Introduction to Nanotechnology and Nanoscience – Class#20

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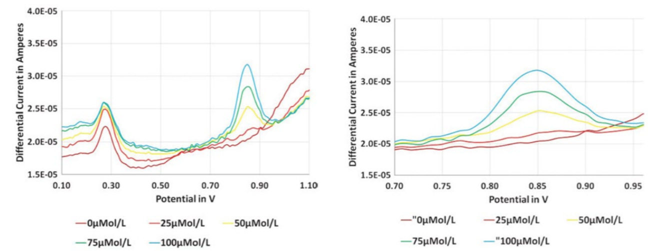
Outline

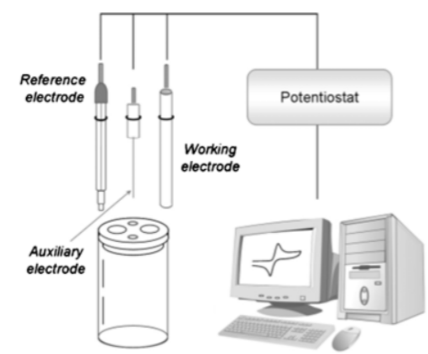
- Electrospinning video
- Small Project Presentations
- Electrospinning Process
- Paper #9

Square Wave Voltammetry for UTI detection from Urine Sample

Ibad Ali
Mohamed Mouhab

- Presence of nitrite in urine is often a sign of a urinary tract infection
- SWV are sensitive to electrode kinetics thus 3 different electrodes are used to determine nitrite presence.
    - Working electrode (pencil lead) coated with MWCNT solution
    - Reference electrode (Ag/AgCl 0.1 M KCl)
    - Auxiliary electrodes (Platinum Wire)
- Other chemicals such as phosphates can be tested for by adjusting the CNT coated electrode.

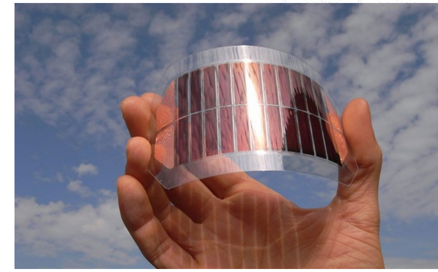




Wendler, Frank, Aurosmit, Paul and Kanoun, Olfa. "CNT-enhanced carbon electrode for nitrite detection and water analysis". *Impedance Spectroscopy: Advanced Applications: Battery Research, Bioimpedance, System Design*, edited by Olfa Kanoun, Berlin, Boston: De Gruyter, 2019, pp. 143-150. https://doi.org/10.1515/9783110558920-014

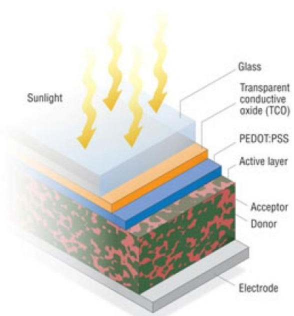
CNT applications in Organic Photovoltaics

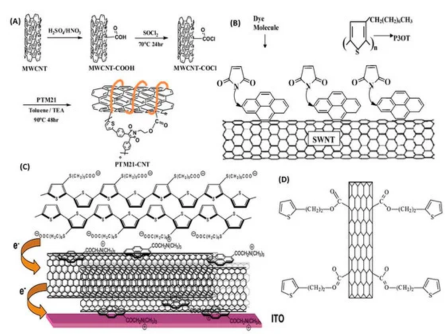
Andrew Cheng, ME 118/218



Problems with ITO electrodes

- Incompatibility with polymer substrates
- Unfavorable mechanical properties
- Limited supply of indium



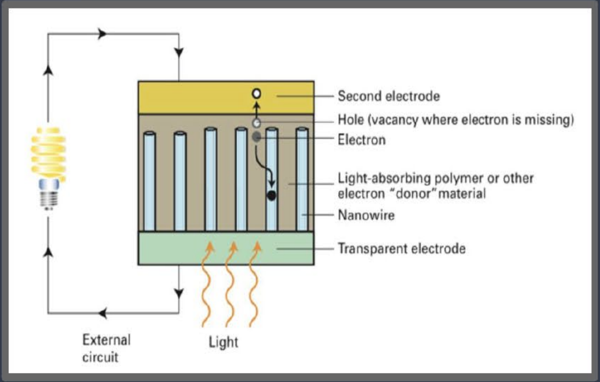


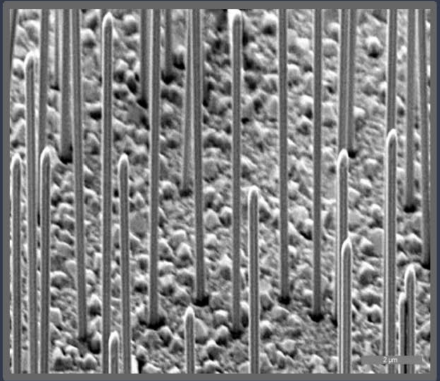
CNT proposal

- Conductive CNT coatings as an alternative to ITO electrodes
- CNTs are transparent, highly conductive, and have high mechanical robustness
- Tunable properties

SWCNT thin films with desirable electrical properties used for hole collection in OPV devices

- *Molecules* **2014**, *19*(11), 17329-17344; **https://doi.org/10.3390/molecules191117329**





Nanowires in Flexible Solar Cells

Problems with Flexible Solar Cells:

- Lower efficiency than rigid solar cells due to less material
- Less durable than rigid solar cells due to their flexibility
- Less power output due to less efficient semiconductor materials

Solutions with Nanowires:

- Use graphene as electrode to replace typical ITO electrode
  - Highly conductive, flexible, robust, and transparent
  - Can attach silicon layer with SiO_2 doping
- Use Gallium arsenide (GaAs) nanowires for donor material
  - More efficient and cheaper than bulk gallium arsenide
  - Can be grown on silicon and even graphene in the future
  - Would allow for layered construction of solar cells
  - More surface area contact with surrounding polymer
  - Polymer would help support delicate nanowires
- Using nanowires for power transmission could lead to smaller size required, allowing for more supporting material

1. *Nanowires and graphene: Keys to low-cost, flexible solar cells, Nancy W. Stauffer*
2. *Nanowires Can Make Solar Panels More Efficient and Cheaper, Redaksjonen Gemini*
3. *Build a Rigid–Flexible Graphene/Silicone Interface by Embedding SiO2 for Adhesive Application, ACS Publications 10.1021/acsomega.7b00017*
4. *Flexible Solar Cells Made of Nanowires/Microwires*
5. *Author links open overlay panel, Jongseung Yoon 1, Yugang Sun 2, John A. Rogers 3*

Filter for blood with Viruses

Problem

- People with viruses cannot donate blood (Hepatitis, HIV/AIDS, Ebola, etc)
- A large population of people cannot donate
- Rare types of blood become even harder to find
- Virus tests can have false negatives

Possible Solution

- Carbon nanotube membranes with highly aligned, low-friction, straight-channels and narrow pore-diameter distributions (0.5-4.5 nm) have been used for hemodialysis
- The smallest viruses measure around 20 nm in diameter
- We can use the same membrane to filter this viruses!
- Allows people with viruses to donate their blood

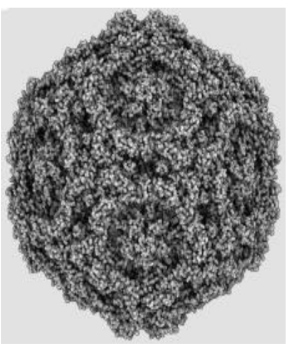
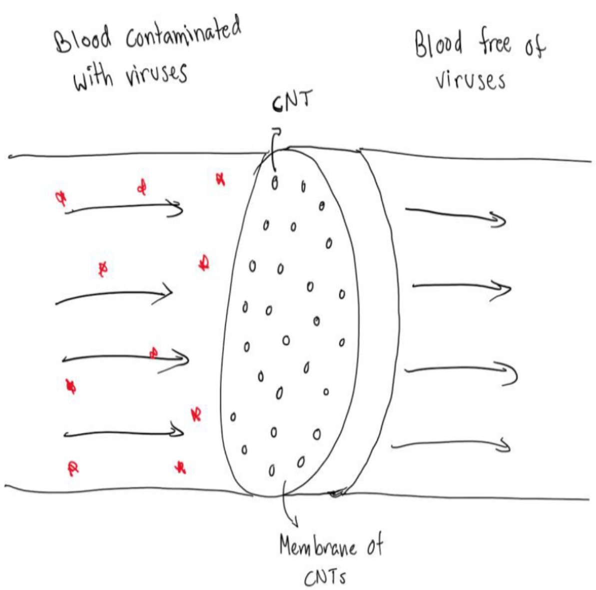


Figure 1: 3D surface reconstruction of the Human Hepatitis B virus.
Illustrations created with QuteMol (IEEE. Trans. Vis. Comput. Graph 2006, 12, 1237–44) using 2G33 (J. Virol. 2006, 80, 11055–61), 1S58 (Proc. Natl. Acad. Sci. U. S. A. 2004, 101, 11628–33), 1K4R (Cell 2002, 108, 717–25), and 1IHM (Science 1999, 286, 287–90) PDB assemblies.



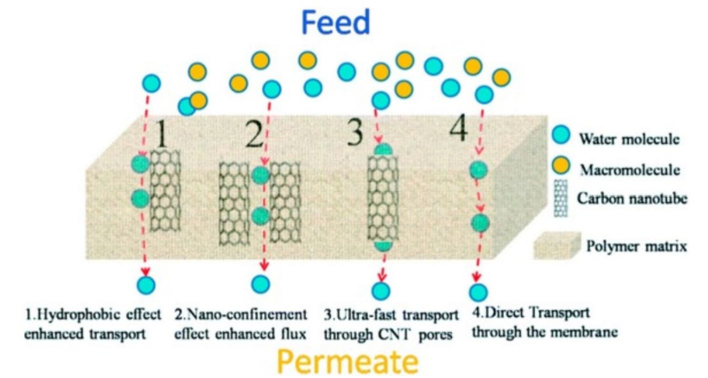
Assumptions

- The viruses will not go through the CNT as the CNT has a smaller diameter
- Important molecules pass easily through the CNT
- The filtration rate of blood is large enough to be useful

1. Louten J. Virus Structure and Classification. Elsevier eBooks [Internet]. 2016 Jan 1 [cited 2024 Mar 18];19–29. Available from: https://www.ncbi.nlm.nih.gov/pmc/articles/PMC7150055/#:~:text=The%20smallest%20of%20viruses%20are,viruses%20that%20are%20infecting%20them.
2. Can I Donate Blood If I Have a Tattoo or Body Piercings? [Internet]. Redcrossblood.org. 2023 [cited 2024 Mar 18]. Available from: https://www.redcrossblood.org/local-homepage/news/article/donor-eligibility-tatoos-piercings-rcbs.html#:~:text=Three%2DMonth%20Waiting%20Period,C%20with%20several%20different%20tests.
3. Cheng P, Ferrell N, Öberg CM, Buchsbaum SF, Jue ML, Sei Jin Park, et al. High-Performance Hemofiltration via Molecular Sieving and Ultra-Low Friction in Carbon Nanotube Capillary Membranes. Advanced Functional Materials [Internet]. 2023 Aug 27 [cited 2024 Mar 18];33(50). Available from: https://onlinelibrary.wiley.com/doi/10.1002/adfm.202304672

Water purification by Vertically alligned carbon nanotube (VACNT) membranes

- Adam Pawel Kosinski



- **Benefits for drinking water filtering :**
  - Tremendous separation performance
  - Low bifouling potential (inactivates bacteria)
  - Ultra-high water flux
- **Issues involve:**
  - CNTs are hydrophobic → Fouling of the membranes
  - Low rejection of small organics and ions (even using SWNTs)
- **Proposal:**
  - Charging surfaces, as rejection coefficient R_{Donnan} depends on the ion concentrations (c_a^b):

$$\mathrm{R}_{\mathrm{Donnan}} = \left(1 - \frac{\mathrm{c}_\mathrm{i}^\mathrm{m}}{\mathrm{c}_\mathrm{i}}\right) = \left(1 - \left(\frac{|z_i|\mathrm{c}_\mathrm{i}}{|z_i|\mathrm{c}_\mathrm{i}^\mathrm{m} + \mathrm{c}_\mathrm{x}^\mathrm{m}}\right)\left|\frac{z_i}{z_j}\right|\right)$$

  - Growth of CNTs using CVD and graft polymerization method (adding functional groups) for improval
  - Additional idea: Using acoustic waves (e.g. ultrasound) to induce cavitation generating jets, clearing the pores

Sources:

1. Fornasiero, F., Park, H. G., Holt, J. K., Stadermann, M., Grigoropoulos, C. P., Noy, A., & Bakajin, O. (2008). Ion exclusion by sub-2-nm carbon nanotube pores. *Proceedings of the National Academy of Sciences*, 105(45), 17250–17255. https://doi.org/10.1073/pnas.0710437105
2. Park, S.-M., Jung, J., Lee, S., Baek, Y., Yoon, J., Seo, D. K., & Kim, Y. H. (2014). Fouling and rejection behavior of carbon nanotube membranes. *Desalination*, 343, 180–186. https://doi.org/10.1016/j.desal.2013.10.005
3. Ihsanullah. (2019). Carbon nanotube membranes for water purification: Developments, challenges, and prospects for the future. *Separation and Purification Technology*, 209, 307–337. https://doi.org/10.1016/j.seppur.2018.07.043
4. Srivastava, A., Srivastava, O. N., Talapatra, S., Vajtai, R., & Ajayan, P. M. (2004). Carbon nanotube filters. *Nature Materials*, 3(9), 610-614. https://doi.org/10.1038/nmat1192

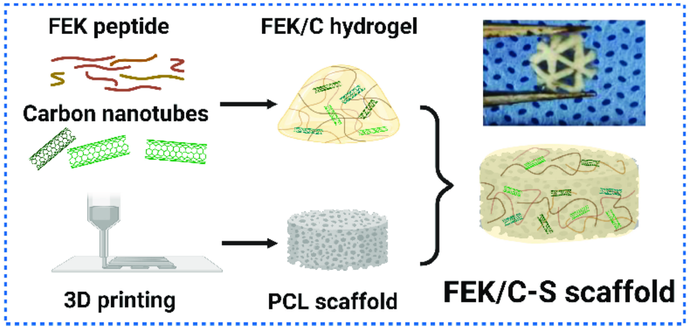
CNT-Hydrogel Composite Cartilage Regeneration

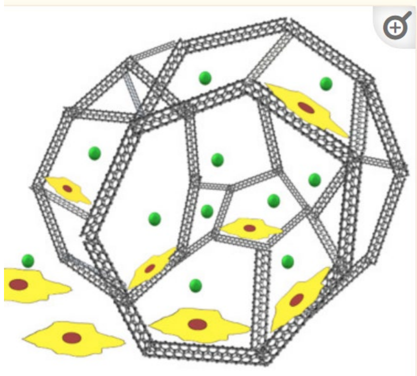
Current Problems with Cartilage Regeneration

- No established procedure to repair damaged cartilage or regenerate cartilage
- Only preventable measures for cartilage degeneration
  - Ex. Osteoarthritis

Proposal: CNT-hydrogel composite scaffolds

- Fibrous nanoscale topography resembling extracellular matrix
- Increase cell adhesion + chondrocyte production
- CNTs biomimics ECM
  - Graphene structure = molecule + nutrient absorption
  - Cell adhesion + cell growth

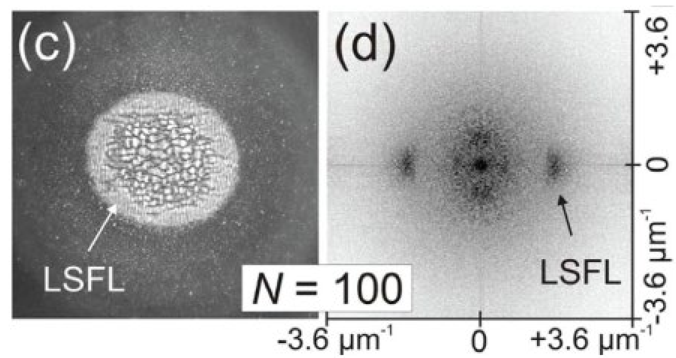


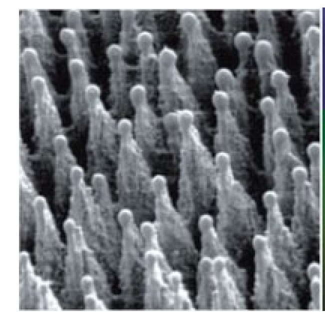


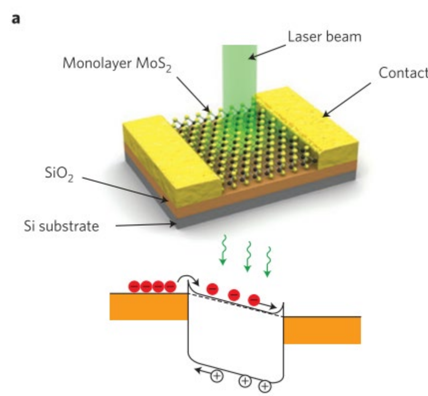
1. Enhanced Cartilage and Subchondral Bone Repair Using Carbon Nanotube-Doped Peptide Hydrogel–Polycaprolactone Composite Scaffolds. Pharmaceutics. 15. 2145. 10.3390/pharmaceutics15082145.
2. Utilization of Carbon Nanotubes in Manufacturing of 3D Cartilage and Bone Scaffolds

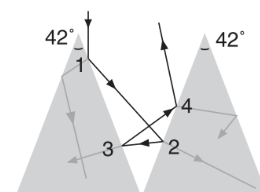
Maskless Fabrication of Surface Periodic Nanostructures on 2D Material for Sensitive Photodetector

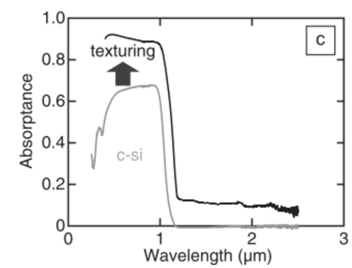
- Laser induced Periodic Surface Structures are a special phenomenon when low power laser pulse hits the surface of a material
- Structured surface enhances photon absorption by geometric trapping and resonance
- The enhancement of absorption applied to 2D materials can be used to make photodiodes or photovoltaic devices







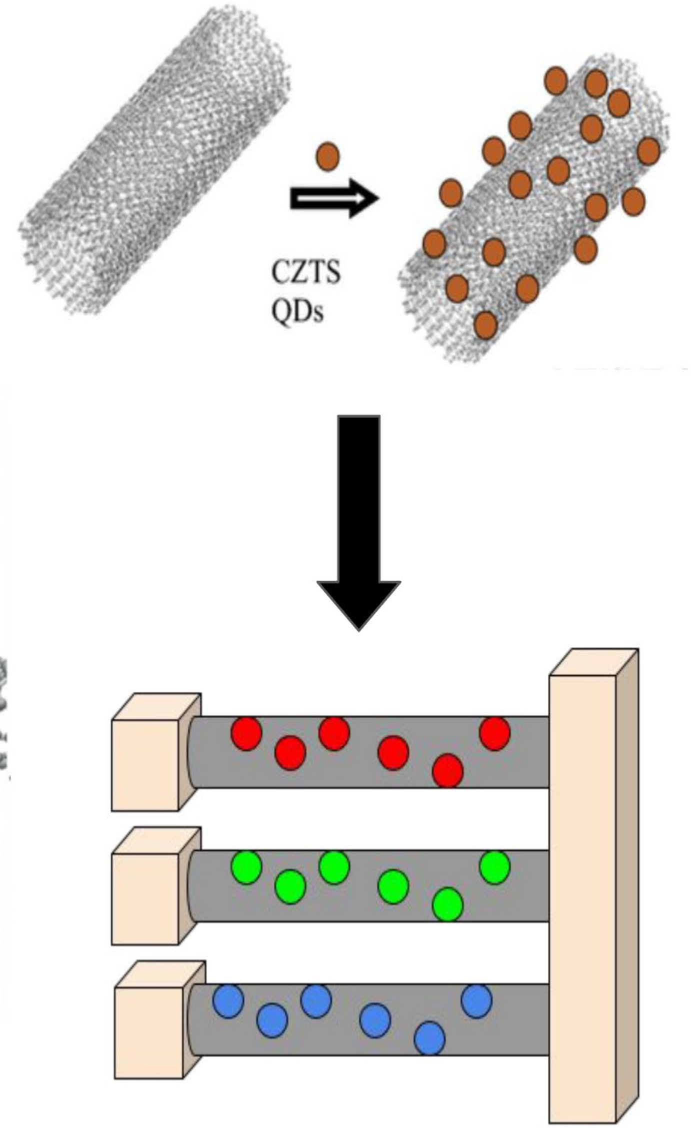


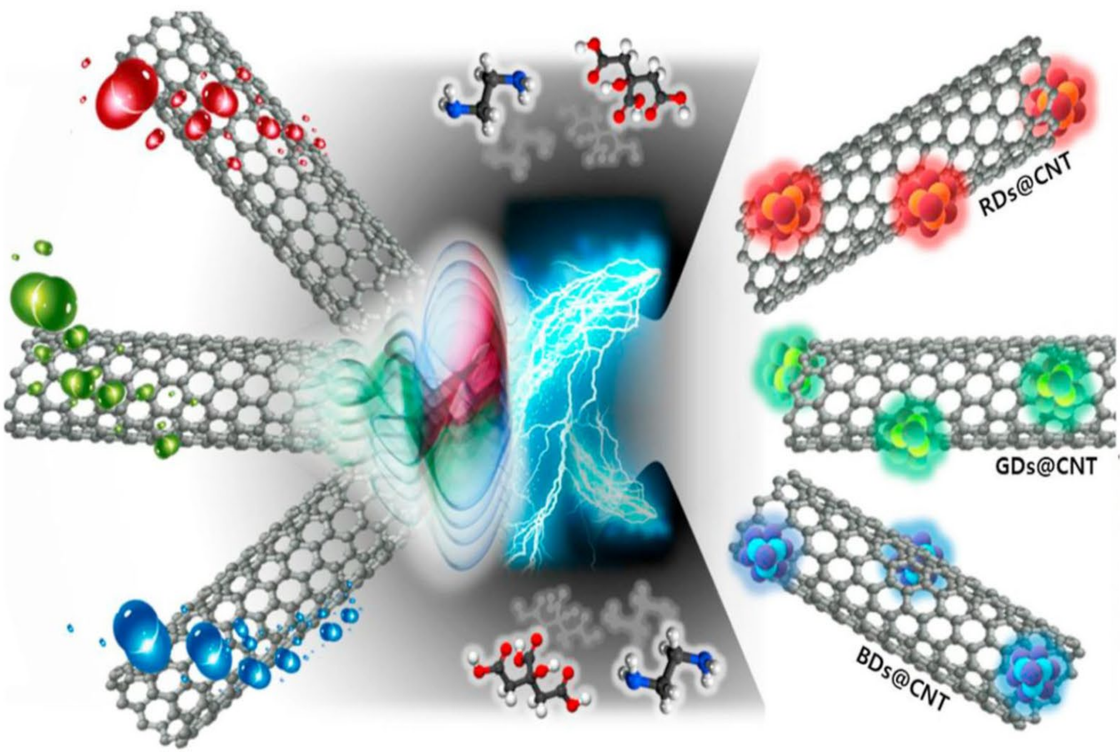


1. J. Laser Appl. 24, 042006 (2012); https://doi.org/10.2351/1.4712658
2. Pulsed-laser hyperdoping and surface texturing for photovoltaics; Meng-Ju Sher , Mark T. Winkler , and Eric Mazur
3. Photonics and optoelectronics of 2D semiconductor transition metal dichalcogenides Kin Fai Mak and Jie Shan

QD Decorated CNT for Nano-LED

- QDs are attached to CNT using DNA
- Different emission spectra for QD
- Selectively choose RGB for light emission





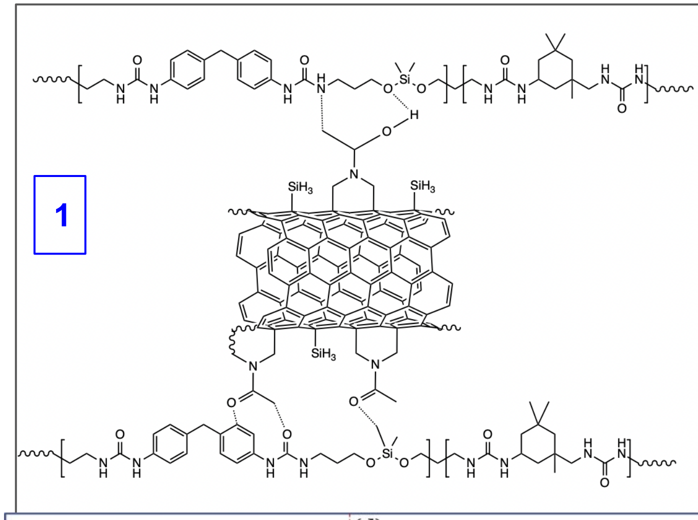
Multi-functional nanocomposite-based self-healing polymers

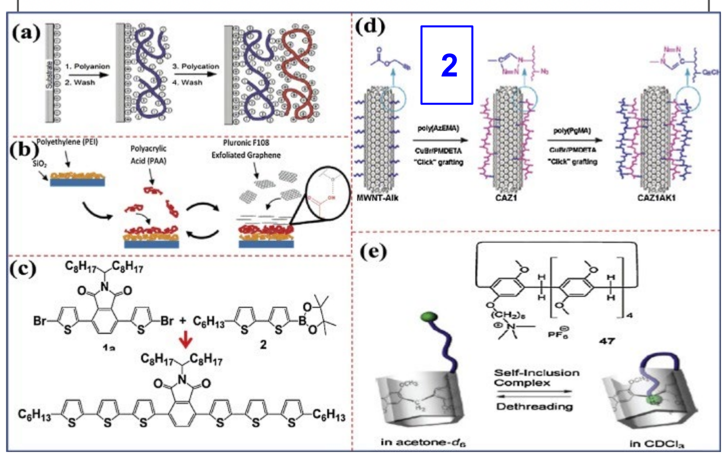
Kai Lyubchenko

Motivation: Self-healing polymers + functionalized nanotubes

Proposal: Introduction of functionalized nanotubes into the polymer matrix to improve the self-healing process and increase the range of possible applications

Goal: CNT's functionalized with silicon and organic groups in a covalent polymer would strengthen the healing properties of the polymer, while also allowing for the incorporation of electronic elements and tuneable polymer properties. Multiple layers of these polymers can be used to make a "second skin" coating for medical and extreme-environment applications.





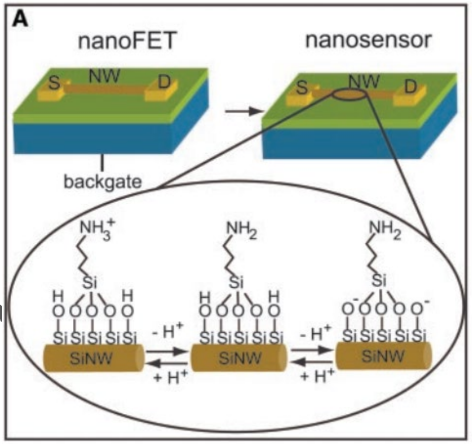
Other possible applications include:

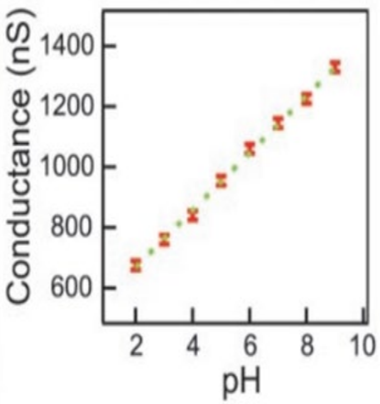
- Conductive and thermally stable coatings for electronics
- Long-lasting anti-corrosive coatings
- UV protection
- Antimicrobial coatings
- Multi-layered customizable composite polymers
- Batteries
- Biomedical coatings

1- My proposed design for functionalized CNT in self-healing polymer

2- Zhang et. al. Progress on the layer-by-layer assembly of multilayered polymer composites: Strategy, structural control and applications, Progress in Polymer Science, Volume 89, 2019, Pages 76-107, ISSN 0079-6700, https://doi.org/10.1016/j.progpolymsci.2018.10.002.

Heavily doped APTES-modified Silicon Nanowire (SiNW) for low pH levels

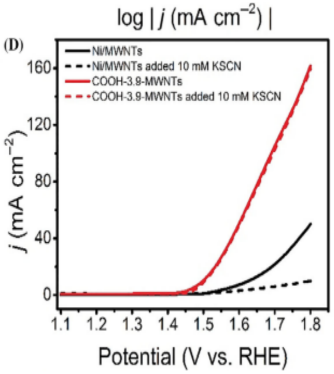




1, 2: *Nanowire Nanosensors for Highly Sensitive and Selective Detection of Biological and Chemical Species*, Cui, et al.

Designed Environment:

- Wanted for biomedical applications specifically in stomach acid areas.
  - pH levels can go as low as 1.5 in that highly acidic region.
- Allows for the transfer of medicines and precise surgical reasons.



3: *Carboxylated carbon nanotubes with high electrocatalytic activity for oxygen evolution in acidic conditions*, Zhang, et al.

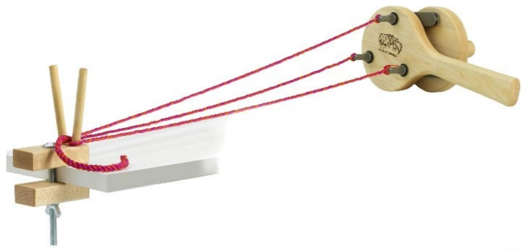
Theory:

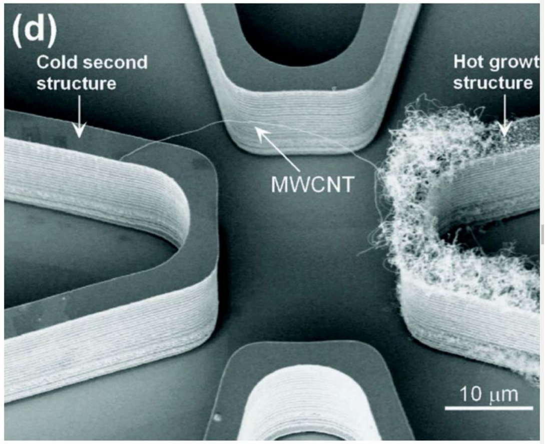
- To create a SiNW pH sensor for low pHs (1-6), we want to heavily dope APTES-modified SiNW with boron to increase the p type charge carriers (holes) in the nanowire. Allows for lower pH resistance (pH 1 - 2).
- As the depletion of holes at low pH will not reduce the conductance enough to cause a nonlinear relationship between conductance and pH.
- Carboxyl functional groups have also been used for CNTs.

Carbon Nanotube “Rope”

Andrew Moncada

- Carbon Nanotubes are well known for their strength-to-weight ratio
- A limitation of CNT’s for applications beyond the nanoscale is their small size
- Solution exists in the macroscale: rope weaving
- Goal: Design a process by which CNT growth and assembly may lead to a “weaved” geometry.





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Aluminum-CNT Composite Passive cooling devices for Photovoltaic Thermal (PV/V) Technology

Orlando Munoz

Motivation:

PV/T tech is a promising technology that combines a solar PV panel with a solar thermal collector. It maximizes solar energy utilization. Main problem for better performance is heat dissipation limits.

Proposal: Introduction of Aluminum-CNT composite as construction material for fin arrays for PV/V tech to improve heat transfer rate for both natural and (mainly) forced convection.

Goal: CNT's thermal properties are well known, but large scale implementation specially for fin required dimensions is troublesome. With the use of Aluminum-CNT composite materials, this can obstacle can be minimized. The presence of such a cheap metal as the composite material combined with the incredibly high thermal conductivity of CNTs would allow for a efficient fin. That is, a high bulk surface area, cheap, and highly conductive material.

Bulk properties for such a composite have been explored for forced convection over plates or conduction [1], but fin arrays with materials have yet to be thoughtfully explored.

(b)

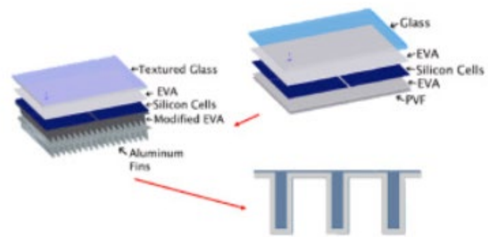
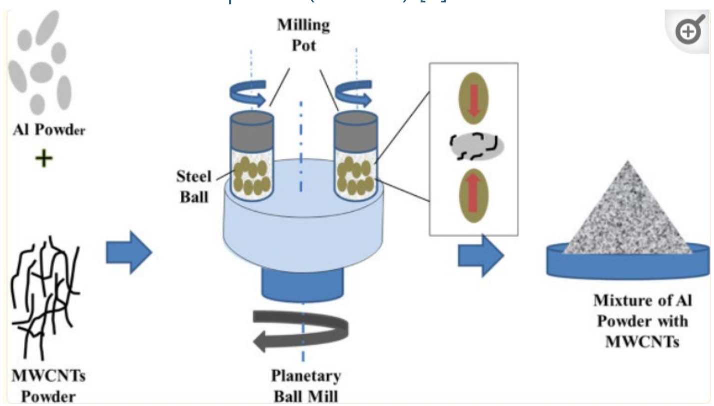


Illustration of fin arrangement for device (above) and Fabrication of Al and MWCNT composite (bottom) [3]



$$\frac{d^2T}{dx^2} - \frac{hP}{kA_c}(T - T_\infty) = 0$$

Heat equation for uniform shape fin. This shows changes in k, Ac, and P could allow for more efficient energy transfer.

Other applications:

Cheap and sturdy material composite for structural reinforcement of same or other structures.

More electrically conductive material.

Higher natural convection to be explored.

Sources:

[1] https://www.sciencedirect.com/science/article/pii/S2214157X23006226#sec4

[2] https://www.ncbi.nlm.nih.gov/pmc/articles/PMC10515603/

[3] https://www.sciencedirect.com/science/article/pii/S166564231630044X#sec0015

Berkeley
UNIVERSITY OF CALIFORNIA

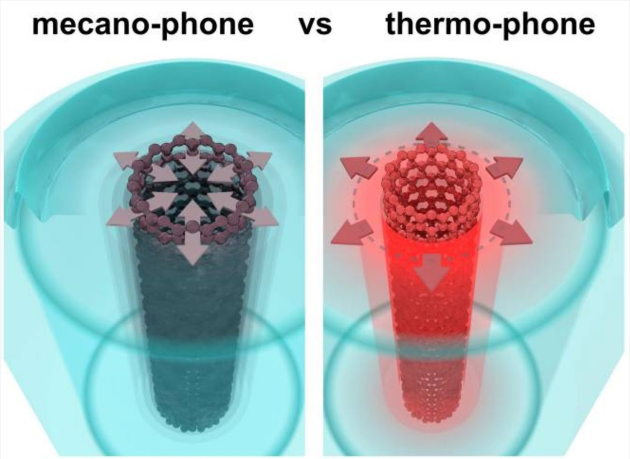
Wave Prediction Using CNTs

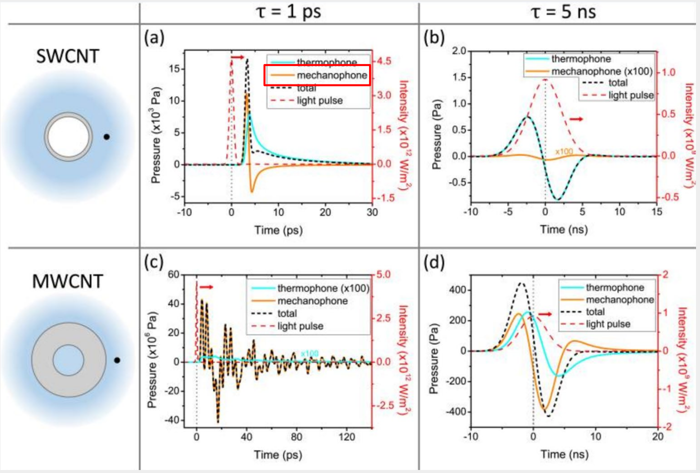
System:

- Underwater acoustic fields can be used to predict and map motion of fluids and resulting surface waves via acoustic propagation and machine learning.
- The unique thermal properties of CNTs allow for high frequency sound waves, which can be employed either by usage as a mecano-phone or thermophone.
    - *Mechano-phone* sends pulses via the expansion of the water surrounding the CNT from thermal energy.
    - *Thermo-phone* sends pulses by expanding the CNT itself from thermal energy.
- In conjunction with a machine learning algorithm, it could be possible to predict wave height and frequency by mounting CNT acoustic propagators on the hull of ships.

Benefits:

- Reduce wind noise and surface scattering by directly sending and reading sonar information underneath the ship.
- Increase response time and accuracy due to ultrahigh frequency allowed by CNTs.
- Decrease space needed to mount and employ radar technology.





Ermoshkin AV, Kosteev DA, Ponomarenko AA, Razumov DD, Salin MB. Surface Waves Prediction Based on Long-Range Acoustic Backscattering in a Mid-Frequency Range. *Journal of Marine Science and Engineering*. 2022; 10(6):722. https://doi.org/10.3390/jmse10060722
Diego M, Gandolfi M, Casto A, Bellussi FM, Vialla F, Crut A, Roddaro S, Fasano M, Vallée F, Del Fatti N, Maioli P, Banfi F. Ultrafast nano generation of acoustic waves in water via a single carbon nanotube. Photoacoustics. 2022 Sep 29;28:100407. doi: 10.1016/j.pacs.2022.100407. PMID: 36263352; PMCID: PMC9574765.

Brian Rodriguez, March 18 2024

CNTS in Hydro Turbines

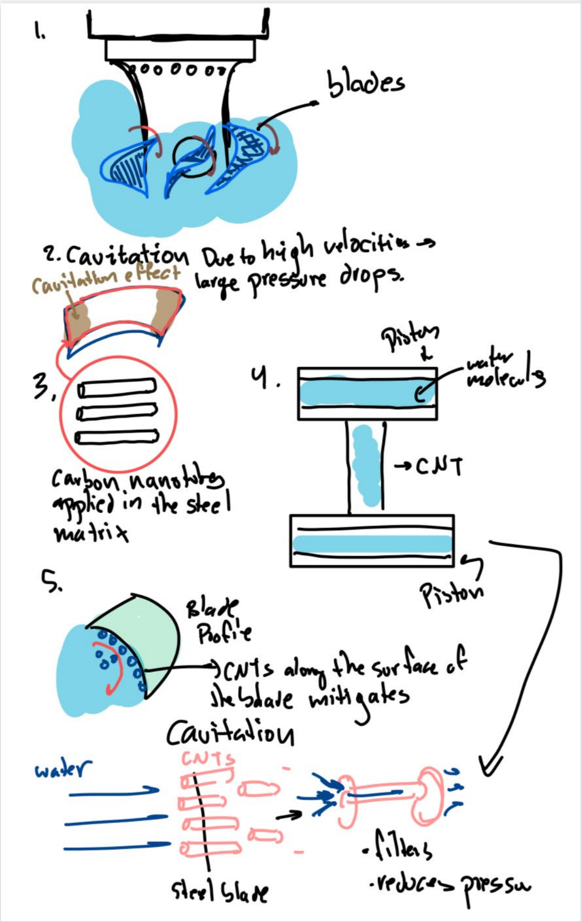
Motivation: Kaplan Turbines require high water flow rate and low head and its performance is hindered by cavitation effects and can damage the ecosystem

Proposed System: Placing CNTs along the profile of the blades could help by

- Filtering the water as only water could pass through the matrix to tackle human caused pollutants in the water
- The hydrophobic nature of CNT walls can serve as surface coatings to increase the steel's lifetime (common turbine material)
- Enhances material properties for reinforcement
- Reduces heat (results in cavitation) as CNTs are good thermal conductors which can dissipate heat away from the blades
- Could output electrical signals that measures pressure to moderate the pressure: optimizes or energy production and risk management

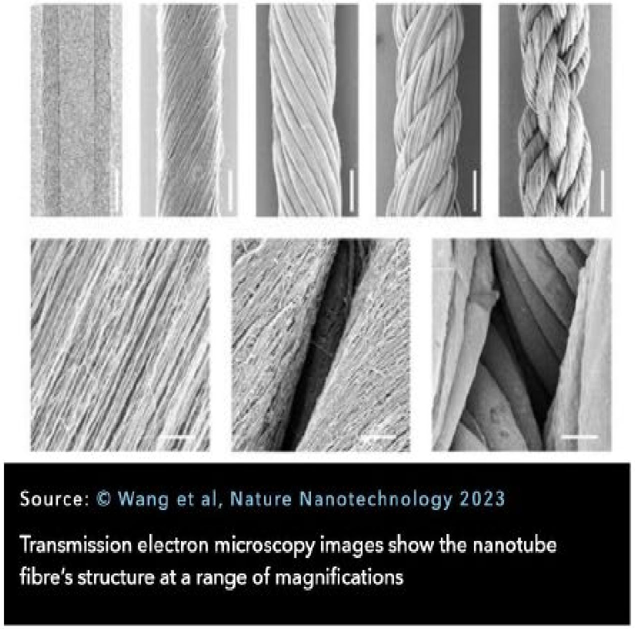
Assumptions:

- CNTs are purposefully impure to allow pressure diffusion.
- CNTs fabrication process are faithful to the structure's geometry , as it is essential for maintaining its efficiency

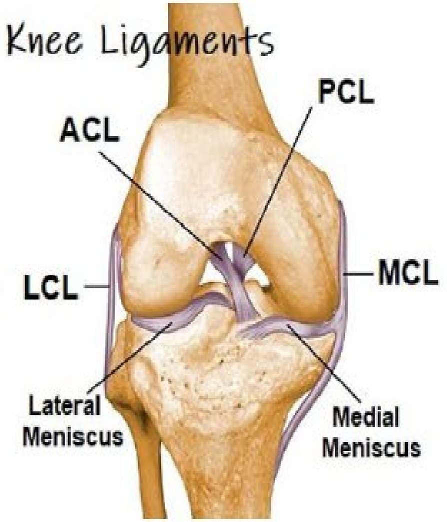


Carbon Nanotubes with ACL Reconstruction

Dylan Rosario



- The anterior cruciate ligament (ACL) is partially responsible for stabilizing the knee, must remain both tough and flexible to support knee bending
- With average length and width of 33 mm and width of 11 mm, the natural ACL has tensile strength about 2200 N [1]
- Current methods involve repurposing existing tendons in the body, may cause medical complications
- Propose ACL reconstruction by replacing with multiwalled carbon nanotubes twisted into a rope [2]
  - Grow MWCNTs with chemical vapor deposition, then twist bundles together, twisting will increase tensile strength, preventing future injury
  - Preliminary research with animals is promising
  - Goal is to mimic natural ACL mechanical behavior
  - To integrate, body must accept material and grow around



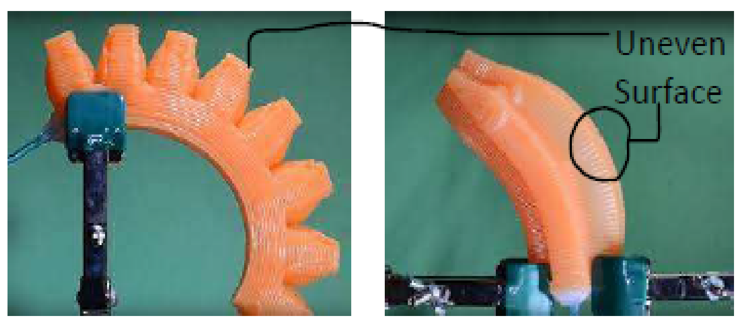
[3]

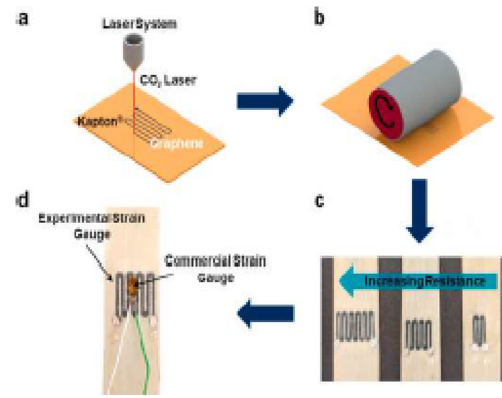
[1] https://spineologychiropractic.com/acl-injuries-and-what-you-need-to-know/
[2] https://www.chemistryworld.com/news/twisted-carbon-nanotubes-make-ideal-replacements-for-damaged-ligaments/4017498.article
[3] https://www.powerfulpt.com/post/acl-mcl-pcl-lcl-what-do-these-letters-stand-for

CNT BASED EMULSIFICATION AND MIXING

1. Idea is to use the LIG resistors to make strain gauges for soft robots and providing a real time feedback to the processors whether the pressure applied infact achieved the desired movement or not.

2. LIG based strain gauges can provide an easy way of transferring the sensors to the soft robotics and this can also be useful especially for 3D printed surfaces as the transferred LIG can provide a better contact and more accuracy then a film based sensor due to the nature of 3DP as shown below. Feedback loop will allow better and more accurate actuation and movements which is not possible right now.





Nanorobotics use for Thrombolysis

Shira Shabtian

Thrombolysis: Procedure used for breaking up blood clots which restrict blood flow in veins and arteries

Problems in Space:

Traditional tools such as pharmaceuticals and catheters may have adverse side effects or may be overly invasive

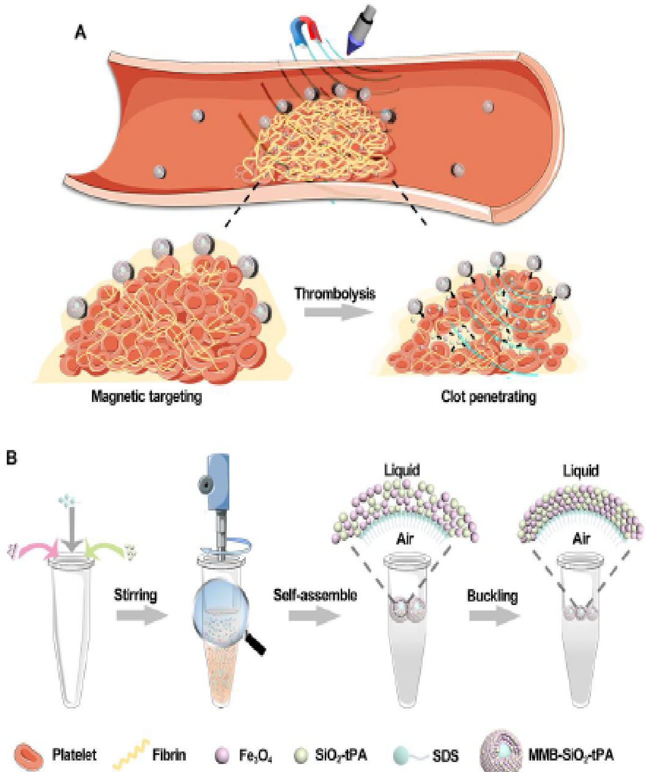


Fig 1. Nanorobot guided thrombolysis

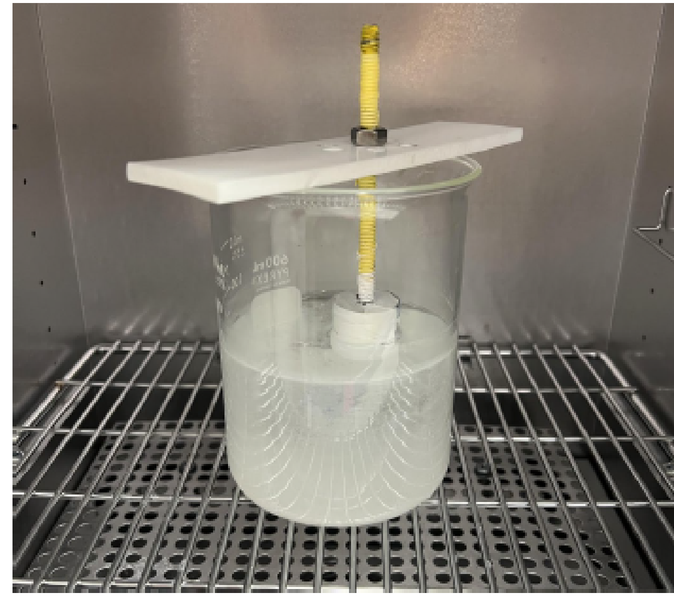
CNT Proposal

- Use ATP Powered Nanodevices for clot penetration either mechanically or through targeted drug delivery
- Nanodevices have been able to convert ATP into mechanical motion.
- Nanorobotics may be able to be used for precision drug delivery
- Can be remotely controlled or preprogrammed for precise navigation, often through magnetic or acoustic guidance
- Made from combination CNTs, biological molecules, and stimuli responsive materials

1. Janmaleki, Mohsen, and Pierre E. Dupont. "Autonomous thrombus removal with a magnetic microrobot." Science Robotics, vol. 5, no. 49, 2020, doi:10.1126/scirobotics.abc7392.
2. Ge, Jiajia, et al. "Nanorobotic Delivery of Antithrombotic Therapy with Surface-Modified Platelets." Nano Letters, vol. 20, no. 9, 2020, pp. 6346–6354, doi:10.1021/acs.nanolett.0c02424.
3. Li, Jian, et al. "Nanorobotic endovascular catheter for atherosclerosis management." Nature Nanotechnology, vol. 6, no. 7, 2011, pp. 156–161, doi:10.1038/nnano.2011.7.

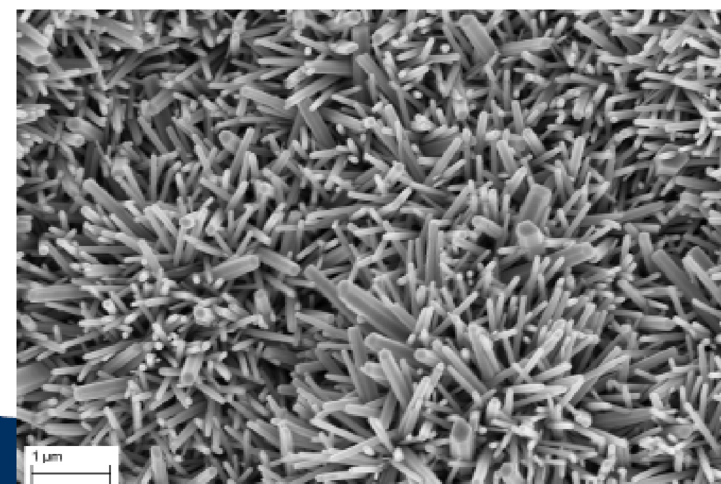
Zinc Oxide Nanostructures for Enhanced Boiling Processes

Anisa Silva



Background

- ZnO grown on copper characterized as superhydrophillic
- Increases wettability and wickability of fluid on surfaces coated with these nanostructures
- Provides an ultra-low contact angle
- Growth process is via deposition of nanoparticles on a substrate followed by aqueous solution growth



Questions

- How does the ultra-low contact angle improve heat transfer performance?
- Nucleation for nano-scale interstitial sites requires high levels of superheat, but nucleation is observed at moderate levels, why?

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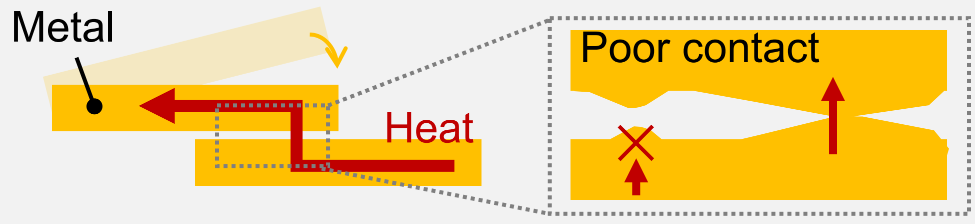
Gecko Thermal Switch Based on CNT Array

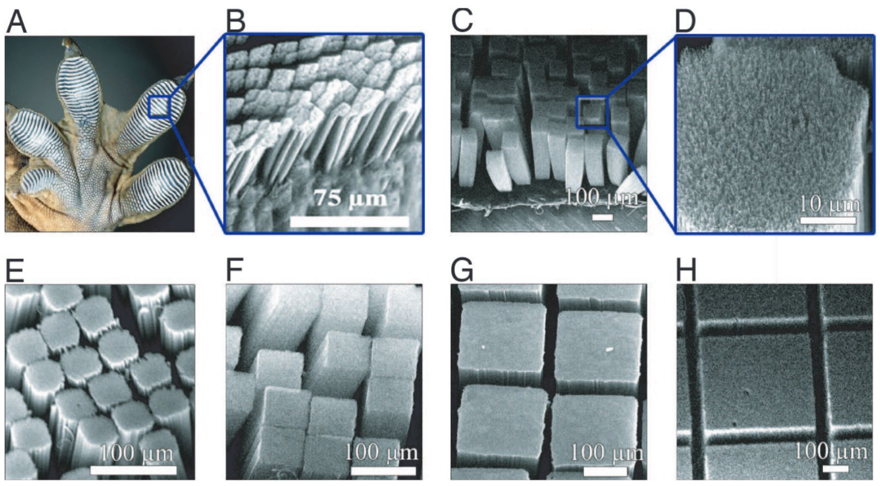
Megan Teng, Peggy Tsao

- ✓ Good Contact
- ✓ Dry and Reversible Adhesion
- ✓ Reusable
- ✓ No Leakage Risk
- ✓ Can Be Used in Space

Bimetallic Thermal Switch

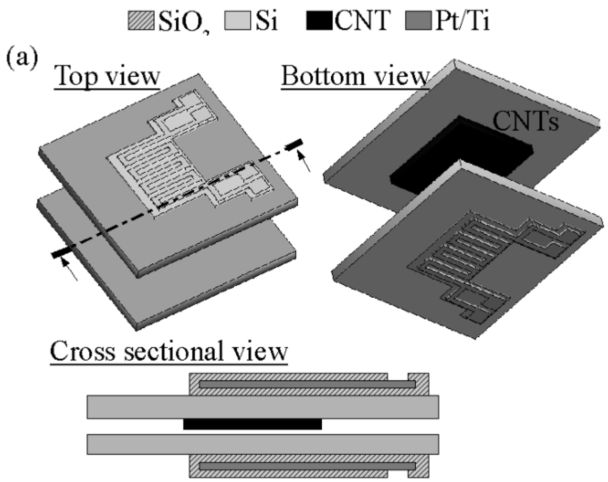


Gecko Pattern



L. Ge, S. Sethi, L. Ci, P. M. Ajayan, and A. Dhinojwala, "Carbon nanotube-based synthetic gecko tapes," Proceedings of the National Academy of Sciences, vol. 104, no. 26, pp. 10792–10795, Jun. 2007

Aligned CNT Thermal Switch



J. Cho, C. Richards, D. Bahr, J. Jiao, and R. Richards, "Evaluation of contacts for a MEMS thermal switch," *J. Micromech. Microeng.*, vol. 18, no. 10, p. 105012, Sep. 2008

3D electrical activity mapping through nanoelectronics in silicon nanowire scaffolding in organoids used to promote recovery in infarcted hearts

Hana Trinh
MECENG118 Small Project
March 18 2024

Research

- Silicon nanowire scaffold to mimic the extracellular matrix in the heart in which stem cells can grow to create an organoid that can be transplanted into damaged tissue of a heart to elicit a much more significant recovery (**Ying Mei**) [1]

- **Charlies Lieber** created a 3D silicon nanowire matrix where stem cells can grow. The matrix contains FET sensors that can measure cell function of lab grown tissue [2]

Proposal

- Combine Ying Mei and Charles Lieber's technology to create a silicon nanowire matrix organoid that can promote regeneration within a damaged heart as well as measure the rate which a damaged heart can heal by measuring cell function and heart-beat

Manufacturing

1. Silicon nanowire manufactured through gold nanocluster-catalyzed VLS

2. Nanoelectric mesh scaffold created
   a) Nickel film deposited on substrate
   b) Photoresist spin-coated over substrate
   c) UV exposure was used to define an array of rectangular pads for nanowire assembly
   d) silicon nanowires transferred through lubricant-assisted (gentle oxygen plasma) contact printing method
   e) Substrate is baked to anchor Si nanowire where they are arranged into FET sensor arrays
   f) The substrate was placed in developer for 1 min
   g) Gentle sonication was carried out to break and remove the free-standing segments of nanowires and SU-8 thin films.
   h) Substrate was hard-baked at 180 °C for 20 min.

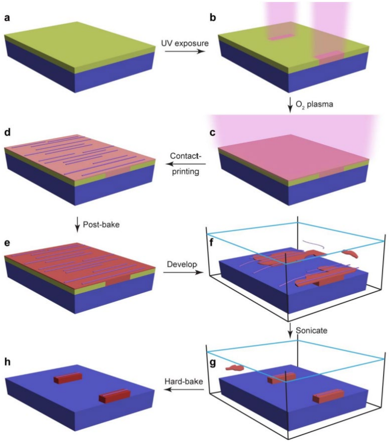


Figure. 2 Photolithography technique

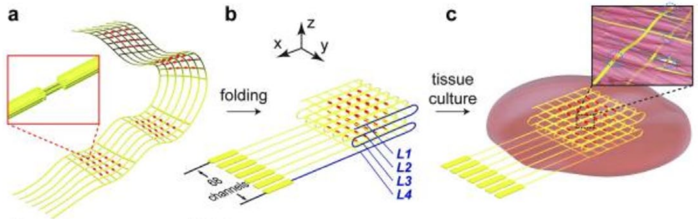


Figure. 1 Schematic of free-standing macroporous nanoelectronic scaffold with nanowire FET arrays (red dots); inset, one nanowire FET.

3. a) 2D polymeric meshes made of silicon nanowire assembly with embedded nanoelectronics (FET) – from 2
   b) 2D mesh is folded into several layers to create 3D scaffold (more than 4 that Lieber did)
   c) Tissue culture is grown on the scaffold

4. Created organoid is injected into damaged tissue and data is measured through the FET in the nanowire mesh

[1] Tan, Yu, et al. "Nanowired Human Cardiac Organoid Transplantation Enables Highly Efficient and Effective Recovery of Infarcted Hearts." *Science Advances*, vol. 9, no. 31, 4 Aug. 2023, https://doi.org/10.1126/sciadv.adf2898. Accessed 18 Mar. 2024.
[2] Dai, Xiaochuan, et al. "Three-Dimensional Mapping and Regulation of Action Potential Propagation in Nanoelectronics-Innervated Tissues." Nature Nanotechnology, vol. 11, no. 9, 27 June 2016, pp. 776–782, https://doi.org/10.1038/nnano.2016.96. Accessed 12 Dec. 2022.

ME218 Project Proposal
Jessica Wu

Towards carbon nanotubes as quantum-light source to trigger artificial photosynthetic processes using light-absorbing nanowires

Motivation

Paper 1:

Carbon nanotubes as emerging quantum-light sources

X. He, H. Htoon, S. K. Doorn, W. H. P. Pernice, F. Pyatkov, R. Krupke, A. Jeantet, Y. Chassagneux & C. Voisin

Nature Materials **17**, 663–670 (2018) | Cite this article [1]

Paper 2:

CHEMISTRY OF MATERIALS — Perspective — pubs.acs.org/cm

Semiconductor Nanowires for Artificial Photosynthesis

Chong Liu,[†,§] Neil P. Dasgupta,[†] and Peidong Yang*[†,‡,§]

[†]Department of Chemistry and [‡]Department of Materials Science and Engineering, University of California, Berkeley, California 94720, United States

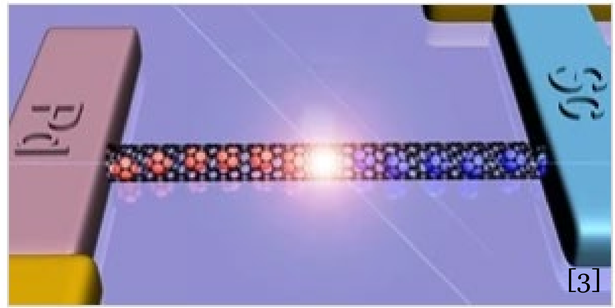
[§]Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States [2]

Idea: what if we combine the two?

Main Research Questions:

1. Can the photons emitted from SCNTs light source be enough to trigger an artificial photosynthetic process utilizing nanowires?
2. Is there a better material(s) as an alternative than TiO2?
3. Can the photons from the CNT emission be redirected via. plasmonic manipulation to target the nanowires?

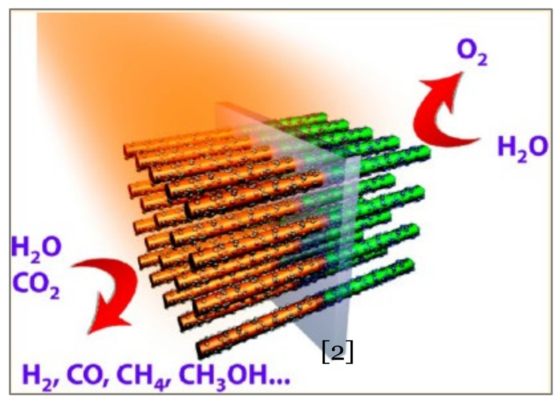
Process Details



CNTs emit light when a pos. charge meets negative (from creation of p-n junction within the nanotube)

photons

- Single-photon source complex previously limited due to scalable integration – SWCNTs exhibit strong anti-bunching and strong photoluminescence
- Photosynthesis occurs at 10,000 photons – lower value than expected and could be explored further
- Quantum light is an exciting topic
- Customize emission wavelength and dielectric encapsulation of SWCNTs for stabilization of optical properties



- Look into ZnO2 and other alternative materials
- Nanowires show promising energy upconversion characteristics (low- to high-energy photon conversion); heterostructures can increase upconversion efficiency by 500x [4]
- Objective: design nanowire device that can effectively scale-up photon emission from CNT, to trigger photosynthesis process

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[1] He, X., Htoon, H., Doorn, S.K. *et al.* Carbon nanotubes as emerging quantum-light sources. *Nature Mater* **17**, 663–670 (2018). https://doi.org/10.1038/s41563-018-0109-2
[2] Chong, L., Dasgupta, N., Yang, P. Semiconductor Nanowires for Artificial Photosynthesis. *Chemistry of Materials* **26, 1,** 415-422 (2014). https://doi.org/10.1021/cm4023198
[3] Carbon nanotubes: A little light. *NPG Asia Mater* (2011). https://doi.org/10.1038/asiamat.2011.40
[4] Jansson, M., Ishikawa, F., Chen, WM., Buyanova, IA. Designing Semiconductor Nanowires for Efficient Photon Upconversion via Heterostructure Engineering. *ACS Nano*.,12666-12676 (2022). doi: 10.1021/acsnano.2c04287.

Targeted Drug Delivery: Combining Drug Delivery properties of CNT with Photodynamic/Photothermal Therapy

Haida Yu

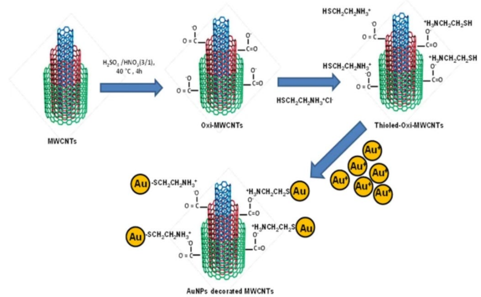
PTT: light absorption and conversion of heat by gold or silver nanoparticles. localized thermal therapy

PDT: Chemicals reacting to certain light localized and selectively perform its function

Gold/silver nano-particles are used for PTT. By attaching CNTs to nano-particles, using CNT to carry medicine, might be able to synthesize photothermal sensitive medicine delivery CNT-nanoparticle compound

Grow CNT (CVD) -> attach to nano particles -> attach to medicine -> Light triggered local releasing/activating of medicine

Figure 1



Schematic illustration for the preparation of Au-MWCNTs.

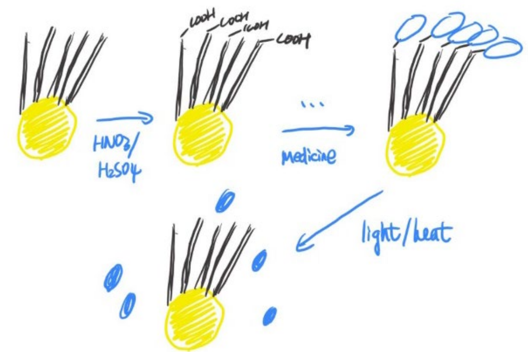


Fig1: Duc Chinh, V., Speranza, G., Migliaresi, C. et al. Synthesis of Gold Nanoparticles Decorated with Multiwalled Carbon Nanotubes (Au-MWCNTs) via Cysteaminium Chloride Functionalization. Sci Rep 9, 5667 (2019). https://doi.org/10.1038/s41598-019-42055-7

Synthesis of functionalized CNT composites

Cassie Young

Motivation:

- CNT properties can lead to composites with properties different than conventional materials useful in new applications

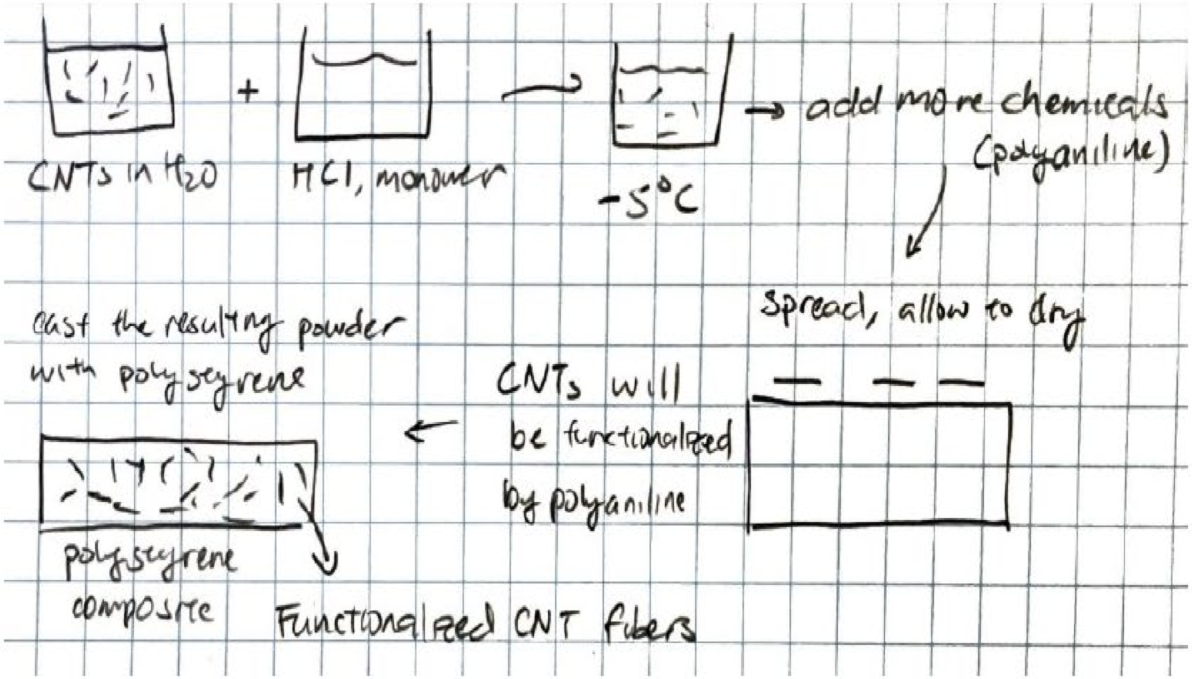
Proposal:

- Functionalized CNTs for increased mechanical, thermal, electrical properties

Goal:

- Differently functionalized MWCNTs could be used for different purposes
- Polyaniline (PA) functionalized CNTs could be used in polystyrene matrices to shield parts from EMI
- Epoxy polymers could have mechanical properties improved via functionalized SWCNTs

Process flow



The general above property is used for other functionalizations and matrix materials

https://link.springer.com/article/10.1007/s11051-012-1415-2
https://onlinelibrary.wiley.com/doi/epdf/10.1002/adfm.200305162

Ag-Nanowires in Medical Thermography

Brendan Unggul, UC Berkeley Department of Materials Science and Engineering
Mechanical Engineering 118

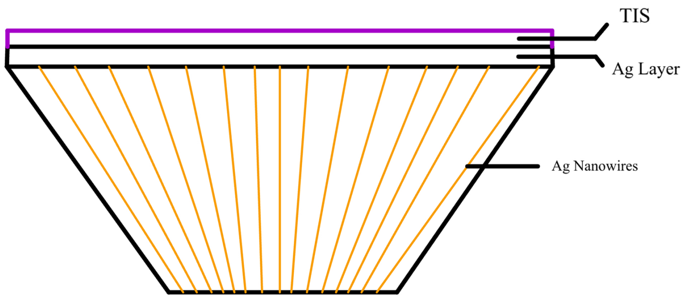


Figure 1: Device Schematic

Currently, one method that is used to detect tumors is medical thermography due to the temperature difference between tumor-affected areas and healthy areas. However, due to limitations in the sensitivity of thermal sensors as well noise (heat) from the surroundings, early detection of tumors is difficult. However, using nanowires directionally embedded in an insulating resin such as PMMA and connected to an Ag sheet layered with Thermal Imaging Sensitizer (TIS), we would increase sensitivity and reduce noise, allowing for earlier tumor detection.

The bottom of the device would be placed on the skin of the patient, and an IR camera would be pointed towards the TIS layer. The IR camera would then generate an image of the temperature field of the surface of the TIS layer, and a temperature anomaly would indicate a potential tumor.

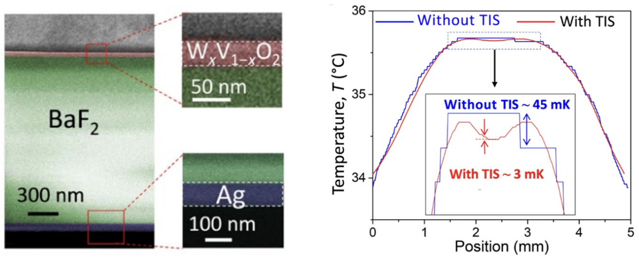


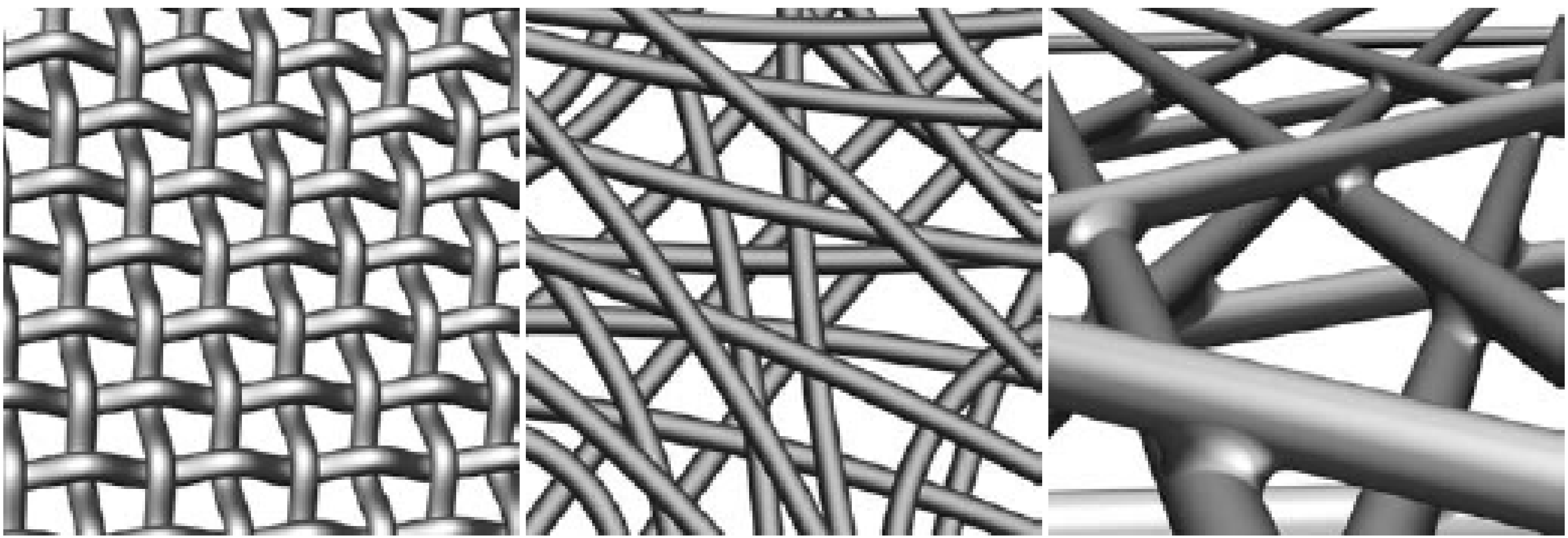
Figure 2: Schematics and Results of TIS

Without this device, measuring directly onto the skin introduces noise from the surrounding tissue. By isolating each nano-region (area connected to the nanowires towards the bottom of the device) and projecting it onto a larger surface area (top of the device), the noise measured would be reduced. The increase in temperature generated by an early tumor is relatively small (~0.1-0.2 K), so the TIS layer is added on top of the Ag sheet to sensitize our readings. The TIS layer amplifies the temperature differences to ensure that the IR camera would be able to capture the temperature differences.

(1) K. Tang, K. Dong, C. J. Nicolai, Y. Li, J. Li, S. Lou, C-W. Qiu, D. H. Raulet, J. Yao, J. Wu, Millikelvin-resolved ambient thermography, in *Science Advances 2020* **6:** eabd8688

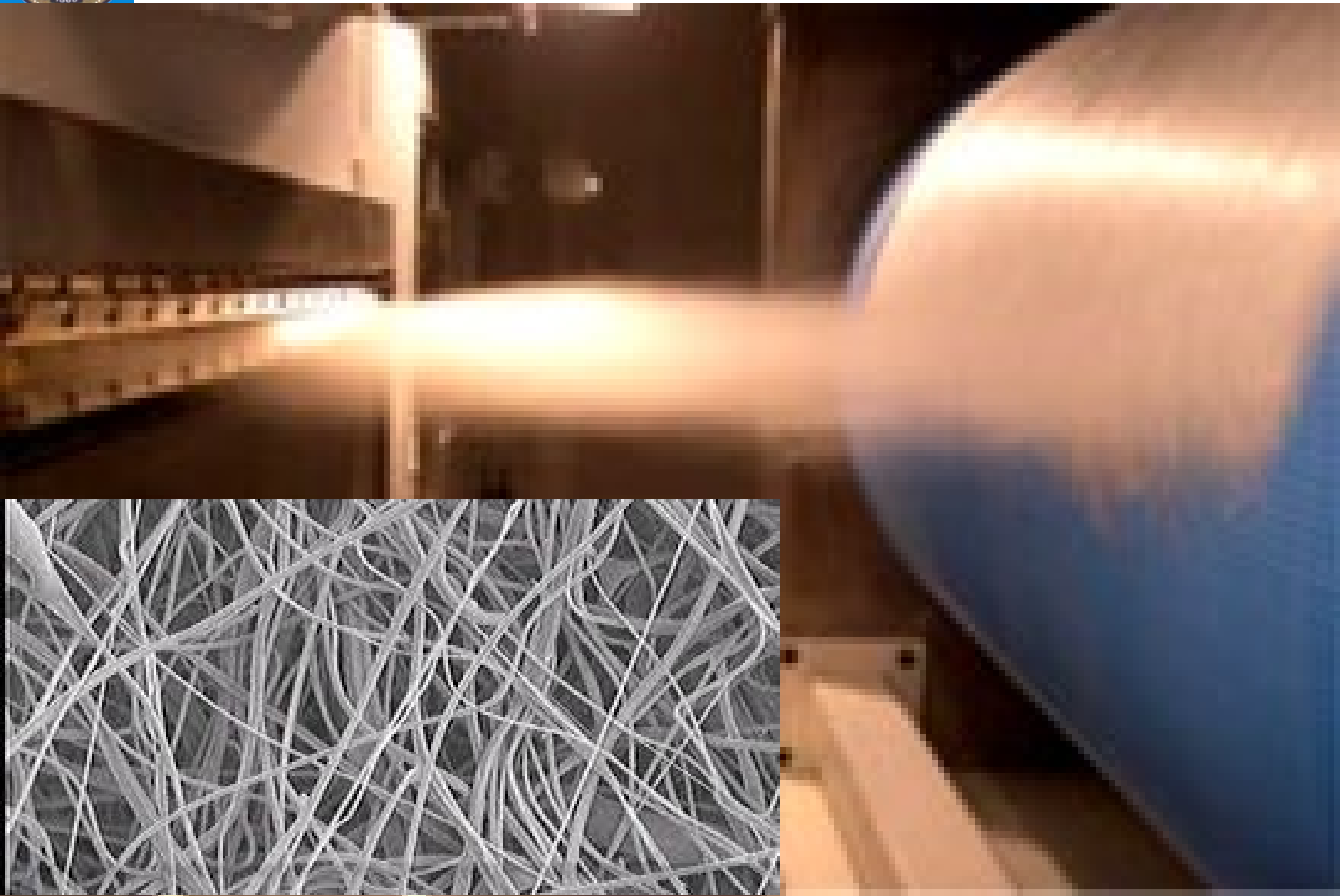
Woven and Nonwoven Fabrics

- Embedded high-modulus fibrous materials (e.g., glass fibers, carbon fibers, carbon nanotubes) for material reinforcement
- Embedding sensors & drug carriers.

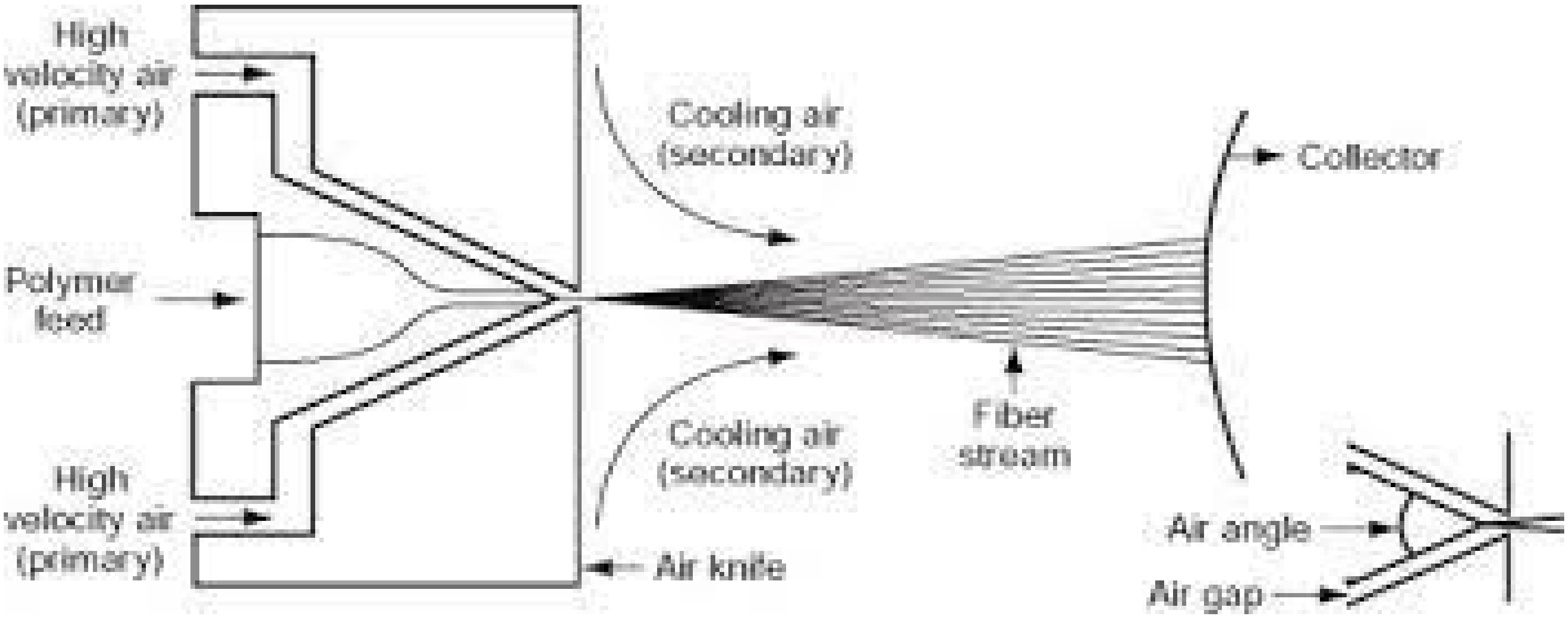


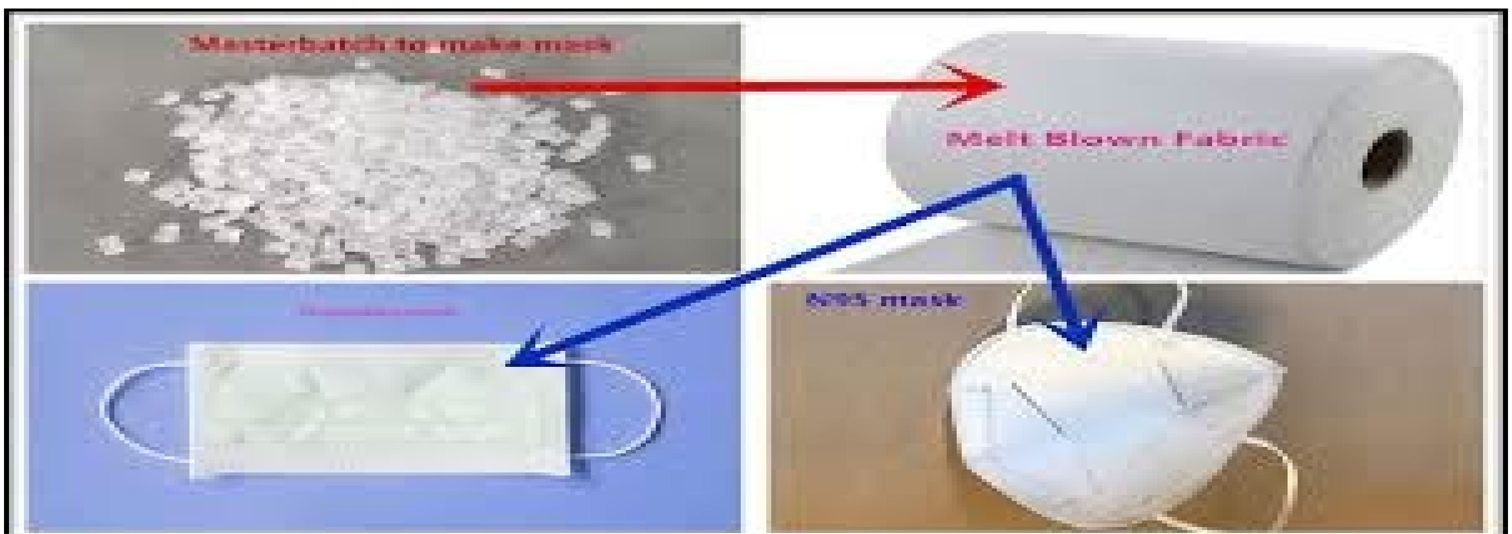
(a) woven fabrics (b) nonwoven fabrics (c) "soldered" junctions

Melt-Blowing Process

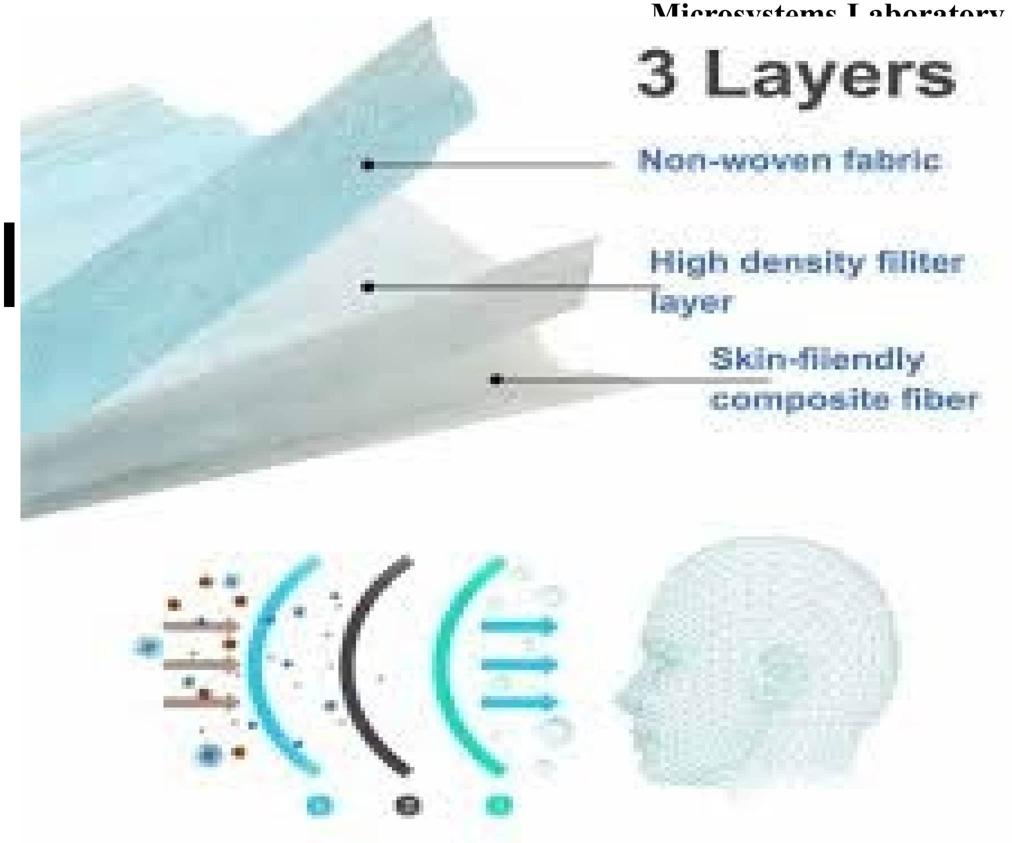


Melt-Blown Fabrics to Face Mask





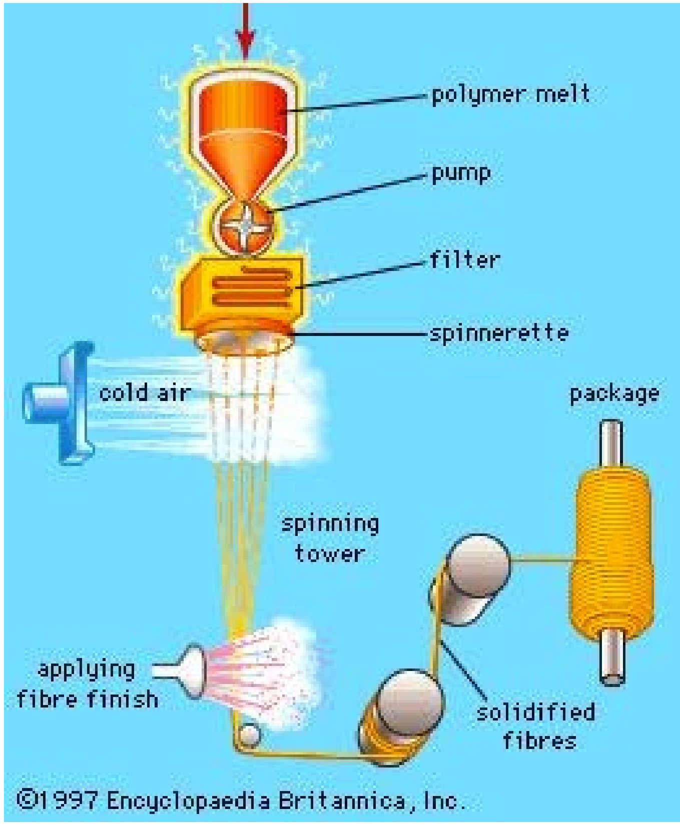
3 Layers Medical Face Mask



Fibres	Fiber Diameter (μm)	Linear Density (dtex)	Specific surface (m^2/g)
Coneventional	10-40	1-30	ca. 0.2
Melt blown	1-5	ca. 0.01	ca. 2
Nanofiber	0.05-0.5	ca. 0.0001	ca. 20

Fiber Fabrication Process

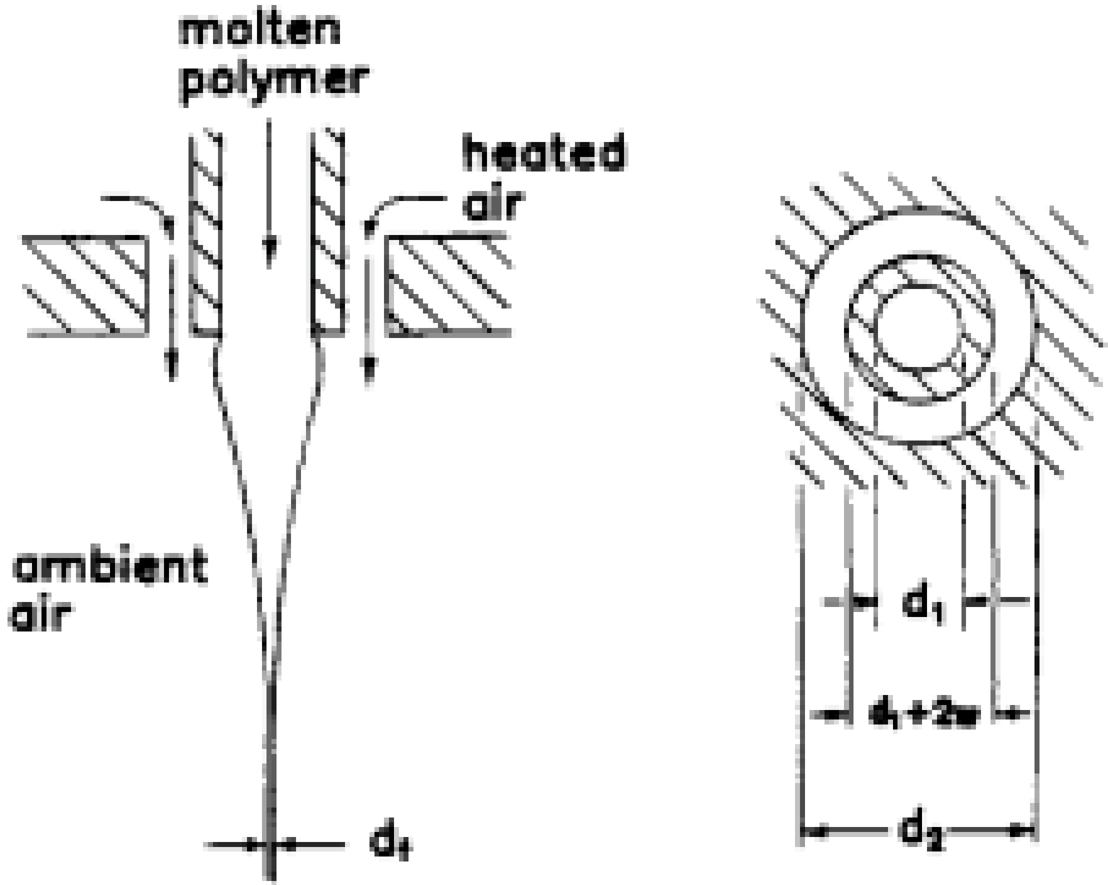
- Produces a Suede-like textile
- Process Explanation
- Can be used to create a range of diameters



http://encyclopedia.che.engin.umich.edu/Pages/PolymerProcessing/FiberSpinning/FiberSpinning.html

Commercial Processes of Non-woven Fabrics

- Foam expansion
- Melt-blowing processes
- Dispersion polymerizatio processes
- Abrasion of polymer surf



http://onlinelibrary.wiley.com/store/10.1002/pen.760301908/asset/760301908_ftp.pdf?v=1&t=j0hmk4x6&s=b4b225b04029e13dcbe500af80f50adf046047c3

Motivation

- Outdated: electrically driven liquid jets have been around since 1934 where polymer solution is deposited into a collector under EF
- Nanotube Diameter <= 100nm through electrospinning
- Limited applications currently: Possible Applications in effect transistors, gas, and optical sensors
- Current Challenge: ES is unstable (figure 3) due to reliance on chaotic motion (uncontrolled) whopping of liquid jets for nanofiber generation
- Proposed Idea: NEAR-FIELD ELECTROSPINNING (NFES)

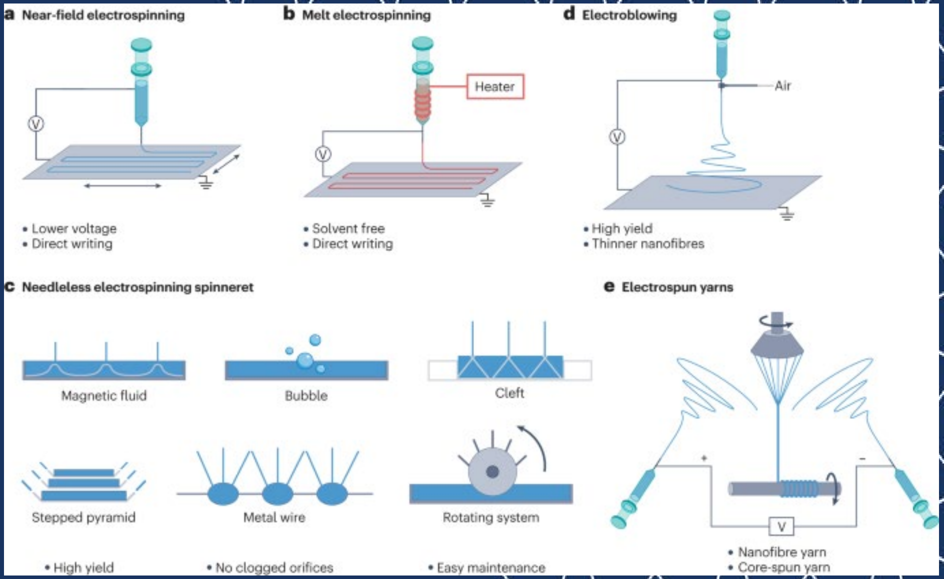


Figure 1: Schematic of a typical electrospinning process for nanowire fabrication

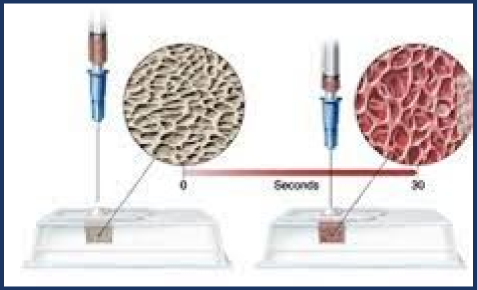


Figure 2: Bio Scaffolding Application

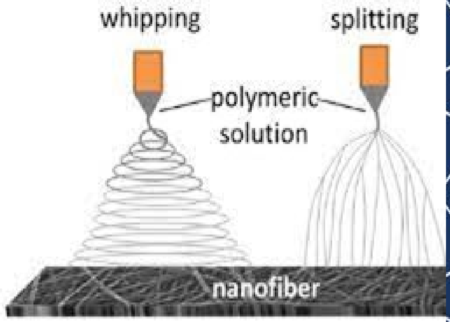


Figure 3: whipping of liquid jets to generate nanofibers

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Near-Field Electrospinning

- A process to deposit solid nanofibers in a direct, continuous, and controllable fashion
- Paper 9's technique:
  - Minimum electrode to collector distance: 500 microns to 3nm to utilize a region of controllable deposition stability for the liquid jets
  - Tungsten electrode with tip diameter of 25 microns constructs a 50-500 nm nanofiber line on silicon based collector as liquid polymer solution simultaneously is supplied like that of a dip pen (sub 100nm resolution)
  - Reduce electrostatic voltage (due to short e to c distance) while maintaining 10^7 volts/m range at the tip
  - Minimum applied bias voltage: 600 V
- This technique allows NFES be a potential tool in direct wire fabrication as charged nanofibers can be ordered as they are collected

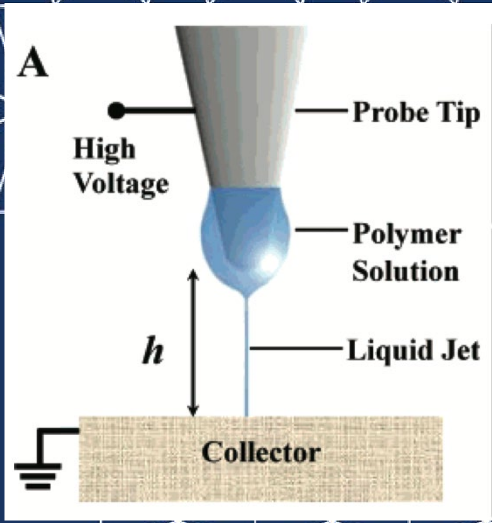

FIgure 4: NFES Schematic

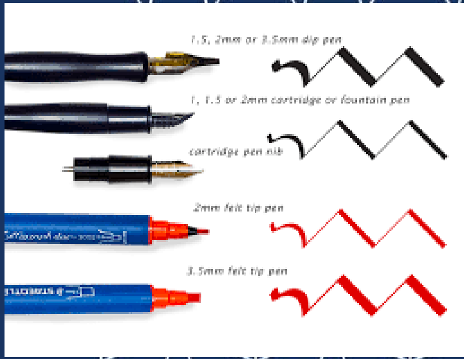

Figure 5: Dip Pen analogy

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Resolution and Competitors

- NFES is not the only direct-wire nanofabrication style to utilize serial material deposition
- DPN uses atomic force microscope tip deposits materials with precise position control (30 nm line width)
  - This is better than electrospinning!
- ES used for large, continuous areas with fast deposition
- NFES, however, provides feasibility of controllable electro spinning for sub 100nm fabrication; thus, allowing it to complement DPN, inkjet, and conventional electrospinning deposition procedures

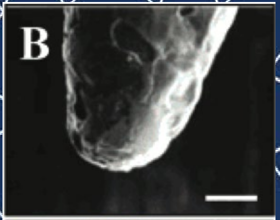

FIgure 6:SEM photograph of Tip diameter 25 microns

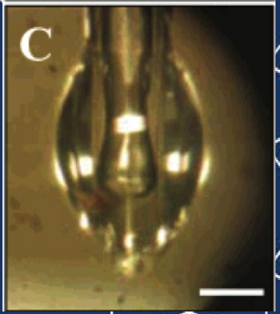

FIgure 7: Optical photograph of 50 micron diameter polymer solution on the tungsten tip

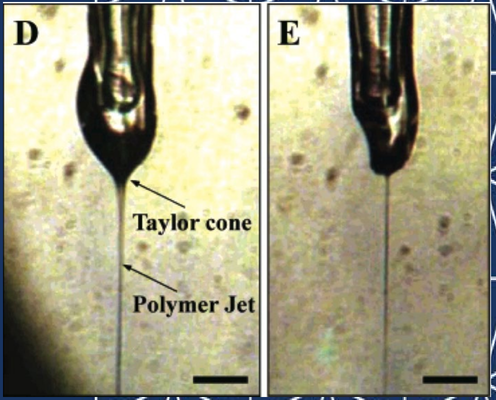

Figure 8: Polymer ejected from the taylor cone under EF after some time

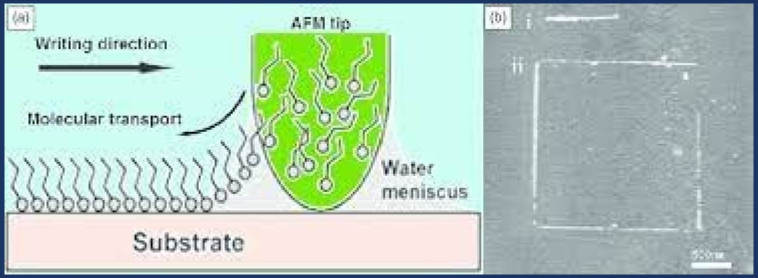

FIgure 9: DPN process

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Nanowires fabricated through NFES

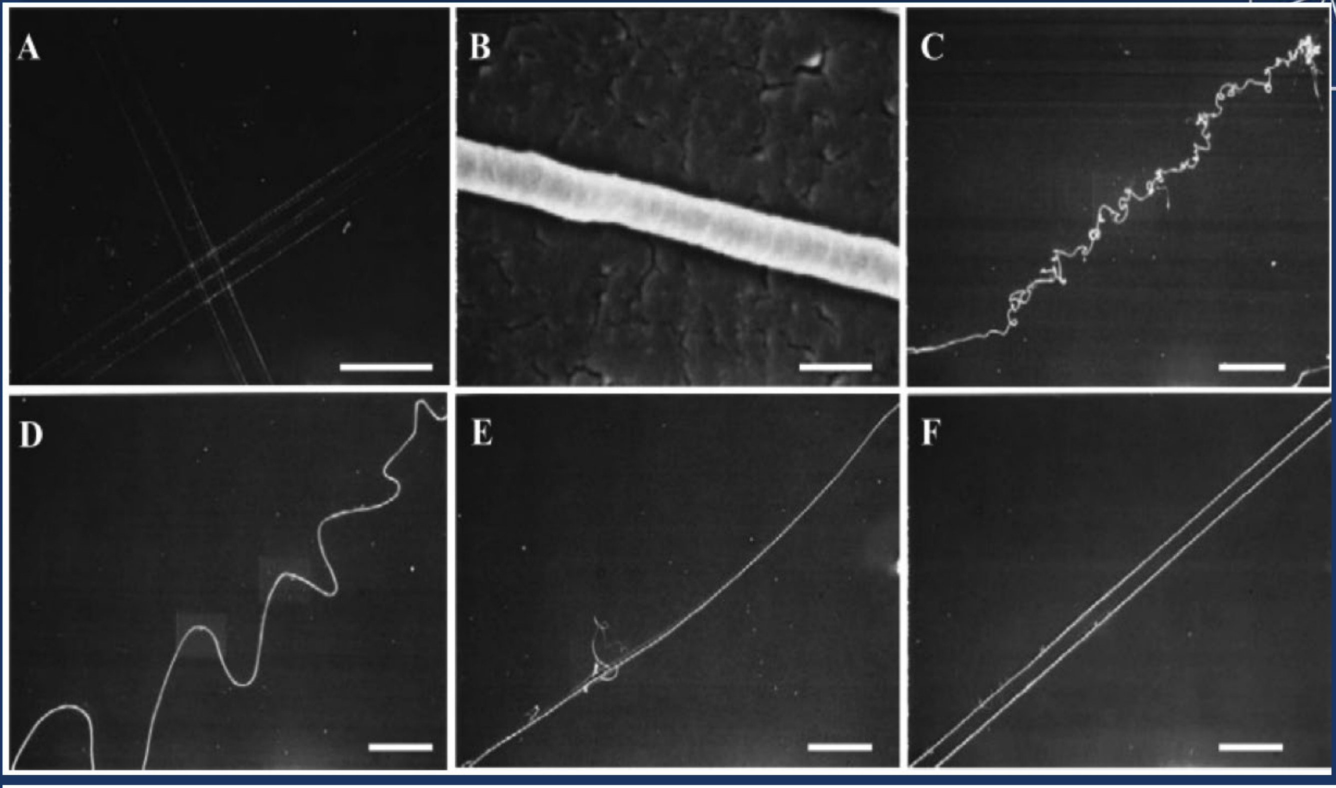

Figure 2. (A) Two groups of parallel lines constructed perpendicular to each other by NFES. Scale bar, 1 mm. (B) Enlarged SEM photomicrograph showing a nanofiber with diameter of 300 nm. Scale bar, 500 nm. (C) NFES result when the collector has a moving speed of 5 cm/s showing "local spiraling". Scale bar, 100 μm. (D) Collector moving speed at 10 cm/s. Scale bar, 100 μm. (E) Collector moving speed at 15 cm/s. Scale bar, 100 μm. (F) Collector moving speed is 20 cm/s, and straight lines can be constructed. The two nanofibers are separated 25 μm away from each other under the control of the $x-y$ stage. Scale bar, 100 μm.

Experiment Conditions/Specifications

- Deposition of Poly ethylene oxide (PEO,M_v = 300,0000)
- Room temperature
- 1 atm pressure
- Finite tip introduced to intensify electrical field: activates electrospinning
- Small diameter liquid jets in the stable region
- Time length ~5 sec

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Near-Field Electrospinning Results

- Factors that affect the morphology of the electrospinning nanofabrication:
  - Droplet size
  - Applied Voltage
  - Electrode to collector distance
- NFES has similar morphology to that of conventional ES processes
  - MORE DATA/EXPERIMENTS ARE NEEDED to characterize morphology factors
- Great Control is shown through drawing straight lines with ease

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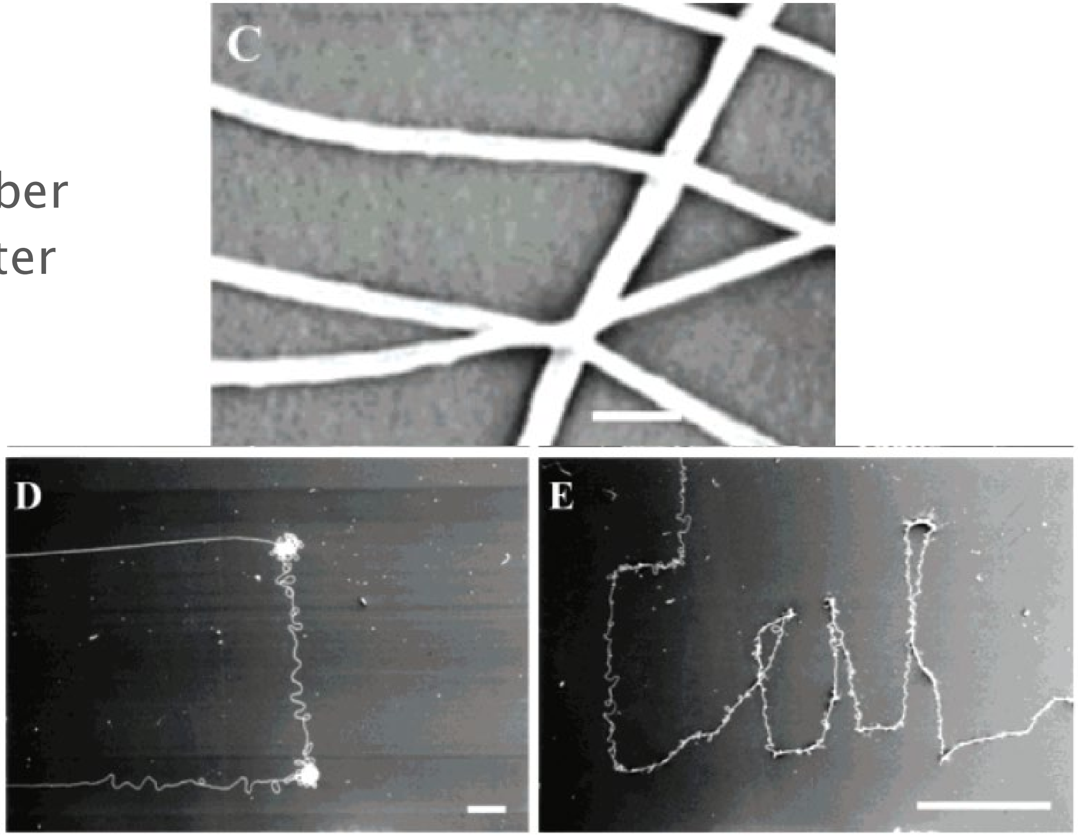
Nanofibers Control

- Greater control when nanofiber electrospinning speed is faster than collector moving speed
- Local spiraling decreases as collector speed increases
- 1.5 μm, typical distance between nanofibers with no external control



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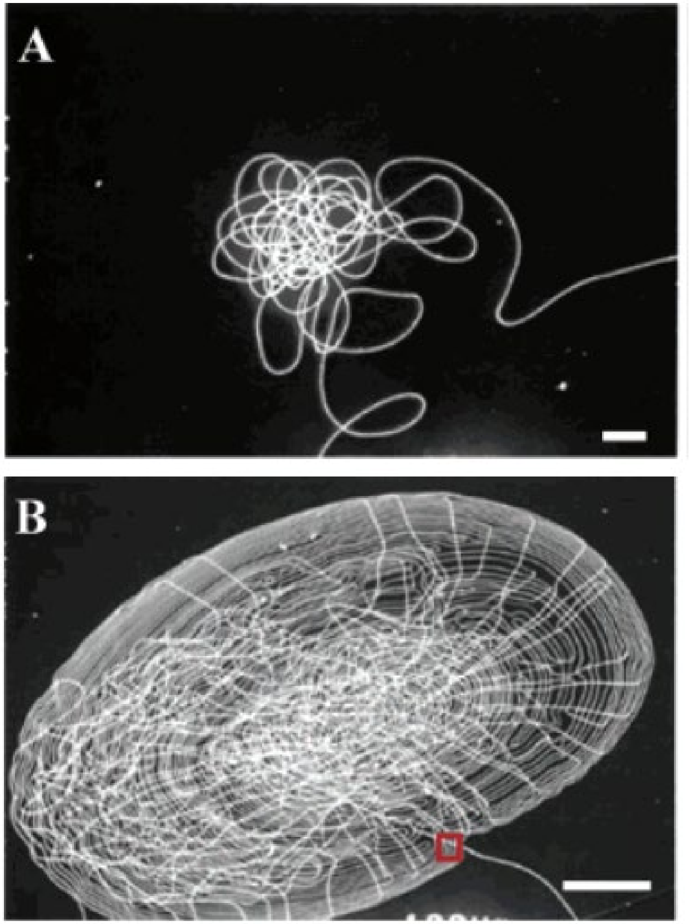
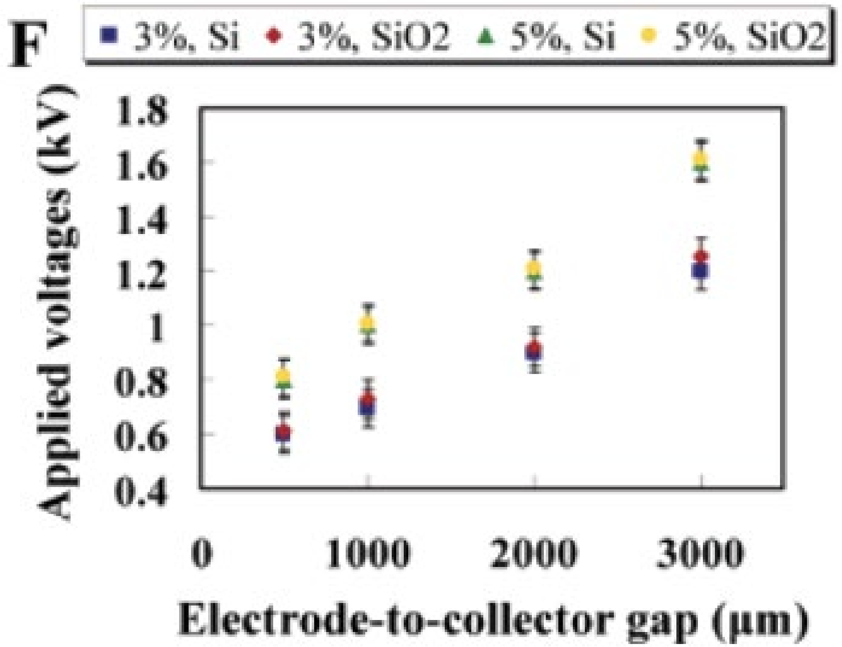
Locational Accuracy

- 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 μm, elliptical pattern of Figure B within 300 μm
- 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 μm utilized



Experiment Conclusions

- Possible to deposit nanofibers with both pattern and location control
- Spiraling effects are minimized when the spinnert 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

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