{E}$$  \hspace{1cm} (Eq. 3)
where $s$ is the total strain, $t$ is the thickness of the nanoribbons and $\Delta t$ is the measured change in the thickness. Total strain can be written in following form according to internal and external physical variables:

$$s = s_{\text{piezoelectric}} + s_{\text{electrostriction}} + s_{\text{thermal}} + s_{\text{pressure}}$$  \hspace{1cm} (Eq. 4)

$$s = d_{33}E - QE^2 + \lambda \Delta T + e_{33}\sigma_{33}$$  \hspace{1cm} (Eq. 5)

where $d_{33}$ is the piezoelectric coefficient, $E$ is the electric field, $Q$ is the electrostriction coefficient, $\lambda$ is the thermal expansion coefficient, $\Delta T$ is the change in the temperature, $e_{33}$ is the elastic coefficient and $\sigma_{33}$ is the stress. 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:

$$s = d_{33}E - QE^2$$  \hspace{1cm} (Eq. 6)

$$\begin{bmatrix} s_1 \\ \vdots \\ s_n \end{bmatrix} = \begin{bmatrix} E_1 & E_1^2 \\ \vdots & \vdots \\ E_n & E_n^2 \end{bmatrix} \begin{bmatrix} d_{33} \\ Q \end{bmatrix}$$  \hspace{1cm} (Eq. 7)

$$\begin{bmatrix} d_{33} \\ Q \end{bmatrix} = \left( \begin{bmatrix} E_1 & E_1^2 \\ \vdots & \vdots \\ E_n & E_n^2 \end{bmatrix} \begin{bmatrix} E_1 & E_1^2 \\ \vdots & \vdots \\ E_n & E_n^2 \end{bmatrix} \right)^{-1} \begin{bmatrix} E_1 & E_1^2 \\ \vdots & \vdots \\ E_n & E_n^2 \end{bmatrix} \begin{bmatrix} s_1 \\ \vdots \\ s_n \end{bmatrix}$$  \hspace{1cm} (Eq. 8)

Figure S13 illustrate the device fabrication steps using PVDF nanoribbons. 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 S14. Theoretical fits to the impedance measurements are done using parallel R-C circuit impedance relation as given in equation 9.

$$|Z_{eq}| = \frac{R}{\sqrt{1 + (\omega RC)^2}}$$  \hspace{1cm} (Eq. 9)
$Z_{eq}$, $R$ and $C$ represents equivalent impedance, resistance and capacitance of the parallel $R - C$ circuit respectively, and $\omega$ is angular frequency. 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. Response of devices under random tapping condition is shown in figure S15 and Video S4. For the first device, maximum output voltage and current is 7V and 3 $\mu$A, respectively. For the second device, maximum output voltage and current is 60V and 10 $\mu$A, respectively. We built an identical device structure using non-piezoelectric amorphous As$_2$Se$_3$ 150 nm in diameter nanowires which produced by thermal fiber drawing in order to confirm and compare with PVDF piezoelectric devices. As shown in Figure S16, 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.
Comparison of PVDF nanowire production techniques

**Table S1.** 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.

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Process conditions for transitions among $\alpha$, $\beta$, and $\gamma$ phases of PVDF

Figure S1. Transition into $\alpha$, $\beta$, and $\gamma$ phases from the molten state or other phases of PVDF are possible by using versatile processes. $\gamma$ 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 $\gamma$ phase transformation by providing the two conditions concurrently.
**Figure S2.** 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.
Finite element simulation results for process of all-polymer fiber drawing

\textbf{Figure S3.} 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 $\gamma$ phase transition in PVDF nanoribbons at high temperatures.
Fiber drawing tower for the iterative size reduction method

**Figure S4.** 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.
**Figure S5.** (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.
Size distribution of nanoribbon width

**Figure S6.** Mean of size distribution in nanoribbon width is calculated from SEM images as $<w> = 309$ nm. Standard deviation of size distribution is $\sigma = 35$ nm. Standard deviation normalized with respect to the mean is $\sigma / <w> \approx 11\%$. 
Ab-initio calculations for modelling γ phase transformation in fiber drawing

Figure S7. 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.
Figure S8. 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.
**Ab initio simulation results for higher temperature**

![Graphs showing phase transformations](image)

**Figure S9.** Ab initio calculations for explaining phase transformation at higher temperatures. Increasing the temperature decreases the required strain for phase transformation accordingly. (a) Transition from $\alpha$ (yellow circle) to $\gamma$ phase (blue triangle), (b) transition from $\beta$ (red square) to $\gamma$ phase with compressive strain and (c) transition from $\alpha$ to $\beta$ phase with tensile strain.
Experimental setup for piezoelectric characterization of PVDF nanoribbons

**Figure S10.** Experimental setup for piezoelectric characterization of the PVDF nanoribbons.
Figure S11. 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 loop on and apply a –60 nN which generate maximum 0.3 nm elastic deformation on the top of the nanoribbons.
Finite element simulations for joule heating

**Figure S12.** 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.
**Fabrication process of the device produced using nanoribbons**

![Diagram of device fabrication](image)

**Figure S13.** 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.
Impedance measurement of the piezoelectric devices

Figure S14. 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.
Measurement of electrical output of the piezoelectric devices

Figure S15. 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.
Confirmation of piezoelectric effect of the devices

**Figure S16.** We produced a device with identical structure using non-piezoelectric amorphous As$_2$Se$_3$ nanowires instead of PVDF nanoribbons in order to confirm that the measured peaks are result of a piezoelectric response.