



# Introduction to Nanotechnology and Nanoscience – Class#21

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# Outline

- A few more small project presentations
- Paper #9 Revisit
- Nanofiber-based Energy Generator

# Intel Invests \$20 Billion In 2 New Arizona Fabs



Intel's Ocotillo manufacturing facility in Chandler, Arizona. INTEL



The second announcement was around what the company is calling IDM 2.0. IDM stands for Integrated Device Manufacturer, which is a company that both designs and manufactures its own semiconductor products. Most of Intel's competition are fabless semiconductor companies relying on foundry manufacturers. According to Mr. Gelsinger, this IDM strategy involves three key pillars – having internal manufacturing, leveraging foundry services, and becoming a foundry service provider.

At the moment, the U.S. makes only 12% of the world's semiconductors; however, that is about to change.

Besides TSMC creating a new fab in Arizona, Samsung is also building a new fab in Austin, Texas. And the news broke this week that Intel, as a part of a major new strategy for manufacturing, innovation, and product leadership, will invest \$20 billion in two new fabs in Arizona over the next three years.

# SMIC reportedly gets US license to purchase chip-making equipment

SMIC reportedly gets US license to purchase equipment

By Global Times

Published: Mar 02, 2021 09:28 PM



China's major chipmaker Semiconductor Manufacturing International Corp (SMIC) has, reportedly, received licenses to import equipment from some US companies for use in its mature processes, an anticipated change as Trump's trade war and wanton sanctions seriously disrupted the global chip supply to the extent of hurting the interests of many manufacturing companies,

But they predicted that the US won't ease restrictions on SMIC for advanced chip technologies, such as 7-nanometer or smaller processes.

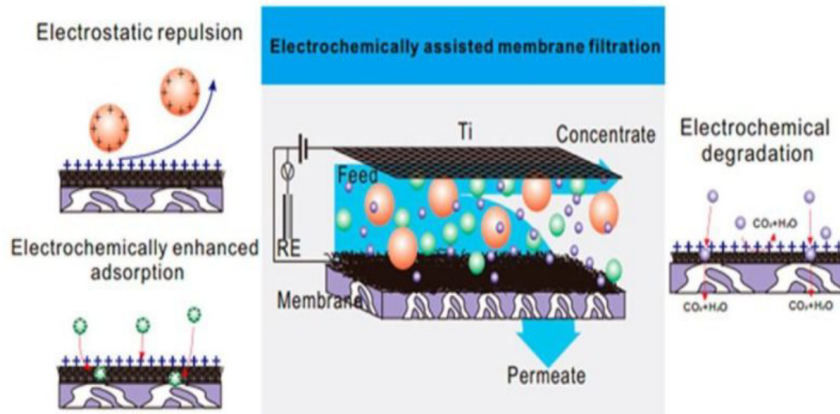
"The US government ban on the Chinese semiconductor sector has not only disrupted global semiconductor supplies but also hurt the interests of its own companies. I believe the Biden administration is moving to correct the situation," Xiang told the Global Times.

# Application of CNT in Water Treatment

Propose:

- Water Desalination
- Membrane Filtration
- Catalysis and Advanced Oxidation Processes

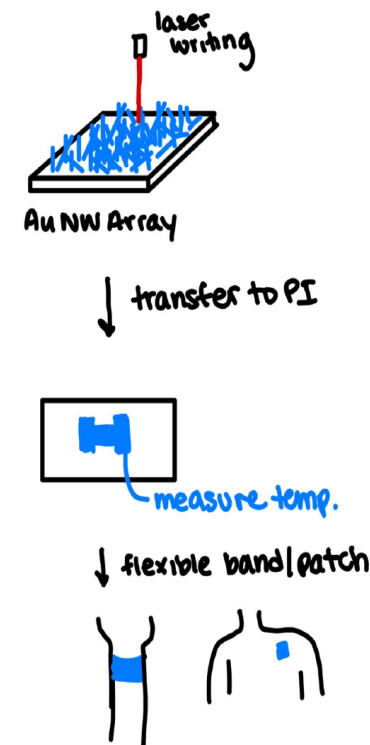
- CNT membranes showed salt rejection and obtained the highest water flux ( $38.91 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ ) and  $\text{Na}_2\text{SO}_4$  rejection (87.25%) at 4 bar
- CNTs- $\text{Al}_2\text{O}_3$  electrochemical separation mechanism to remove pollutants
- ~100% removal efficiency at +1.5V
- the composite membranes exhibited a 94.2% removal for Cr(VI) and 78.2% removal for  $\text{Cd}^{2+}$
- exhibit high catalytic activity, stability, and selectivity for the degradation of organic pollutants
- generate reactive oxygen species (ROS) under redox reactions



Membranes (Basel). 2017 Mar; 7(1): 16.

# NW Sensors in Wearable Technology

- Gold Nanowires would increase accuracy of recorded data
  - NWs provide more flexibility which increases the accuracy of recording data
    - Current material is stiff and causes inaccurate and loss of data
  - High sensitivity that can be changed into a measurable signal
- Incorporate biosensors, temperature sensors, etc.
  - Monitor heart beat, body temperature, muscle spasms to enhance training and/or prevent diseases
- Fabrication process: VLS to grow AuNWs, laser direct writing to form sensors, and place onto PI film



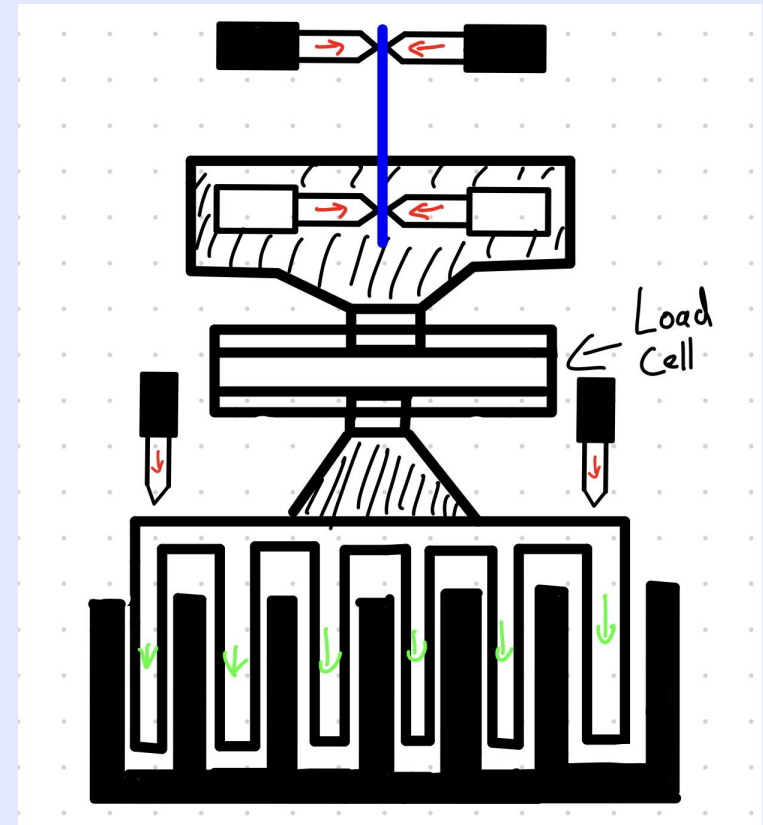
1. *Gold Now Has a Golden Future in Revolutionizing Wearable Devices*, POSTECH
2. *Recent Advances in Nanowire-Based Wearable Physical Sensors*, Gu et al.





# Micromaterial Testing Rig

- Thermoactuator Grippers
- Comb Resonator for cyclical fatigue loading
- Single Wall CNT strain gauge for very precise measurement of the applied loads to the material
- Can test small fibers or structure under specified loading conditions



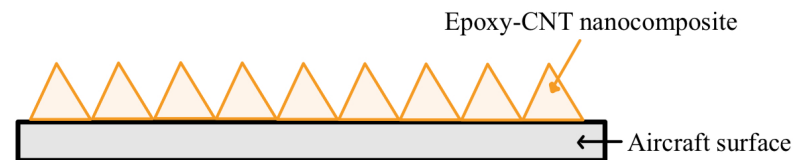
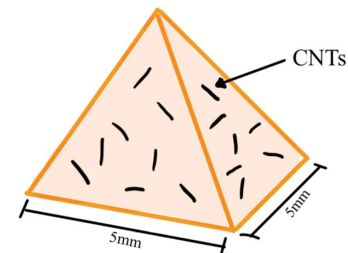
# SWCNTs for Radar Absorption on Stealth Aircraft

## Process

- Use CVD to synthesize a forest of SWCNTs
- Separate the metallic SWCNTs from the semiconducting SWCNTs using dielectrophoresis
- Create a mold of many pyramidal holes, into which a mixture of epoxy and the metallic SWCNTs will be poured into.
- The Epoxy-CNT nanocomposite will then be binded to the surface of the aircraft using a layer of epoxy resin

## Properties

- Metallic SWCNTs absorb the microwaves that RADAR systems emit and convert them to heat
- Metallic SWCNTs have a high thermal conductivity, so they are able to quickly dissipate the heat generated in order to avoid being detected by the thermal signature that is produced



## Advantages

- Lighter weight than metallic radar absorbing material
- The pyramidal shape of the nano-composite serves to deflect the unabsorbed radar waves away from the RADAR system that emitted it

# Analysis of multi-functional nanocomposite-based self-healing polymers

Kai Lyubchenko

**Problem:**

- Polymeric coatings degrade with use over time, and lose their functionality
- Many such coatings are expensive to re-apply, and are used in electronics where they are difficult to replenish

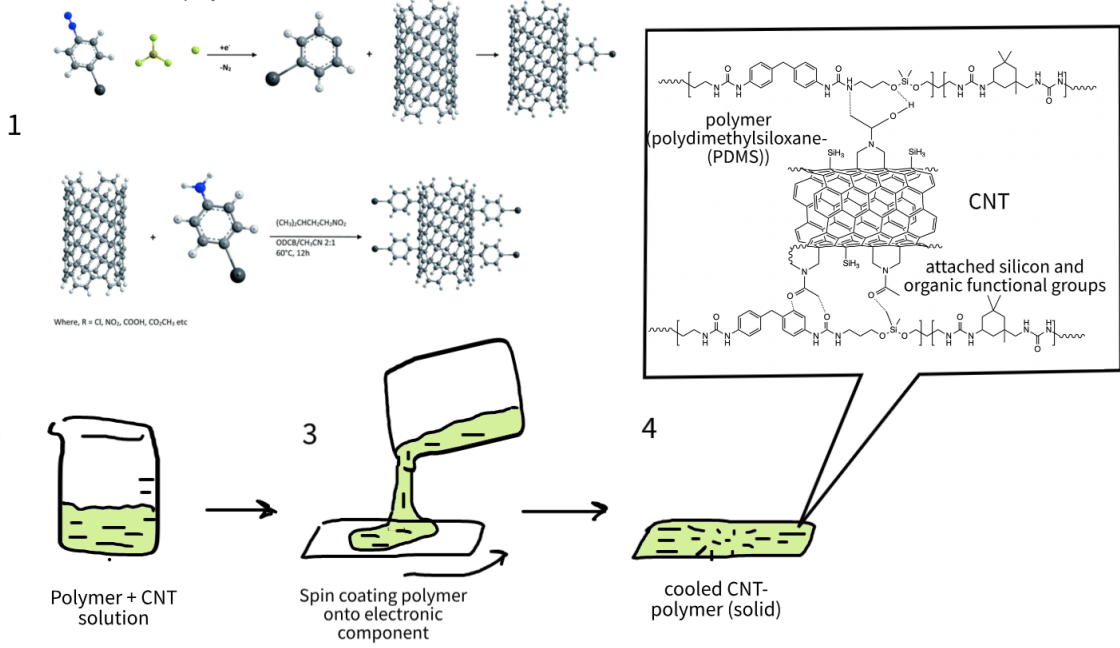
**Objective:** Combine self-healing polymers with functionalized carbon nanotubes to create more durable self-healing composites for long-term use in electronic and medical devices

**Background:** Self-healing polymers rely on a variety of chemical bonding methods to autonomously repair damage and regenerate degraded areas.

Functionalized carbon nanotubes can be combined with these polymers and reinforce the self-healing process by introducing more covalent character to the polymer, as well as making the polymer more durable.

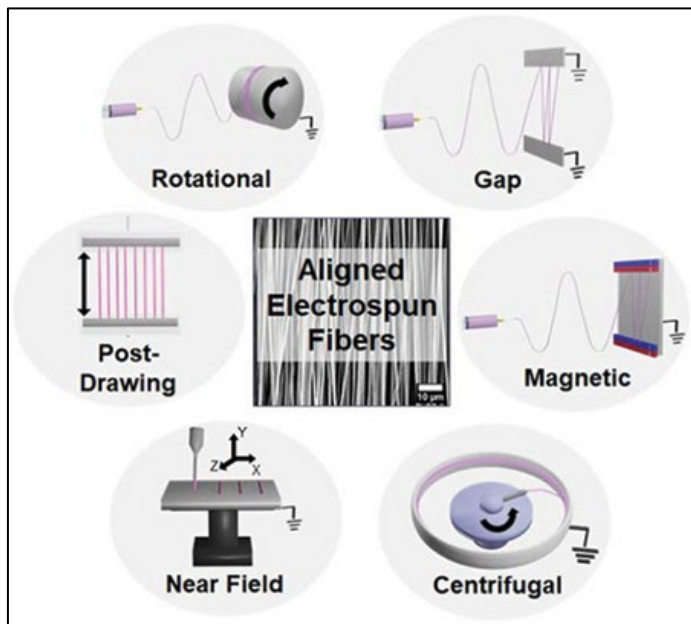
1) Christopher B. Cooper *et al.*, Autonomous alignment and healing in multilayer soft electronics using immiscible dynamic polymers. *Science* 380, 935-941 (2023). DOI: 10.1126/science.adh0619  
 2) J. L. Bahr, J. Yang, D. V. Kosynkin, M. J. Bronikowski, R. E. Smalley and J. M. Tour, *J. Am. Chem. Soc.*, 2001, 123, 6536-6542  
 3) Yuxin Jiang, Margaret Minett, Elizabeth Hazen, Wenyun Wang, Carolina Alvarez, Julia Griffin, Nancy Jiang, and Wei Chen *Langmuir* 2022 38 (41), 12702-12710 DOI: 10.1021/acs.langmuir.2c02206

functionalization of nanotubes before addition to polymer

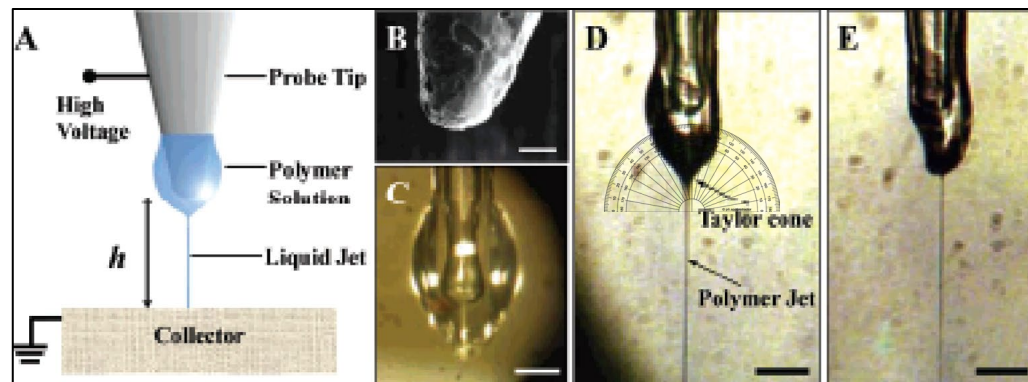


**Results:** Analysis and method development for the synthesis and application of a variety of CNT polymers, as well as the classification and characterization of these materials.

# Near Field Electrospinning : TES vs NFES



Various Fiber Alignment Methods in Electrospun fibers



(A) NFES Schematic (B) SEM photomicrograph of tungsten tip diameter of 25  $\mu\text{m}$ . (C) 50  $\mu\text{m}$  diameter polymer solution droplet (D) jet is ejected from the apex of a Taylor cone under electrical field (E) Decrease in droplet size during electrospinning process.

Method	Forms	Distance (cm)	Voltage (kV)	D <sub>fiber</sub> ( $\mu\text{m}$ )
TES	SES; MES	5–50	10–30	0.01–1
NFES	solution NFES; melt NFES	0.05–5	0.2–12	0.05–30

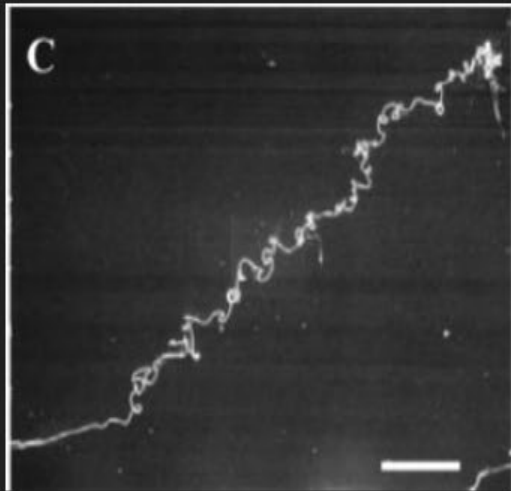
Ju Young Park

[1]A. J. Robinson, A. Pérez-Nava, S. C. Ali, J. B. González-Campos, J. L. Holloway, and E. M. Cosgriff-Hernandez, ‘Comparative analysis of fiber alignment methods in electrospinning’, *Matter*, vol. 4, no. 3, pp. 821–844, Mar. 2021.

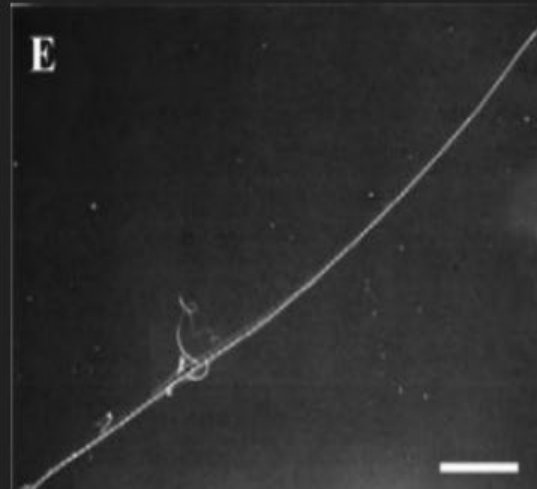
[2] A. Frenot and I. S. Chronakis, ‘Polymer nanofibers assembled by electrospinning’, *Curr. Opin. Colloid Interface Sci.*, vol. 8, no. 1, pp. 64–75, Mar. 2003.

[3]X.-X. He *et al.*, ‘Near-field electrospinning: Progress and applications’, *J. Phys. Chem. C Nanomater. Interfaces*, vol. 121, no. 16, pp. 8663–8678, Apr. 2017.

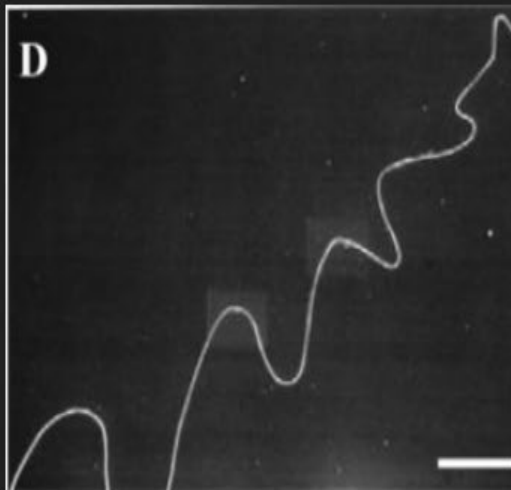
# Nanofiber Electrospinning in Straight Line at 4 Different Speeds



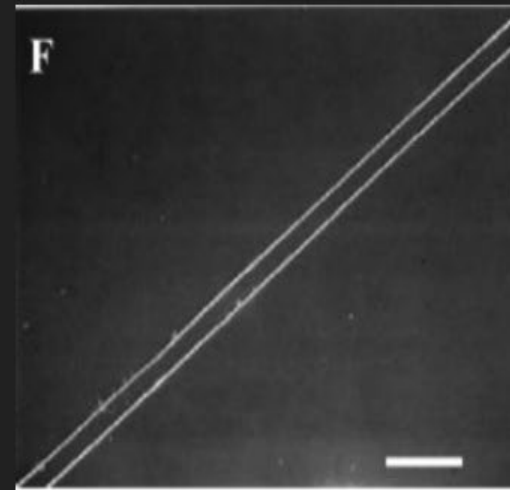
5 cm/s



15 cm/s

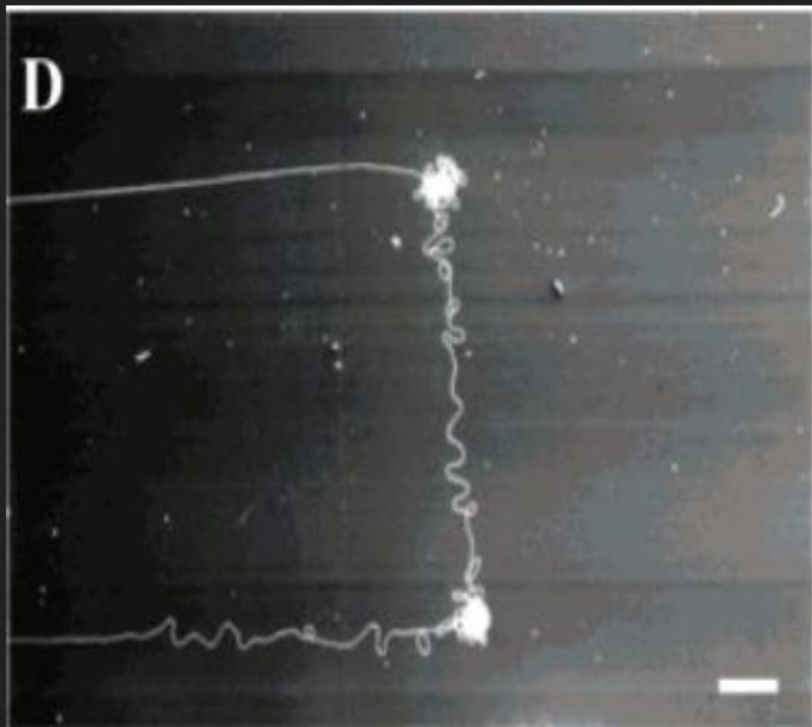


10 cm/s



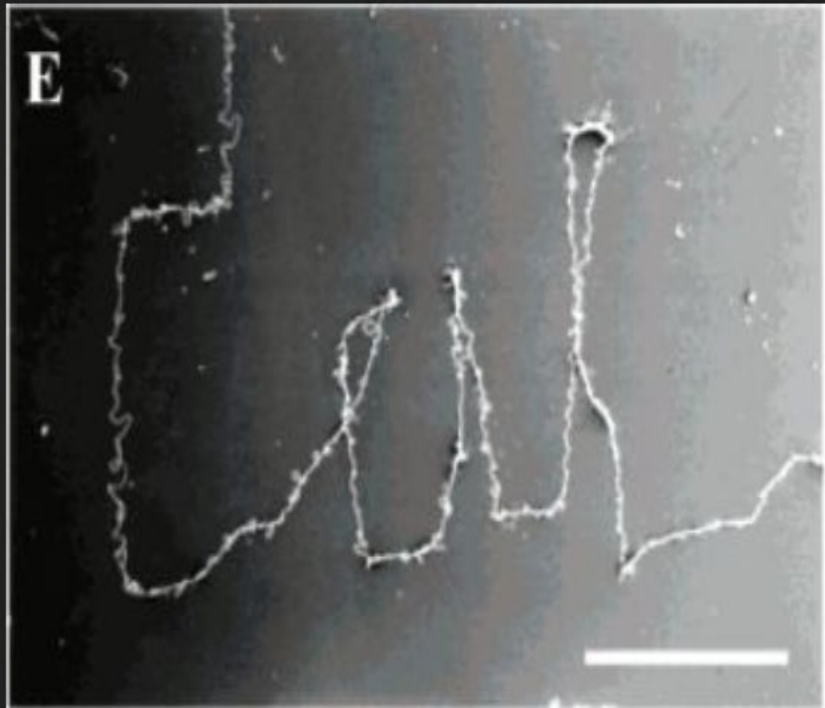
20 cm/s

# U-Shaped Nanofiber



- Produced in 3 motions: High-speed collector movement for the first branch and slower speeds for the second and third ones
- 0.5 sec between each branch create dots in corners
- Slower speeds of later branches meant to create and explore “local spiraling”
- “**Local Spiraling**” occurs when excess material is deposited in a location

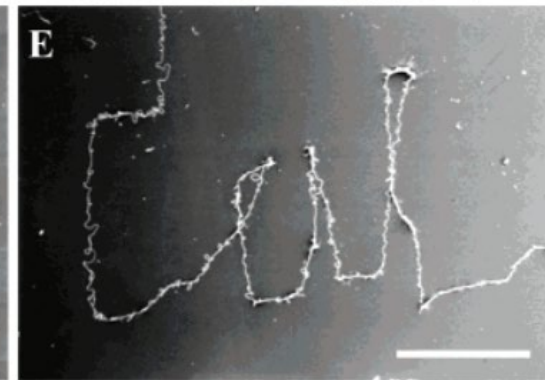
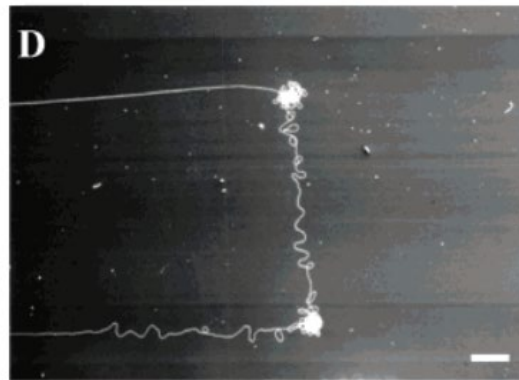
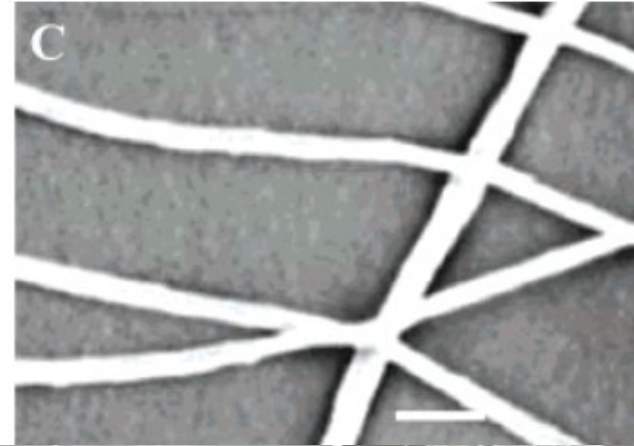
# Cal-Shaped Nanofiber Pattern



- More complicated geometry forces slower speeds
- Each character  $\sim 1 \times 2 \text{ mm}^2$  in size (Scale Bar: 1mm)
- Each character took  $\sim 1$  second to write
- Entire process was done in one NFES process

# Nanofibers Control

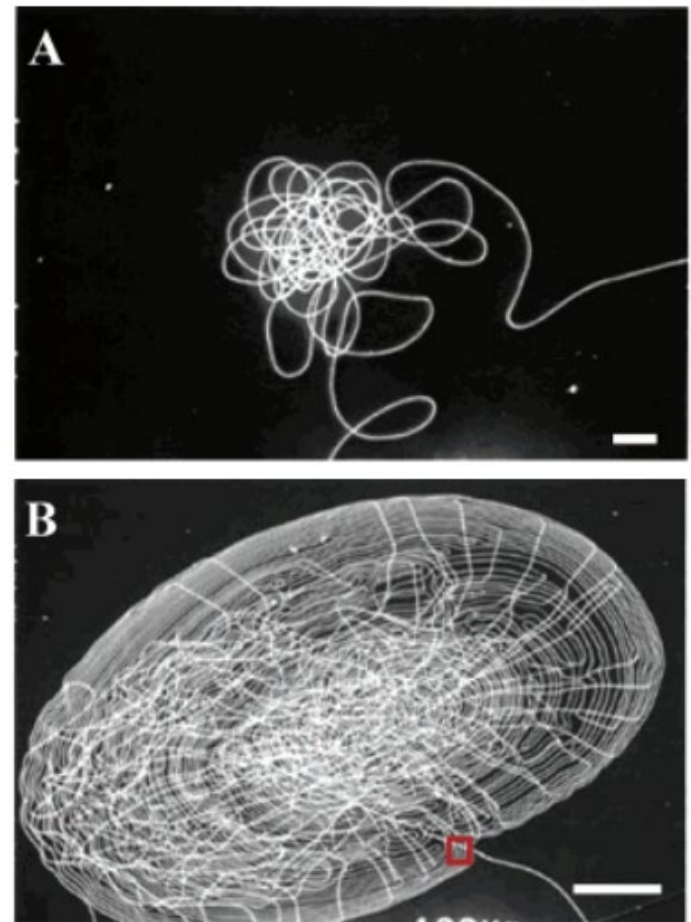
- Greater control when nanofiber electrospinning speed is faster than collector moving speed
- Local spiraling decreases as collector speed increases
- 1.5  $\mu\text{m}$ , typical distance between nanofibers with no external control





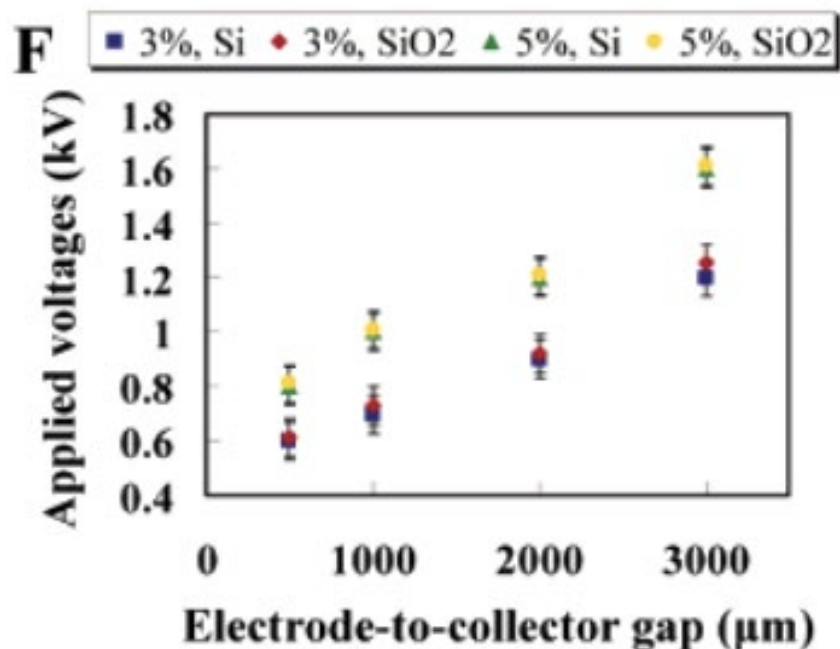
# Locational Accuracy

- Spinneret and collector held stationary, local spiraling due to electrical charge of nanofibers and self-repelling
- Traditional electrospinning creates a much more widespread result
- Figure A demonstrated radial spread of just 50  $\mu\text{m}$ , elliptical pattern of Figure B within 300  $\mu\text{m}$
- Suggests the ability for locational control on conductive collectors



# NFES Power Required

- Minimum required voltage increases as electrode-collector gap increases, or polymer solution concentration increases
- Silicon-oxide collectors require more voltage than just silicon
- Nominal polymer droplet diameter of 50  $\mu\text{m}$  utilized



# Experiment Conclusions

- Possible to deposit nanofibers with both pattern and location control
- Spiraling effects are minimized when the spinneret and collector have comparable speed
- Experiment factors include:
  - Viscosity, conductivity and surface tension of the polymer solution
  - Applied electrical field
  - Tip diameter of the spinneret
  - Size of the droplet
  - Temperature, humidity, and air velocity.

# Future of NFES

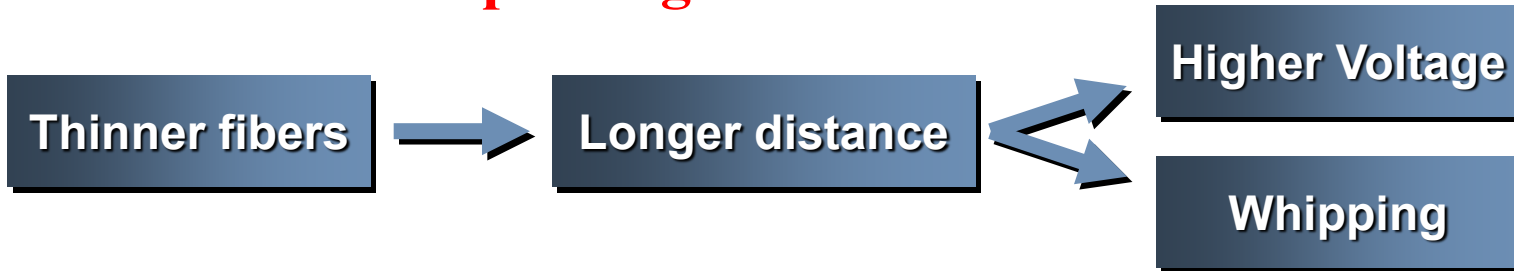
- Provides similarly effective, significantly less expensive alternative to industry standard lithography tools
- Potential use to integrate nanoscale devices in microelectronics and MEMS
- Formulate large area, nonwoven nanofibers



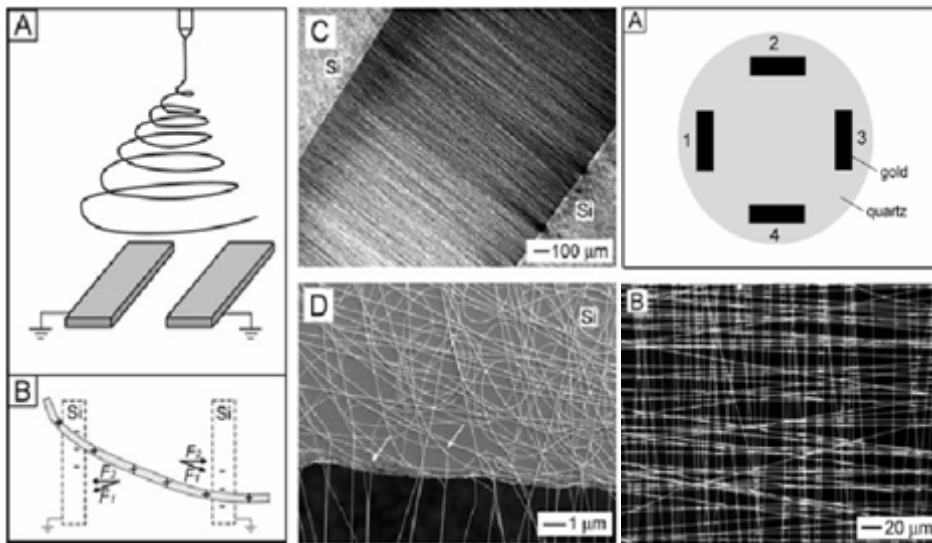


# What's the limitations?

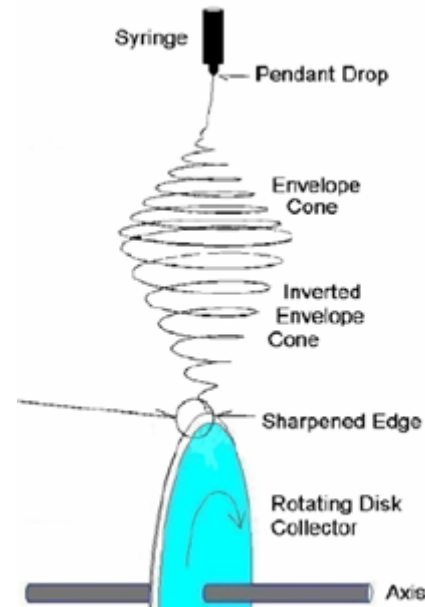
## Conventional Electrospinning for smaller fibers:



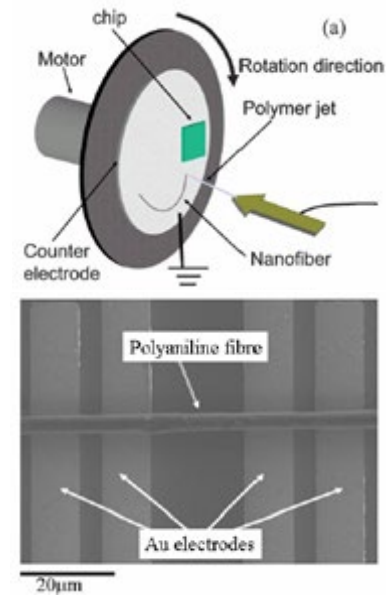
□ Alignment of nanofibers.



D. Li et al, 2004



A. Theron et al, 2001

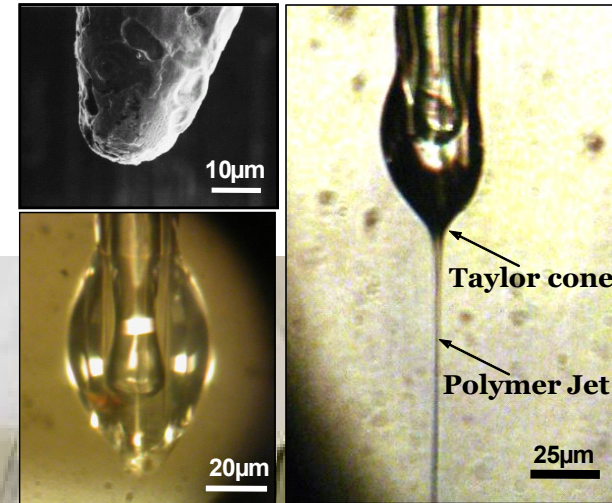
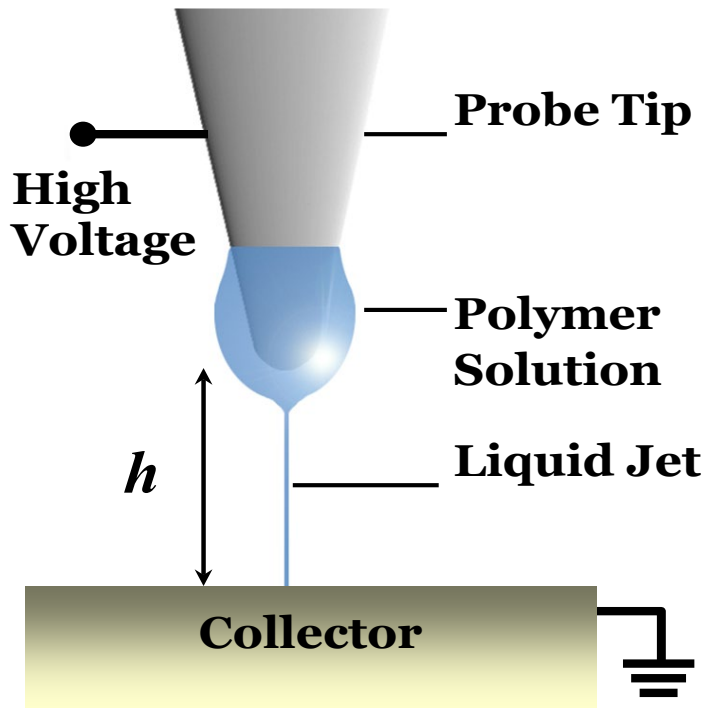


J. Kameoka et al, 2004




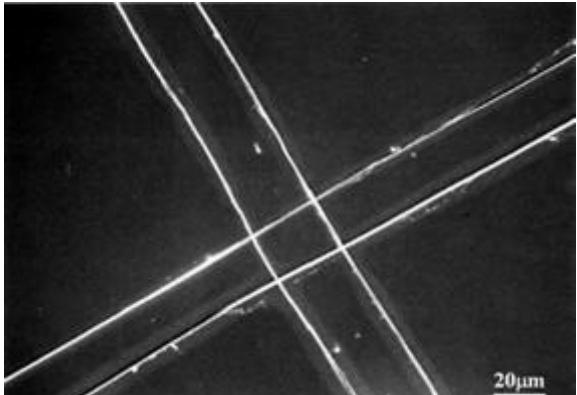
# Near-Field Electrospinning

- Electrode-to-collector distance: 500–1000  $\mu\text{m}$
- Drive voltage: 600–1500 V
- Tip diameter: 25  $\mu\text{m}$  or smaller



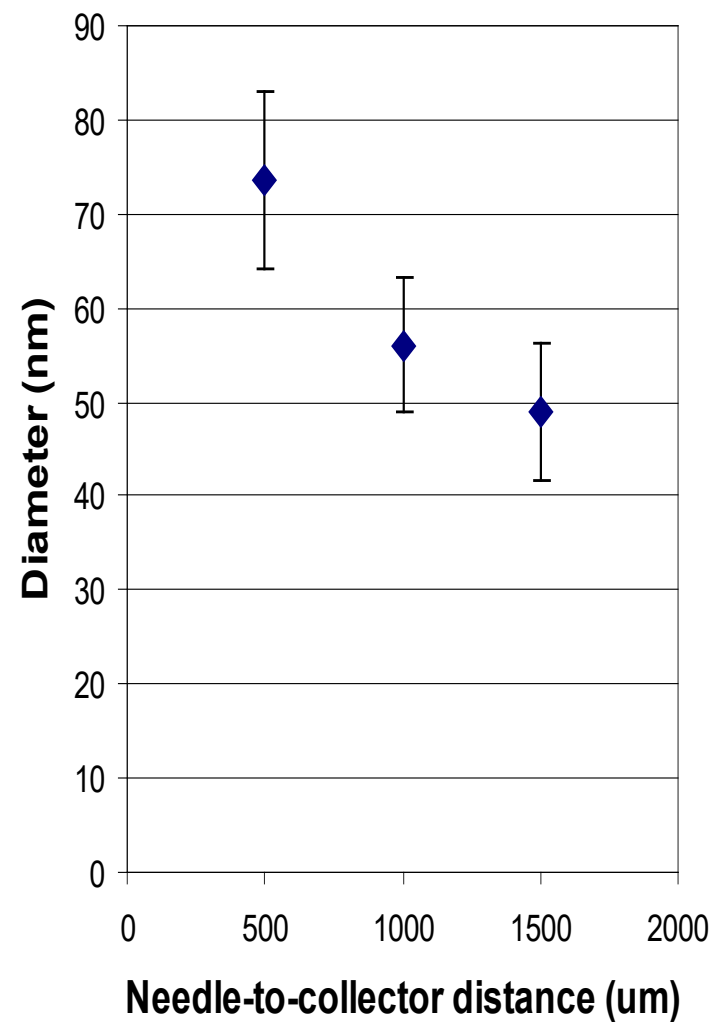
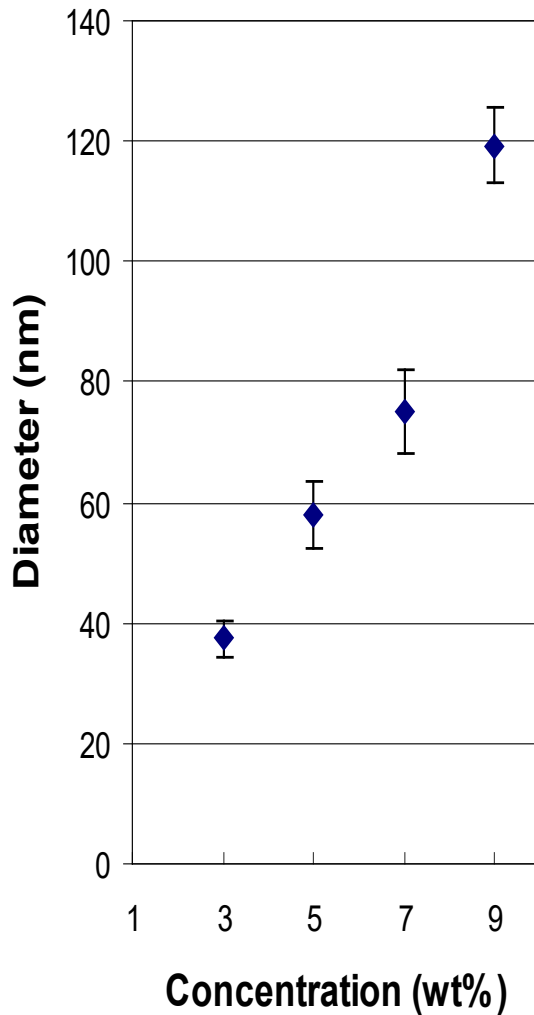
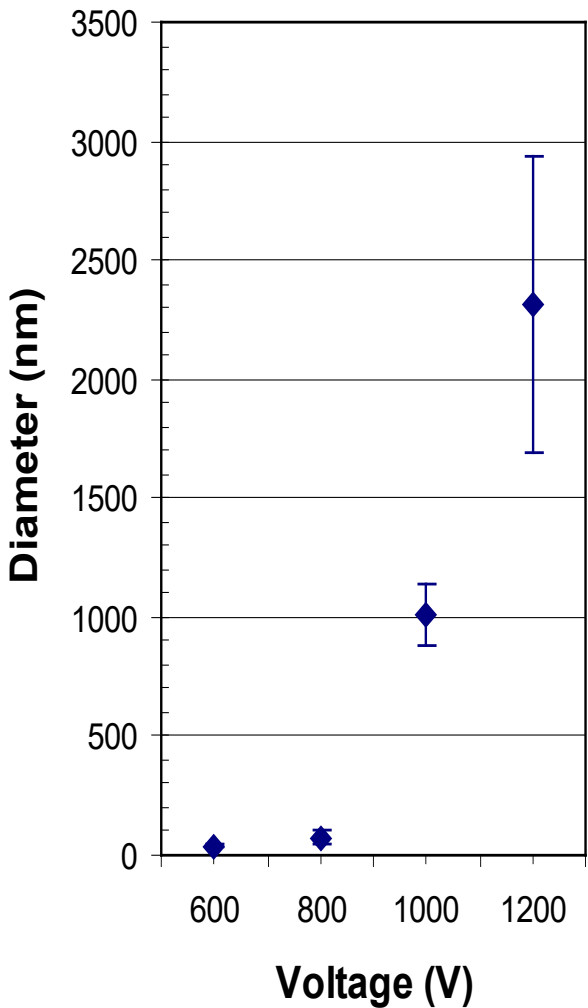


# Comparisons

<b>Conventional</b>	<b>Electrospinning</b>	<b>Near-Field</b>
<b>Needle</b>	<b>Spinneret</b>	<b>Metal probe tip</b>
<b>Several hundred <math>\mu\text{m}</math></b>	<b>Spinneret Diameter</b>	<b>25 <math>\mu\text{m}</math> or smaller</b>
<b>Continuous supply</b>	<b>Polymer Supply</b>	<b>Dip pen</b>
<b>10–30 KV</b>	<b>Applied Voltage</b>	<b>As low as 600 V</b>
<b>Very long</b>	<b>Nanofiber Length</b>	<b>Centimeter to meters</b>
<b>10–50 cm</b>	<b>Electrode-to-collector Distance</b>	<b>500–1000 <math>\mu\text{m}</math></b>
	<b>Controllability</b>	



# Characterizations

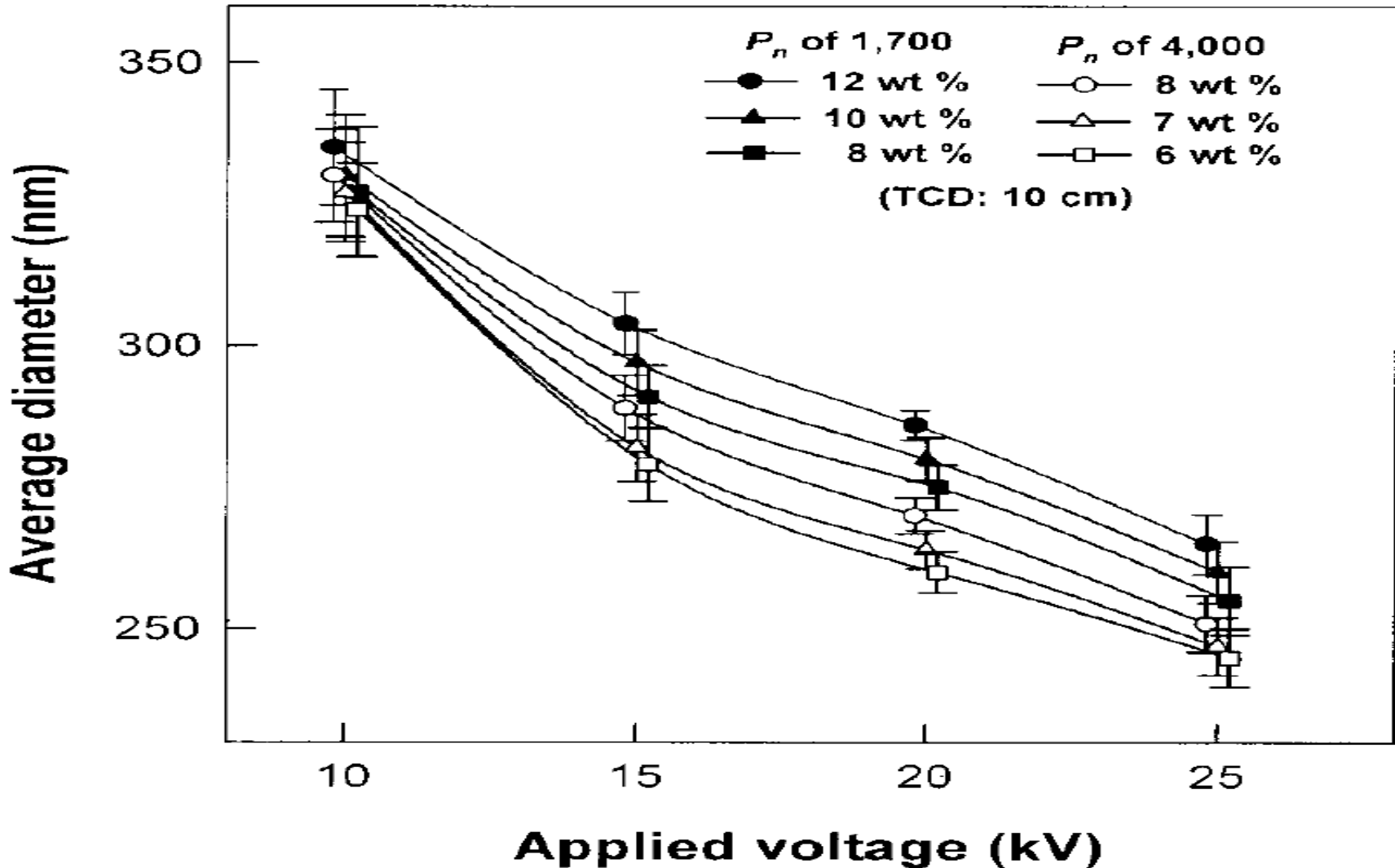






# Conventional Electrospinning

- J. S. Lee, K. H. Choi, H. Do Ghim, S. S. Kim, D. H. Chun, H. Y. Kim, and W. S. Lyoo, J. Appl. Polym. Sci. **93**, 1638 2004.





# Other Direct Write Deposition Methods

Microsystems Laboratory  
UC-Berkeley, ME Dept.

- DPN**
  - **Uses AFM to deliver collections of molecules**
  - **Better than 30nm line width**
- Inkjet printing**
  - **Large area, fast deposition**
- NFES complements the two for controllable sub-100nm fabrication**

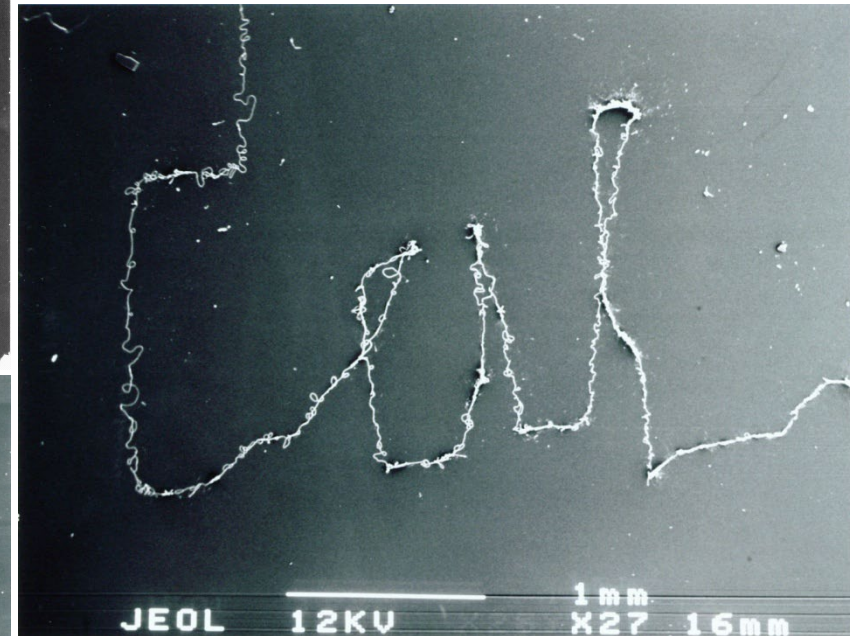
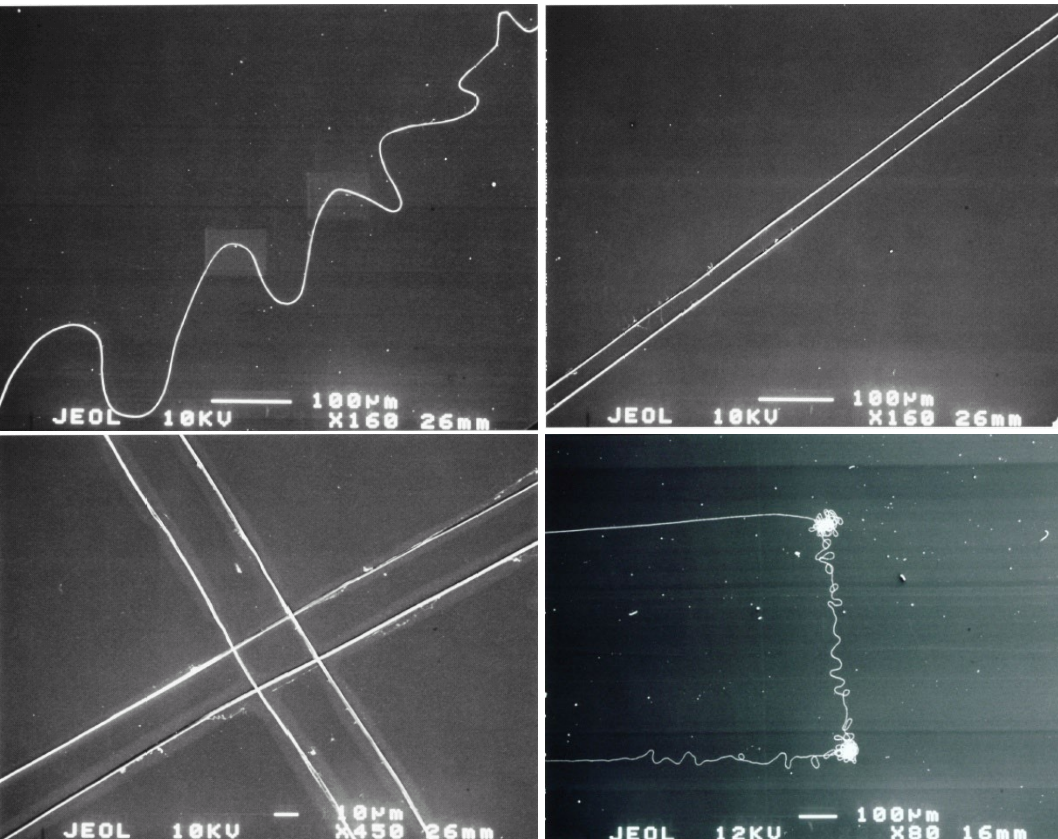
As soon as I mention this, people tell me about miniaturization, and how far it has progressed today. They tell me about electric motors that are the size of the nail on your small finger. And there is a device on the market, they tell me, by which you can write the Lord's Prayer on the head of a pin. But that's nothing; that's the most primitive, halting step in the direction I intend to discuss. It is a staggeringly small world that is below. In the year 2000, when they look back at this age, they will wonder why it was not until the year 1960 that anybody began seriously to move in this direction.

Richard P. Feynman, 1960



# Results & Limitations

- 3~7 wt % Polyethylene oxide (PEO)
- Nanofiber diameter: 50nm– 2 $\mu$ m
- **Manual control**

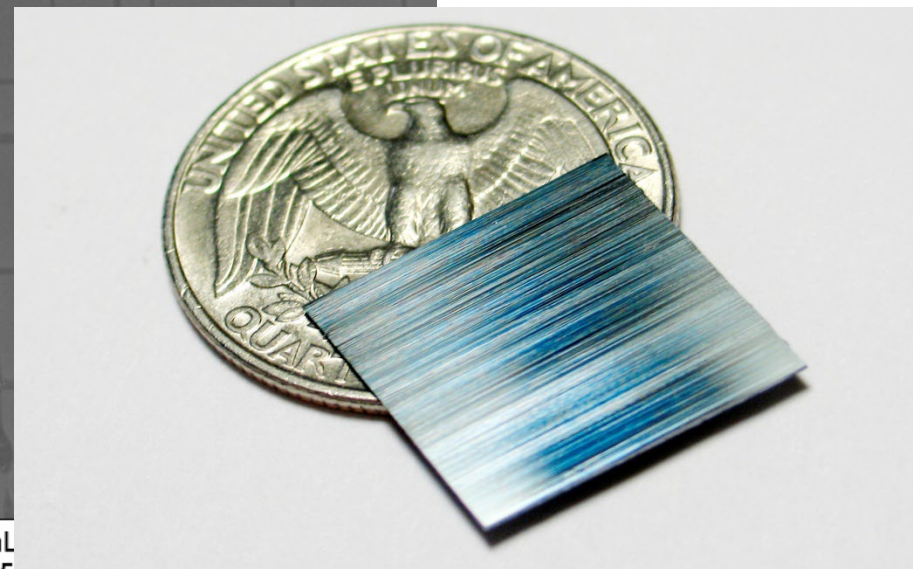
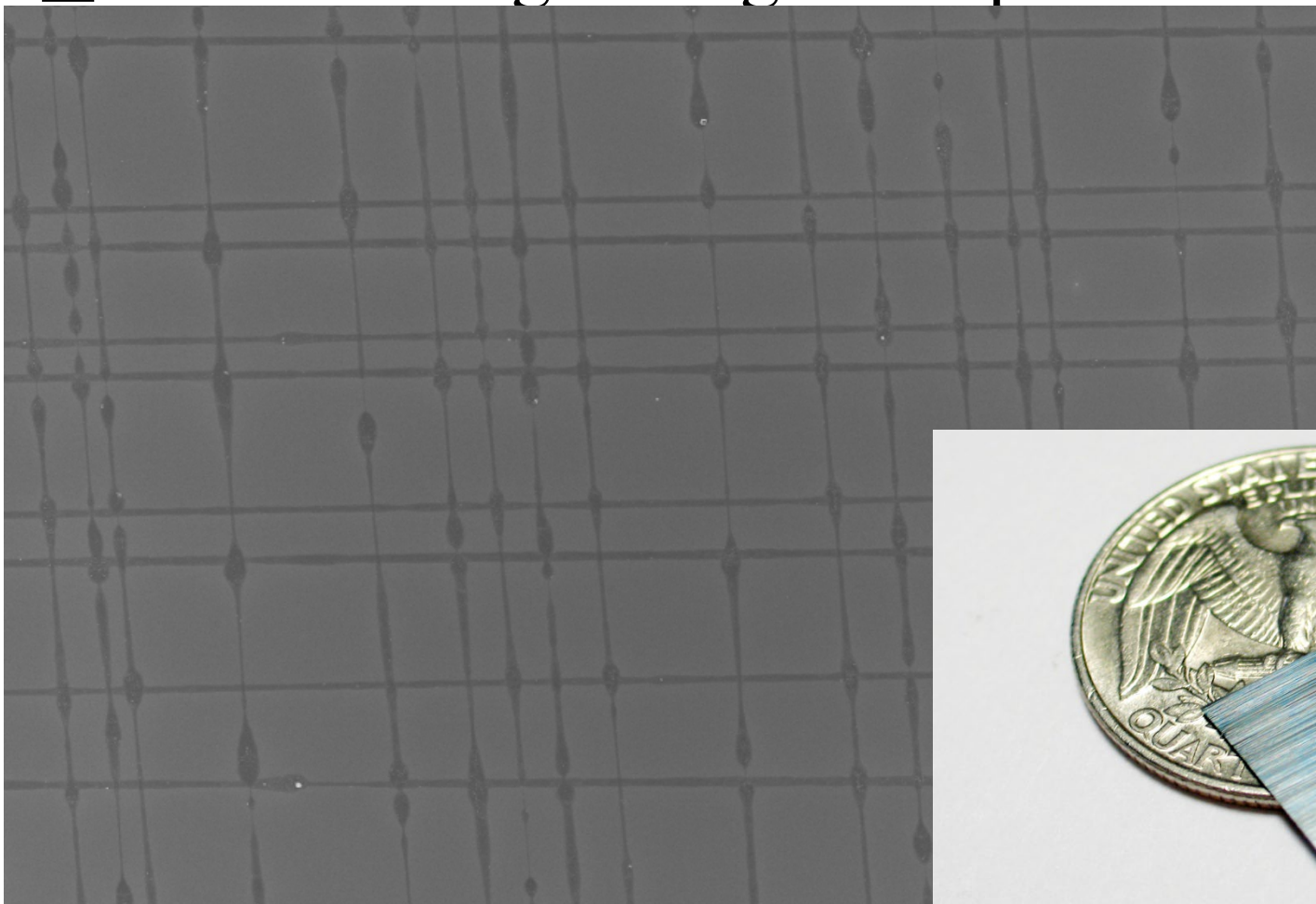




# Continuous Near-Field Electrospinning

Microsystems Laboratory  
UC-Berkeley, ME Dept.

- Direct writing of large area patterns



Mag = 132 X      100µm      EHT = 5.00 kV      Signal A = InL  
WD = 5 mm      Photo No. = 551      Time: 20:38:49



# Large Area Deposition

- A single nanofiber in a designed trajectory
  - 4X4 cm<sup>2</sup> area
  - 15 min deposition period for a total length of 108 m, nanofiber has a diameter of 700 nm

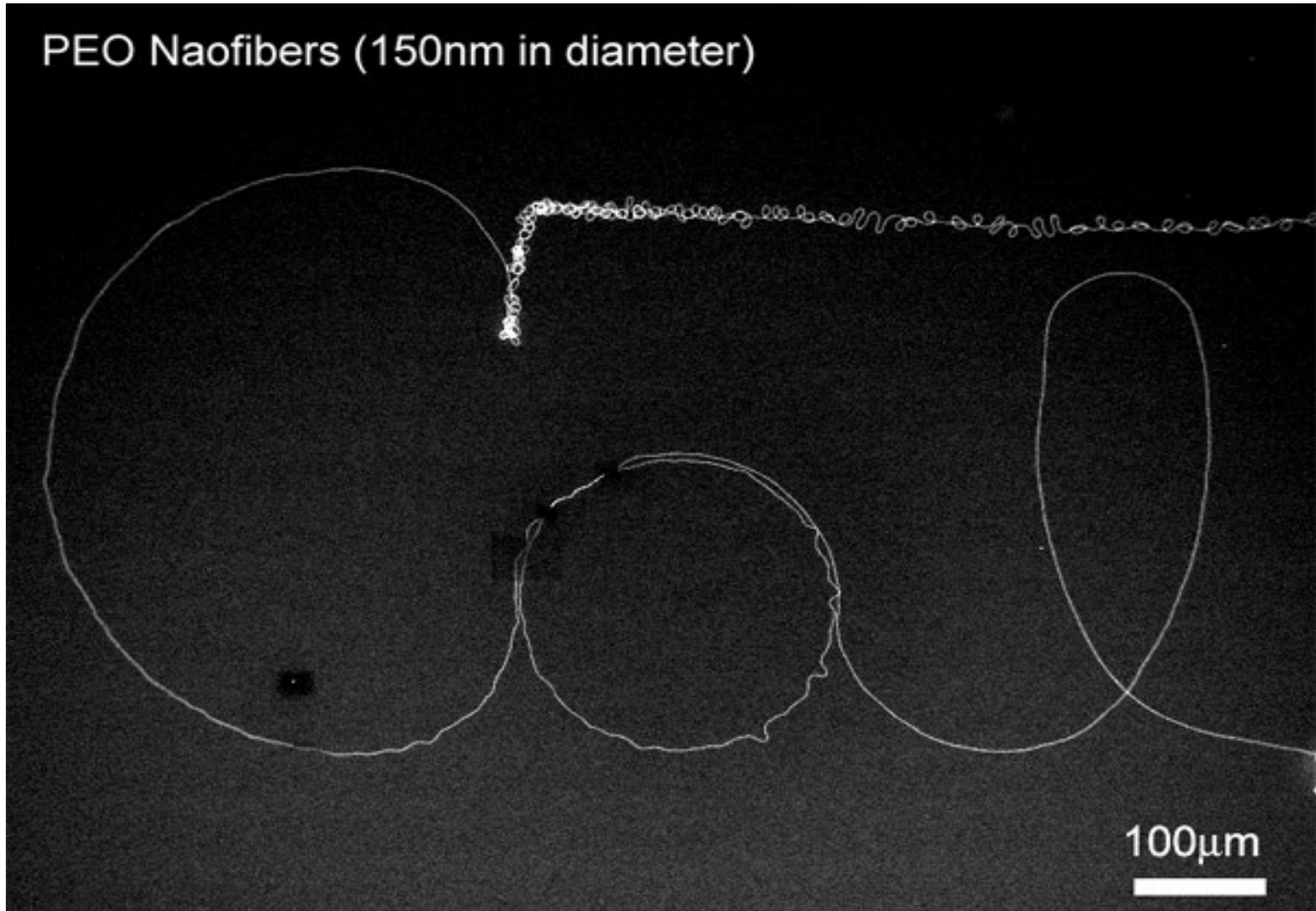






# Potential

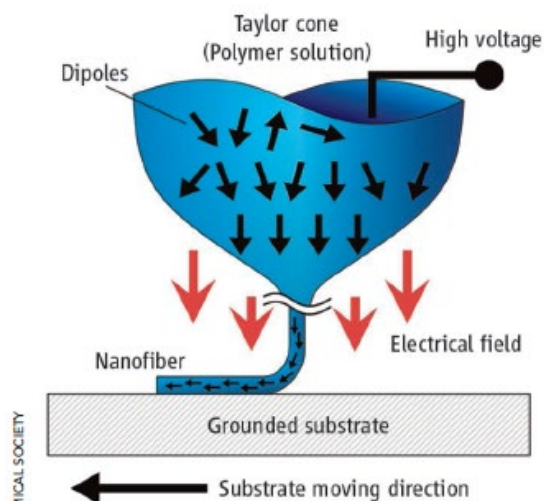
## □ Machine-controlled electrospinning



## ENGINEERING

# Nanogenerators Tap Waste Energy To Power Ultrasmall Electronics

Tiny devices that convert movements into electricity won't power cities. But they may soon be efficient enough to power arrays of invisible sensors and hand-held electronics

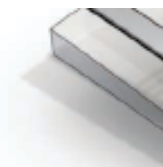


**Power threads.** A large electric field orients electric dipoles in a polymer being drawn into fibers.

ERICAN CHEMICAL SOCIETY

on that goal. At the University of California, Berkeley, another nanogenerator group, headed by mechanical engineer Liwei Lin, is making nanogenerators out of long polymer fibers that one day may be woven into cloth. “This technology could eventually lead to wearable ‘smart clothes’ that can power hand-held electronics through ordinary body movements,” Lin says.

For their nanogenerators, Lin and his colleagues start with a polymer called polyvinylidene fluoride (PVDF) that can be processed to separate electrical charges. Other groups have previously made PVDF generators from thin films of the polymer. But PVDF films are typically inefficient, converting only 1% to 2% of kinetic energy to electricity. Lin and his colleagues also reported in the 10 February issue of *Nano Letters* that when they used a technique called electrospinning to spin PVDF into threadlike fibers as little as 500 nanometers across, the resulting fibers converted 10





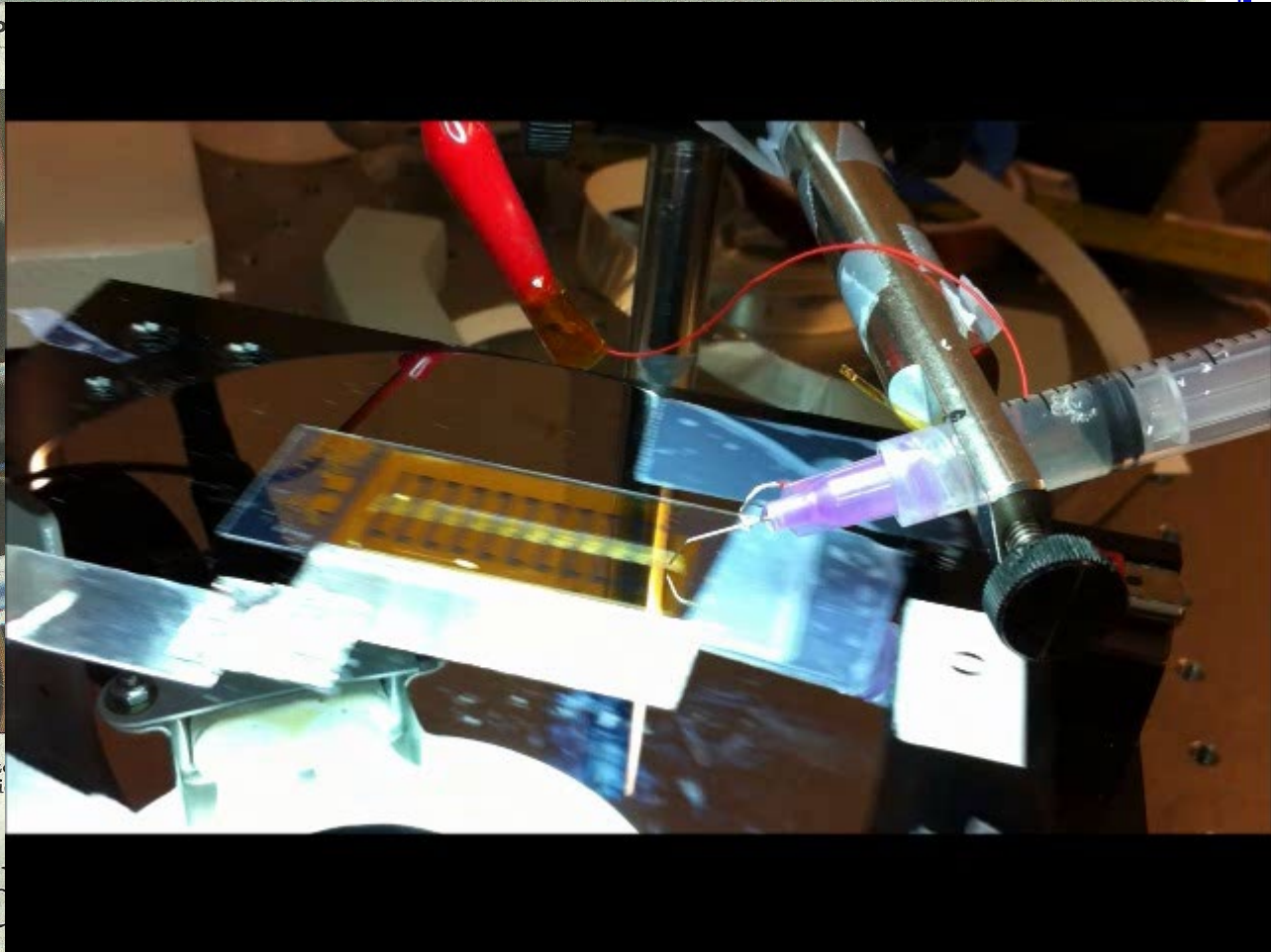
# BUSINESS

THURSDAY, MAY 20, 2010 :: LATIMES.COM/BUSINESS

DOW 10,444.37 ▼ 66.58 | S&P 500 1,115.05 ▼ 5.75 | NASD



**ENERGIZER:** UC Berkeley professor Liwei Lin works in his laboratory. Lin and his team are developing the microscopi



## Ragged stock

American Apparel's share price, weekly closes and latest



## TECHNOLOGY

# One of the things that may power your iPod

Employees' Retirement System board, said the fund needs to assess the consequences of the huge hike on California





# How Does It Work?

## □ Piezoelectric Property of PVDF

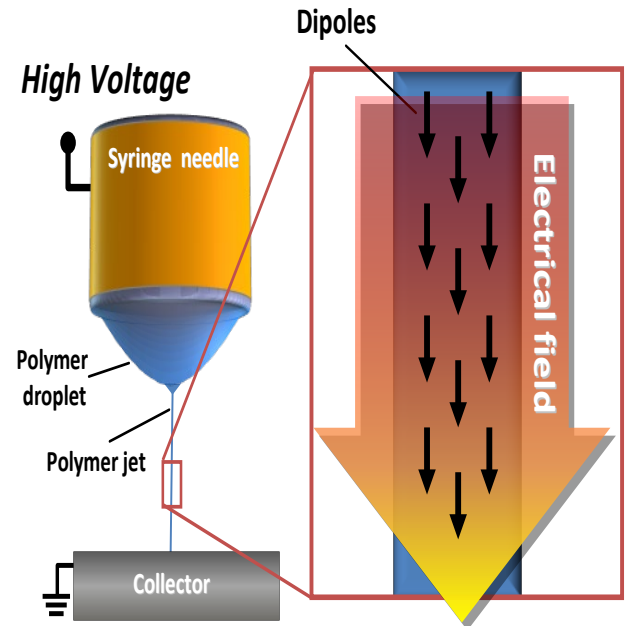
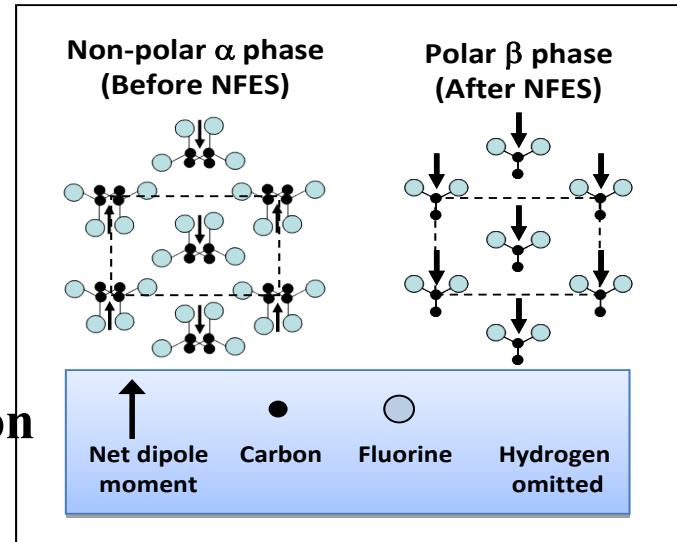
- Mechanical Strain  $\leftrightarrow$  Electrical Potential
- PVDF exists in several forms:  $\alpha$ ,  $\beta$ , and  $\gamma$  crystalline phases
- $\beta$  phase is primarily responsible for piezoelectric properties  $\rightarrow$  **Dipole orientation**

## □ Poling process

- Bulk or thin film PVDF
  - Stretching and strong electric field

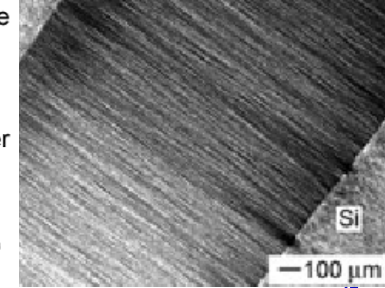
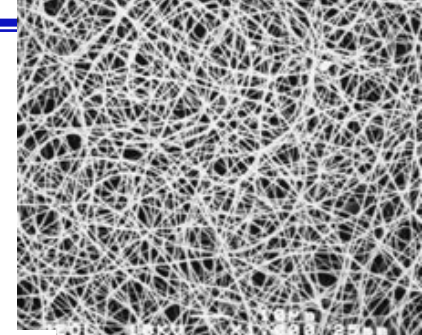
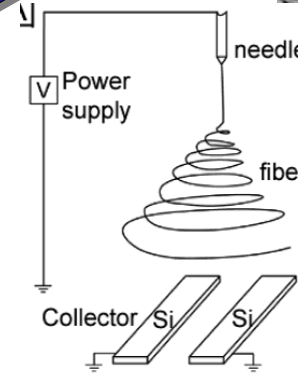
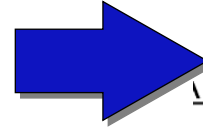
## □ Electrospinning $\rightarrow$ In-situ poling process

- Electrospinning of PVDF from its solutions promoted the formation of  $\beta$  phase.
- In contrast, only the  $\alpha$  and  $\gamma$  phases were detected in the spin-coated samples from the same solutions

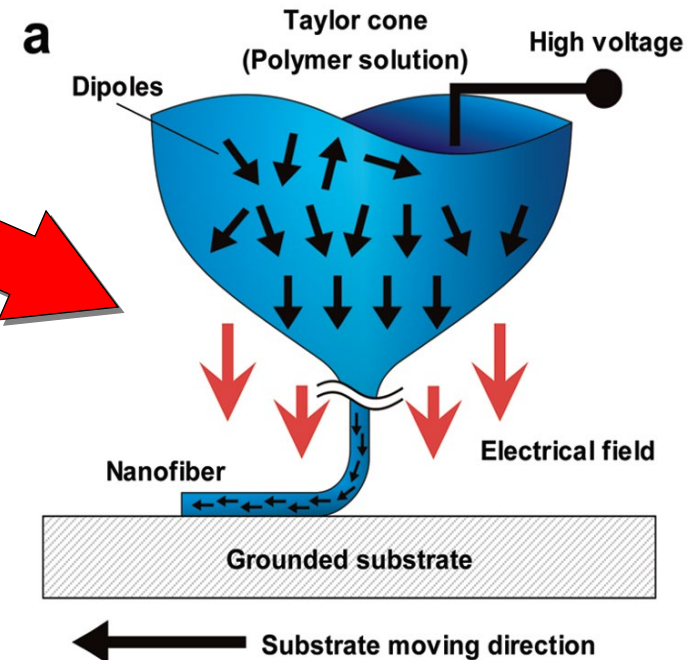
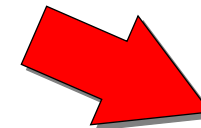


# What's the Challenge?

- **Conventional electrospinning**
  - Random orientation
    - The polarities of these nanofibers mostly cancel out each other and the net piezoelectric output is close to zero



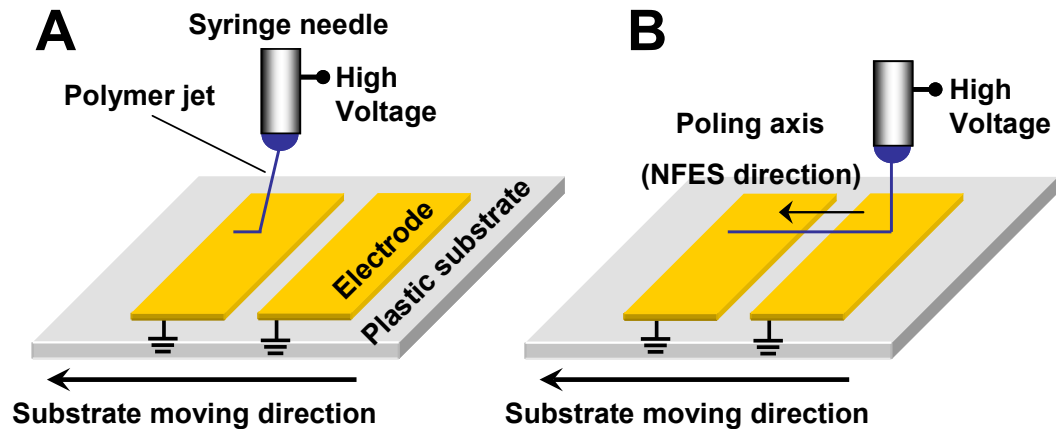
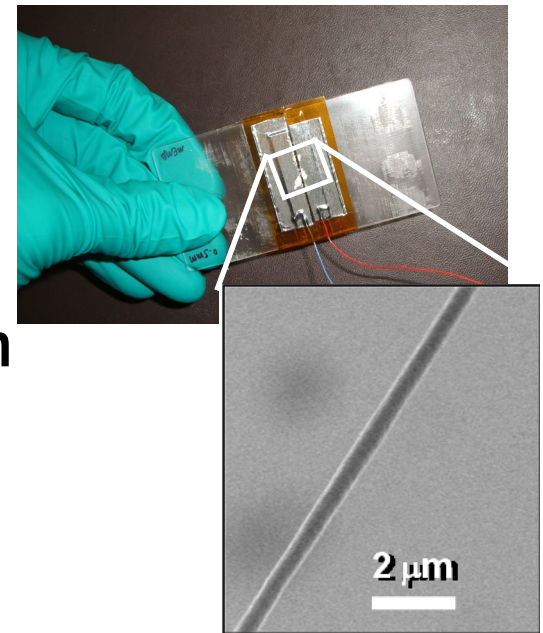
- **Near-field electrospinning**
  - Orderly nanofiber patterns with controlled direction of polarity



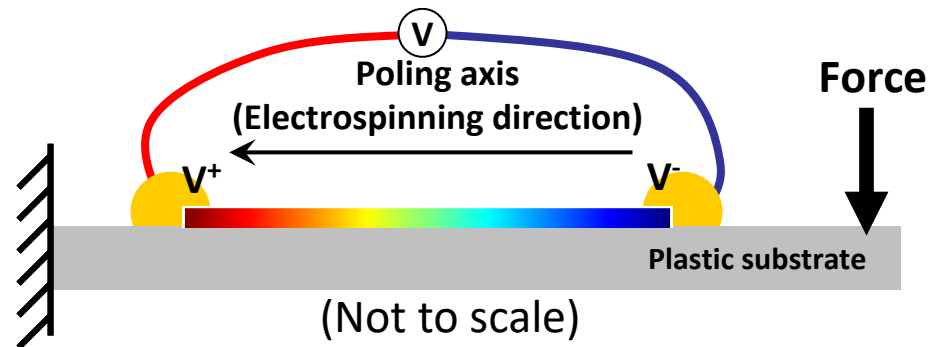
# PVDF Nanogenerator

*Nanoletters*, Vol. 10, pp. 726-731, 2010

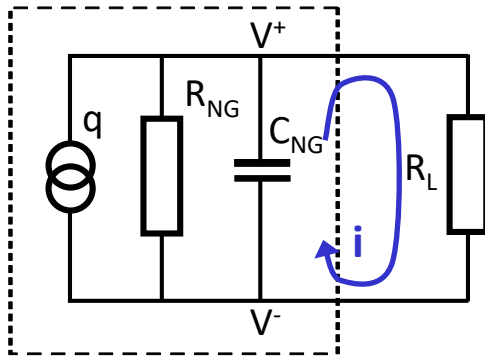
- Fabrication process
  - Spacing between electrodes: 100~500 $\mu\text{m}$
  - Fiber diameter: 500nm~3 $\mu\text{m}$



- Experimental setup
  - Inside a Faraday cage



# Mechanism - Piezoelectric Response

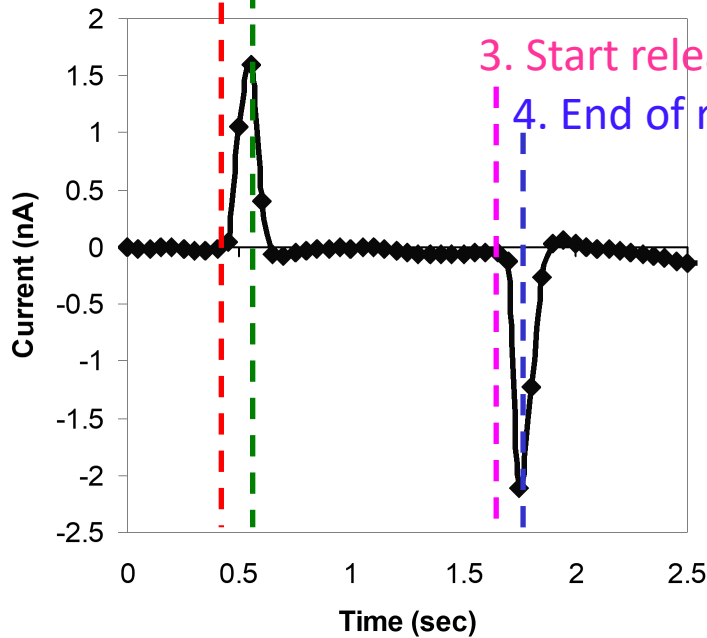


1. Start stretching

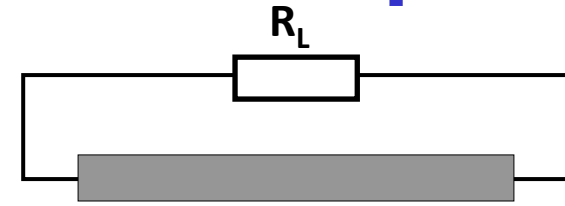
2. Hold stretching

3. Start releasing

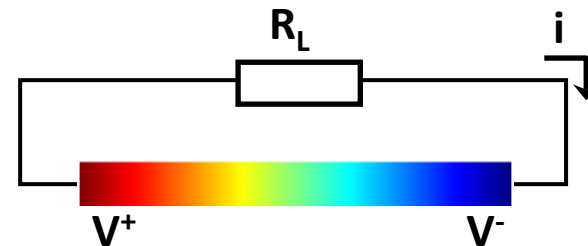
4. End of release



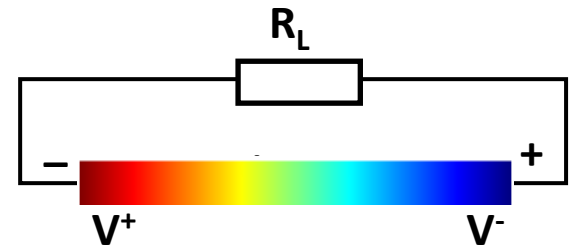
1.



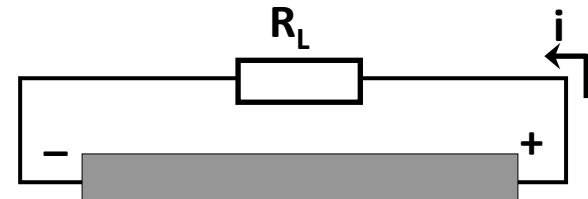
2.



3.



4.



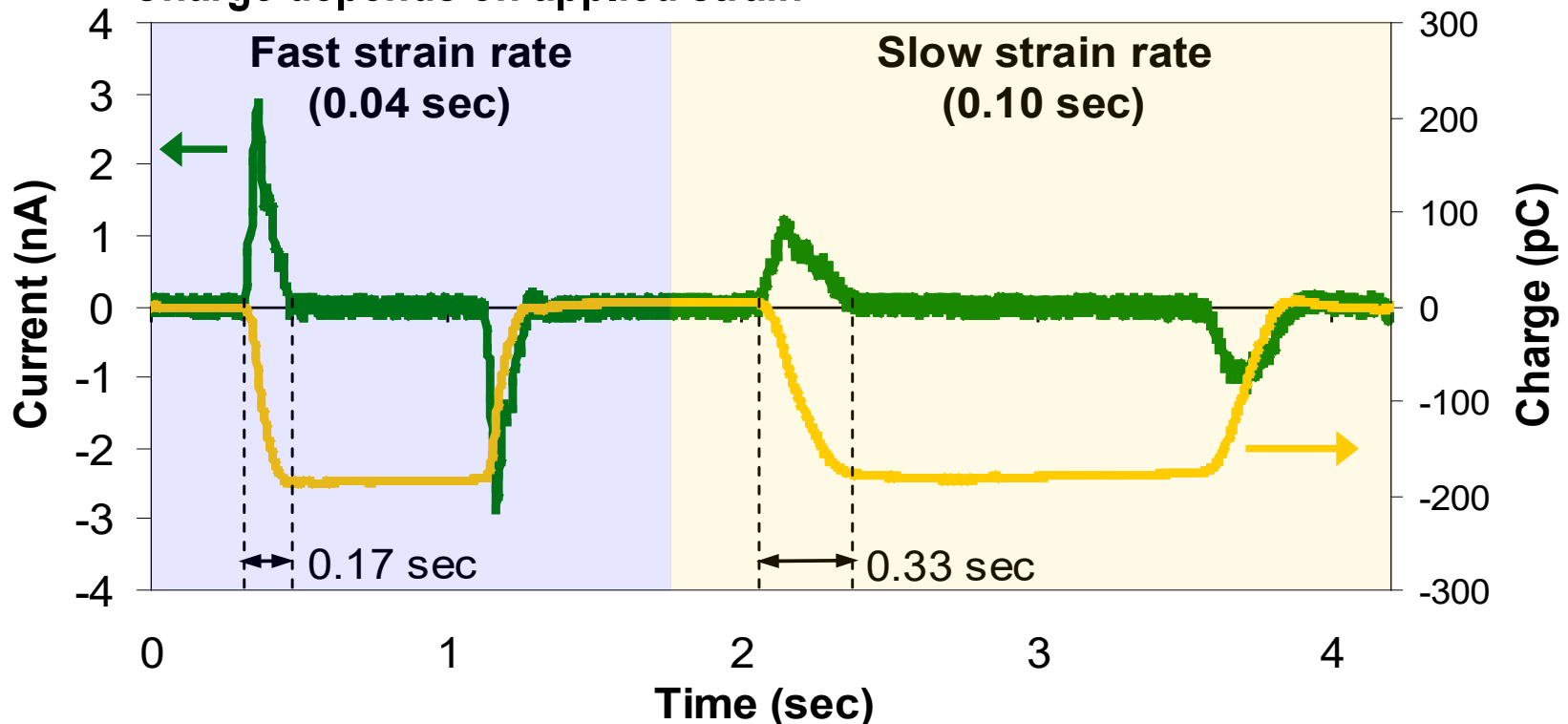
# Effect of Strain Rate

- The current generated by strain in poling direction

$$i = \dot{q} = d_{33}EA\dot{\epsilon}$$

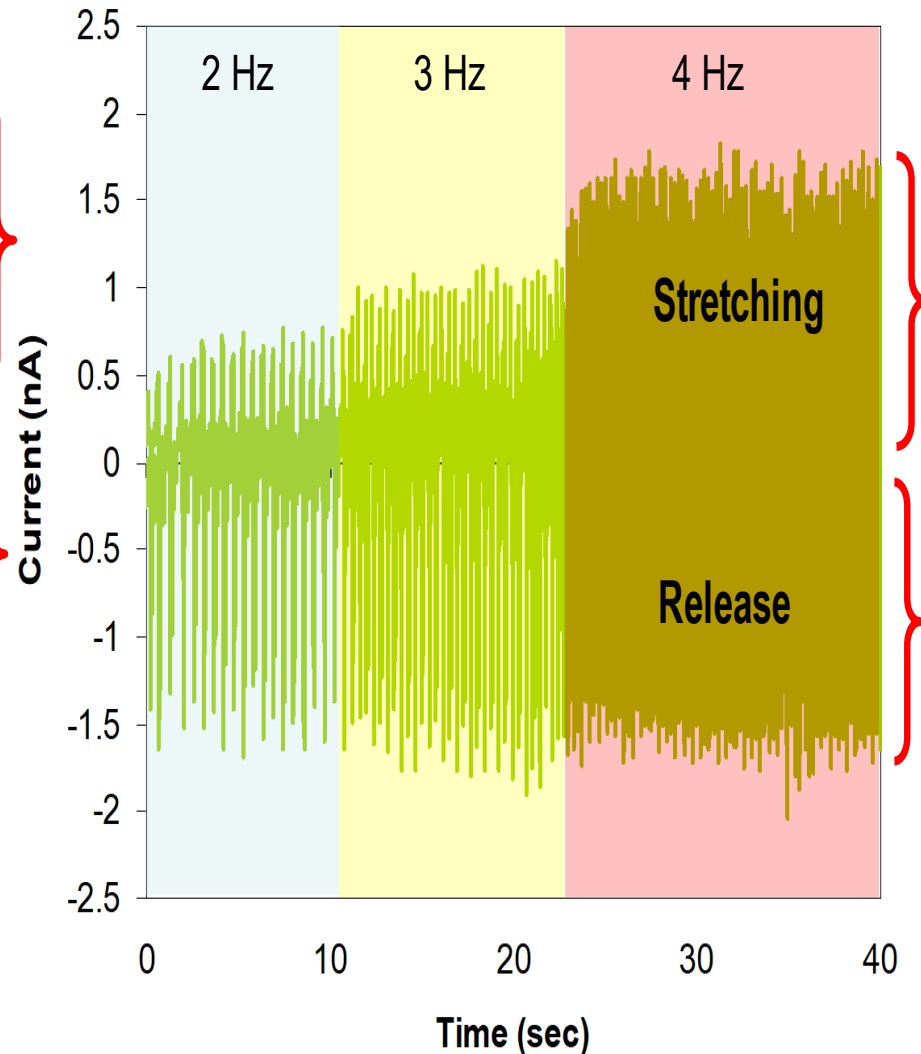
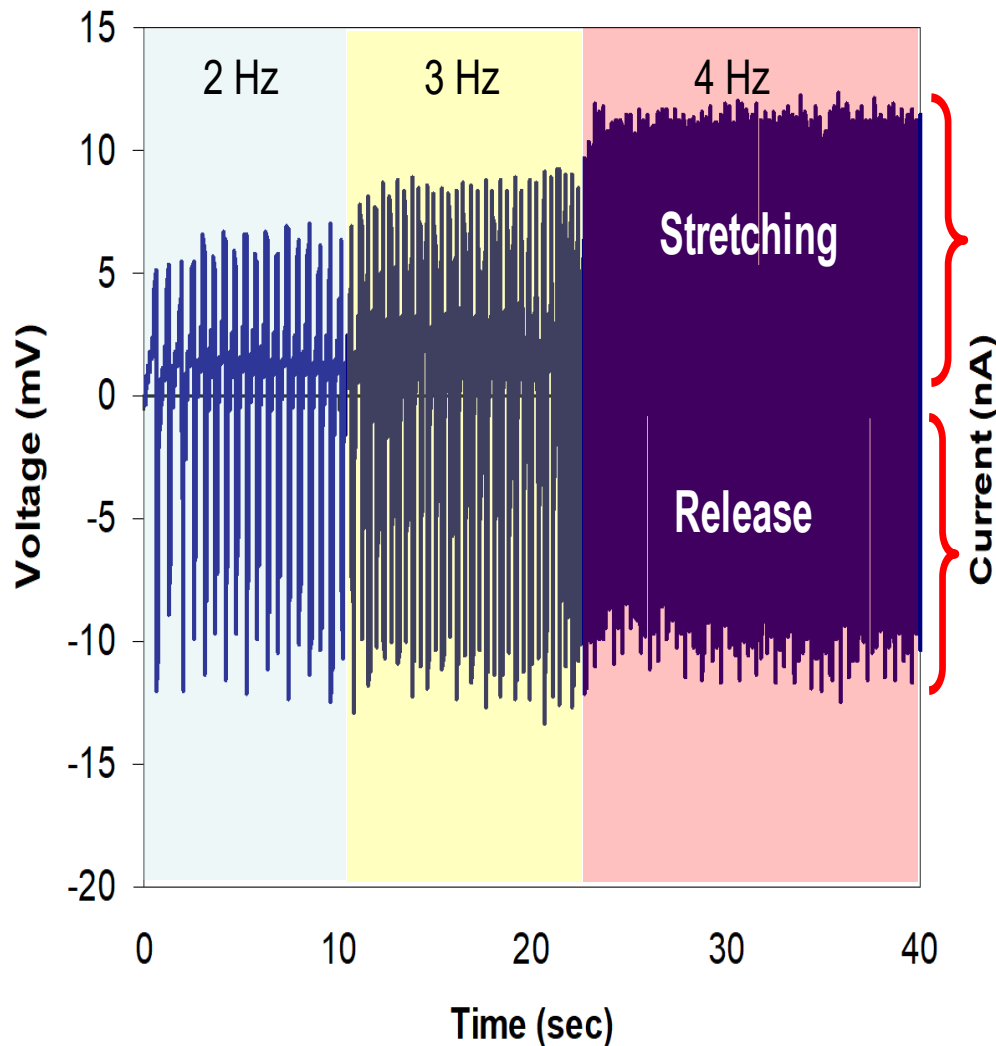
$d_{33}$ : piezoelectric constant      E: Young's modulus      A: cross sectional area

- Current output depends on strain rate
- Charge depends on applied strain



# Effect on Stretching Frequency

- Higher frequency → Higher electric output



# Long Term Stability Test

- 0.04% strain applied at a frequency of 0.5Hz for 100 min

