Welcome

المعهد العالي للصناعات البلاستيكية
Higher Institute For Plastics Fabrication

منسق الدورة

د. علي الدلبجي — الأستاذ المساعد بقسم الكيمياء – جامعة الملك سعود
وكيل معهد الملك عبدالله لتقنية النانو

أ. راضي العيد — نائب المدير التنفيذي - المعهد العالي للصناعات البلاستيكية

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جـامـعـة الملك سعود
King Saud University
1957

Workshop on

Electrospinning, Simple and Effective Approach in Nanotechnology

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Date : Monday; January 1, 2017
Time : 10 – 13
Location : Petrochemical Research Chair, Department of Chemistry
Building 5, Rm 2B87 and Lab AA7

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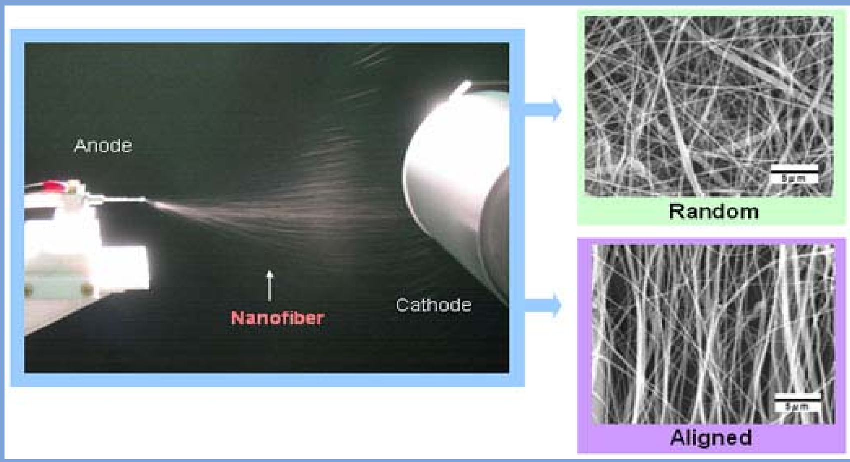
Electrospinning process

The process of spinning fibers with the help of electrostatic forces.



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Workshop Outlines

- ❖ Historical Background.
- ❖ Electrospinning Technique.
- ❖ Electrospun Nanofibers Architectures & Control of Various Morphologies
- ❖ Factors Affecting the Preparation of Electrospun Nanofibers
- ❖ Nanofibers Made From Polymers And Metal Oxides.
- ❖ Large Scale Production of The Electrospun Nanofibers
- ❖ Applications of Electrospun Nanofibers.
- ❖ Electrospinning at KSU; Petrochemical Research Chair.

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Background

- Electrospinning = Electrostatic spinning
- Electrospinning uses an electrical charge to draw very fine (*typically on the micro or nano scale*) fibers from a liquid.
- Electrospinning can be viewed as a special case of electrospraying.

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Historical Background

- Electrospraying

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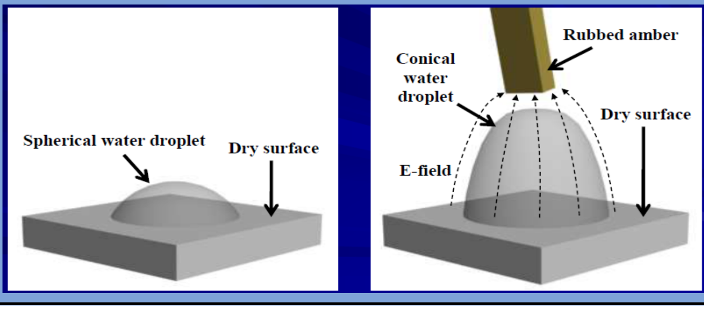
Historical Background

- **William Gilbert (1500s)**

(24 May 1544 – 30 November 1603), was an English physician, physicist and natural philosopher.

- o He set out to describe the behavior of magnetic and electrostatic phenomena.
- o He observed that when a suitably *electrically charged piece of amber was brought near a droplet of water* it would form a cone shape and small droplets would be ejected from the tip of the cone: *this is the first recorded observation of electrospraying*.



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Historical Background

- **Raleigh (1885)**
  - o The amount of charge required for the deformation of droplets was described by Lord Raleigh.
- **J.F. Cooley (1902) and W.J. Morton (1903)**
  - o In 1902 and 1903, Cooley and Moore *described in patents, apparatus for spraying of liquids by use of electrical charges*.

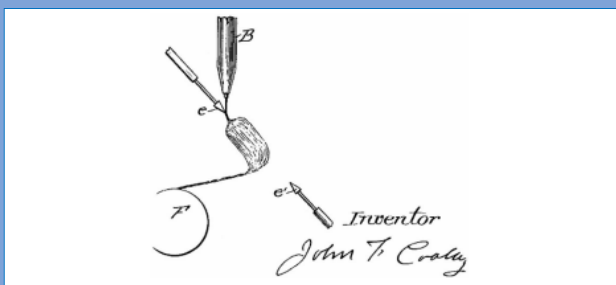

Figure 1.1 A solution of polymer (e.g., collodion or cellulose nitrate in ether or acetone) delivered into the high-voltage direct current (DC) electric field via tube *B* to form electrospun nanofibers collected on a drum *F*. (*Source*: Cooley 1902, Fig. 5 of U.S. patent 692, 631.)

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Historical Background

- **John Zeleny (1914)**
  - His effort began the attempt to *mathematically model the behavior of fluids under electrostatic forces*.
  - Zeleny reported that *the fine fiber-like liquid jets could be emitted from a charged liquid droplet in the presence of an electrical potential*, which is considered to be **the origin of principle for the modern needle Electrospinning**.
- **Hagiwaba (1929)**
  - The preparation of artificial silk by electrical charges was described by Hagiwaba.

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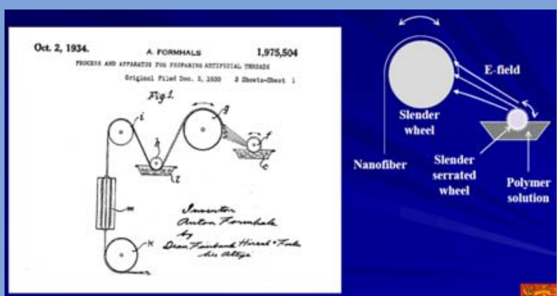
Historical Background

- **Anton Formhals (1934-1944)**
  - In 1934, a crucial patent, revealing the experimental apparatus for the practical production of artificial filaments using electrical field was issued for the first time by Formhals.



Fabrication of textile yarns and a voltage of 57 kV was used for electrospinning cellulose acetate using acetone and monomethyl ether of ethylene glycol as solvent.

- **C.L Norton (1936)**
  - Electrospinning from a melt rather than a solution was patented by C.L Norton using an air-blast to assist fiber formation.

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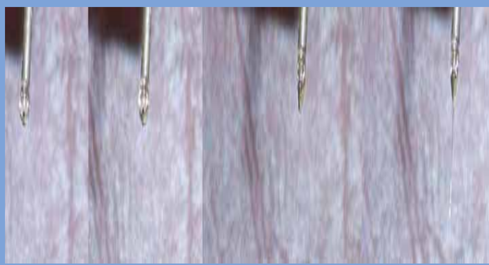
Historical Background

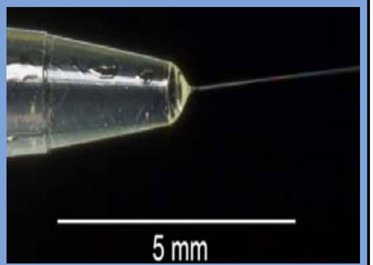
❑ Geoffrey Ingram Taylor (1960s)

Geoffrey Ingram Taylor (7 March 1886 – 27 June 1975) was a British physicist and mathematician

- Taylor produced the theoretical underpinning of electrospinning.
- Taylor's work contributed to electrospinning by *mathematically modelling the shape of the cone formed* by the fluid droplet under the effect of an electric field. (Taylor cone)



Taylor cone is a consequence of induced charge relaxation to the free surface of the liquid at the exit of the nozzle



When a small volume of electrically conductive liquid is exposed to an electric field, the shape of liquid starts to deform from the shape caused by surface tension alone.

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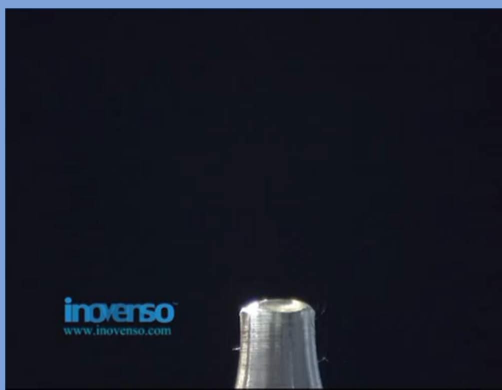
Historical Background

❑ Taylor cone



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Historical Background

1970s

- Some attempts at commercialization were undertaken.

  For example:

  - Simm, from the Bayer company, submitted a series of patents on electrospinning of plastics.
  - Companies such as Donaldson Company and Freudenberg have already applied the outcome of electrospinning process in their air filtration products since past two decades.

- A variety of electrospinning setups were suggested in early electrospinning setups that have some similarities to recent efforts.

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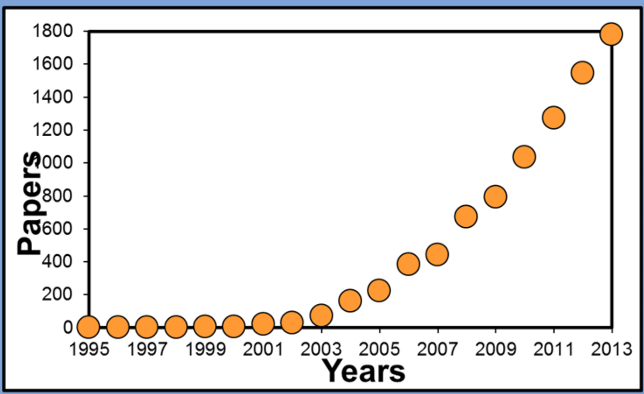
Historical Background

Industry *vs.* Academia

- Academia picked-up electrospinning slowly in the 1990s.
- Several research groups, especially the Reneker's group (*The University of Akron*), revived electrospinning by demonstrating the fabrication of ultra-thin fibers from various polymers.



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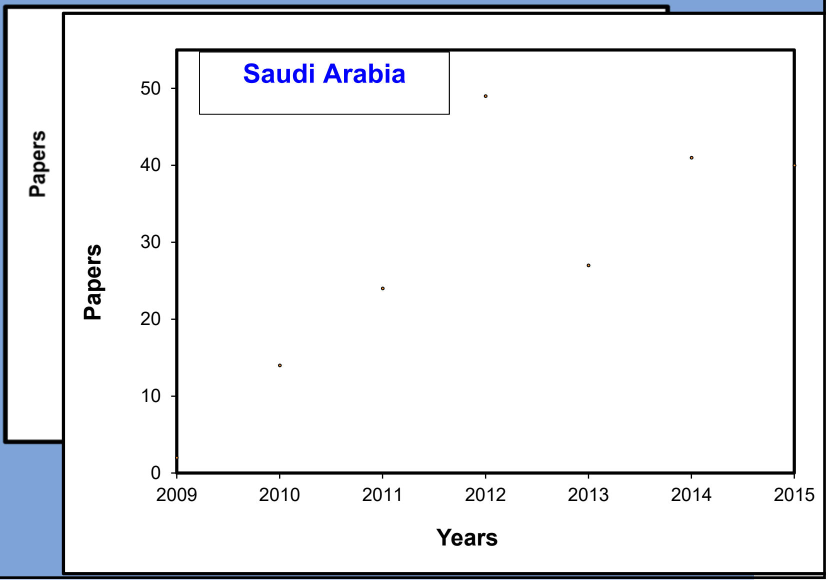
Historical Background

❑ **Growing Popularity of Electrospinning (1994-2013)**



Historical Background

❑ **Milestone in Electrospinning**

- 2008 • Biomimetic extracellular matrix nanofibrous scaffolds
- 2007 • **Emulsion electrospinning**
- 2006 • Growth factor released nanofibrous scaffolds
- 2005 • Guiding effect of aligned electrospun nanofibers on human cells
- 2004 • Drug eluting nanofibers
- 2003 • **Core-shell electrospinning**
- 2002 • Drug delivery and Ceramic nanofibers
- 2001 • Scaffolds for tissue engineering
  • Aligned nanofibers
- 2000 • Theoretical model for electrospinning Jet formation
- 1999 • Electrospinning nanocomposites
- 1981 • **Melt electrospinning**
- 1902 • **Solution electrospinning**

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- ❖ Applications of Electrospun Nanofibers.
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ELECTROSPINNING TECHNIQUE

❑ **Electrospinning Process**

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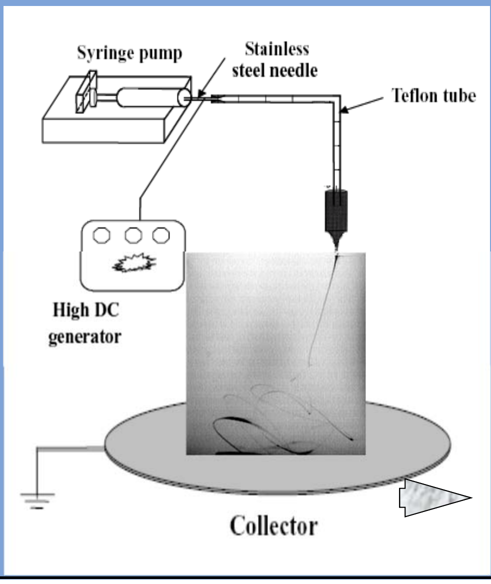
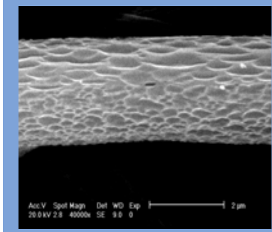
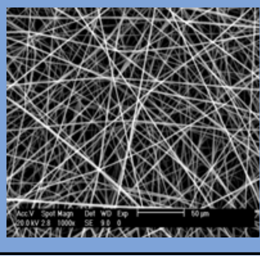
Electrospinning Technique

- Typical Electrospinning







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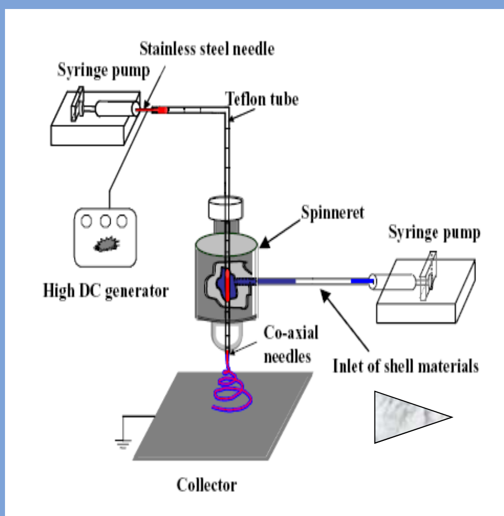
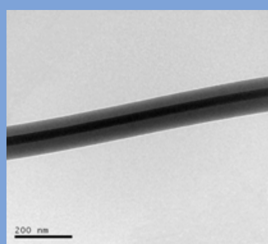
Electrospinning Technique

- Coaxial Electrospinning





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Electrospinning Technique

❑ **Coaxial Electrospinning**

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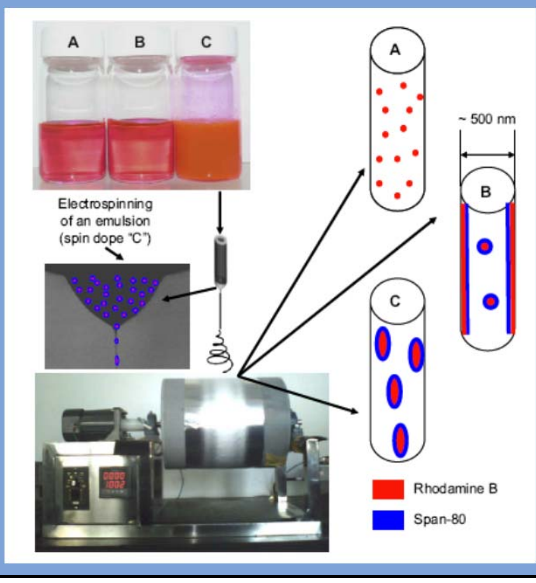
Electrospinning Technique

❑ **Emulsion Electrospinning**



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Electrospinning Technique

- ❑ **Electrospinning process – Needleless**

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Electrospinning Technique

- ❑ **Electrospinning process - stationary wire electrode**

stationary wire electrode system as found in industrial

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Electrospinning Technique

❑ **Welcome To World Nanofibers**

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Workshop Outlines

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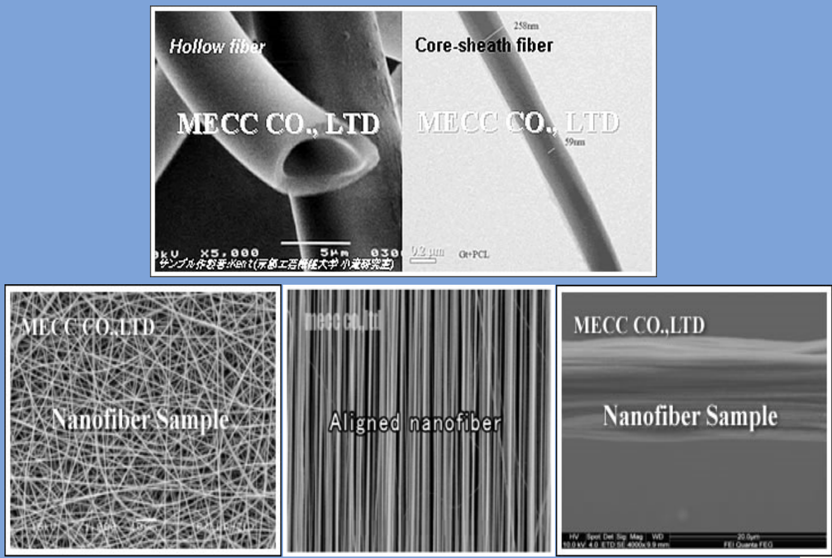
Electrospun Nanofibers Architectures



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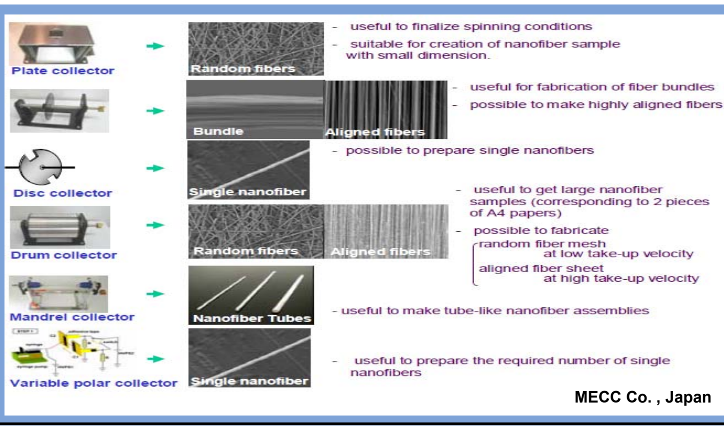
CONTROL OF VARIOUS MORPHOLOGIES

As for controlling of morphologies, design of spinnerets and collectors are very important.

All electrospinning equipments accept 5 types of collectors such as plate, rotating disc, drum, mandrel, and variable polar collectors.

Each collector can be replaced with other one.
Users can select the suitable collector up to their requirements



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Factors affecting the preparation of Electrospun nanofibers

A. Solution Parametres

1. Concentration
2. Molecular Weight
3. Viscosity
4. Surface Tension
5. Conductivity/Surface Charge Density

B. Processing Parameters

1. Voltage
2. Flow Rate
3. Collectors
4. Tip-to-Collector Distance (TCD)

C. Ambient Parameters

1. Humidity
2. Temperature

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Factors affecting the preparation of Electrospun nanofibers

A. Solution Paramètres

1. Concentration

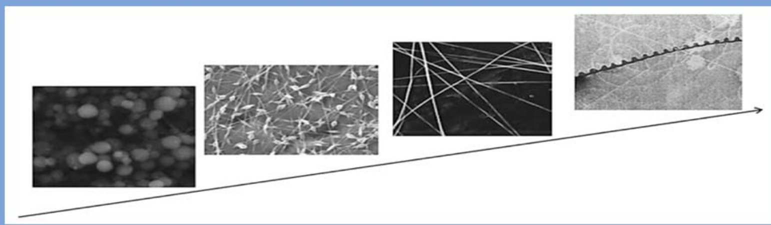
The concentrations of polymer solution play an important role in the fiber formation during the electrospinning process.

1. Very low concentration;

- Polymeric micro (nano)-particles will be obtained.
- *At this time, electrospray occurs instead of electrospinning owing to the low viscosity and high surface tensions of the solution.*

2. Little higher concentration;

a mixture of beads and fibers will be obtained



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Factors affecting the preparation of Electrospun nanofibers

A. Solution Paramètres

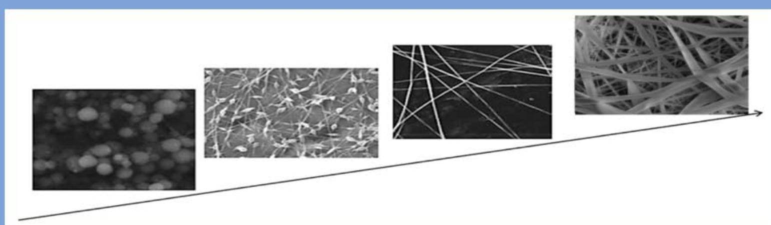
3. Suitable concentration;

Smooth nanofibers can be obtained.

4. Very high concentration;

not nanoscaled fibers, helix-shaped microribbons will be observed

- *Usually, increasing the concentration of solution, the fiber diameter will increase if the solution concentration is suitable for electrospinning.*
- *Additionally, solution viscosity can be also tuned by adjusting the solution concentration.*



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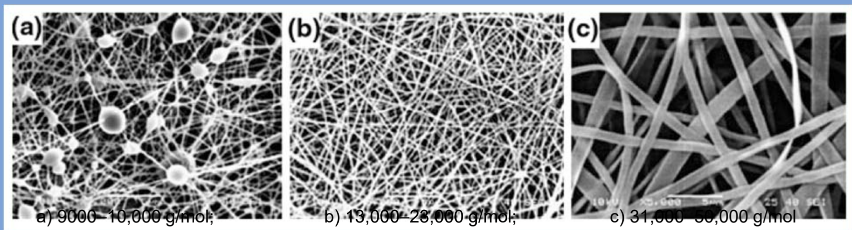
Factors affecting the preparation of Electrospun nanofibers

A. Solution Paramètres

2. Molecular Weight

Molecular weight reflects the entanglement of polymer chains in solutions, namely the *solution viscosity*.

- Lowering the molecular weight of the polymer trends to form beads rather than smooth fiber.
- Increasing the molecular weight, smooth fiber will be obtained.
- Further increasing the molecular weight, micro-ribbon will be obtained



a) 9000–10,000 g/mol; b) 13,000–23,000 g/mol; c) 31,000–50,000 g/mol

(solution concentration: 25 wt. %)

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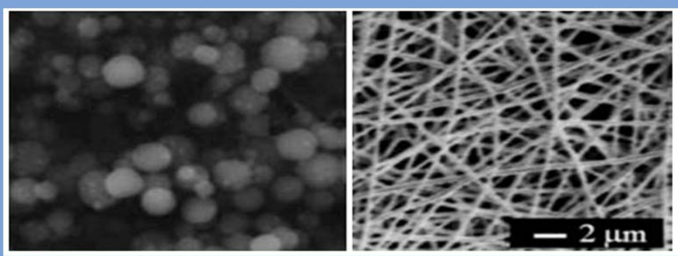
Factors affecting the preparation of Electrospun nanofibers

A. Solution Paramètres

3. Viscosity (*determining the fiber morphology*)

- Continuous and smooth fibers cannot be obtained in very low viscosity.
- Very high viscosity results in the hard ejection of jets from solution, namely there is a requirement of suitable viscosity for electrospinning.

Generally, the solution viscosity can be tuned by adjusting the polymer concentration of the solution; thus, different products can be obtained.



1.3 wt. % 15 wt. %

Electrospun PAN (The molecular weight of PAN is 150,000)

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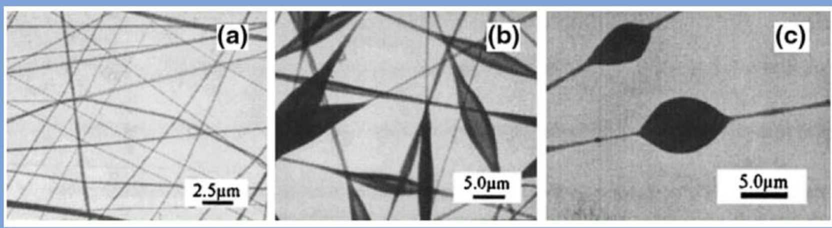
FACTORS AFFECTING THE PREPARATION OF ELECTROSPUN NANOFIBERS

A. Solution Paramètres

4. Surface Tension

In 2004, Yang and Wang systematically investigated the influence of surface tensions on the morphologies of electrospun products with PVP as model with ethanol, DMF, and MC as solvents.

Solvents may contribute different surface tensions.



a) Ethanol; b) MC; c) DMF
TEM images of the PVP nanofibers electrospun from respectively.
The concentration is 4 wt. %.

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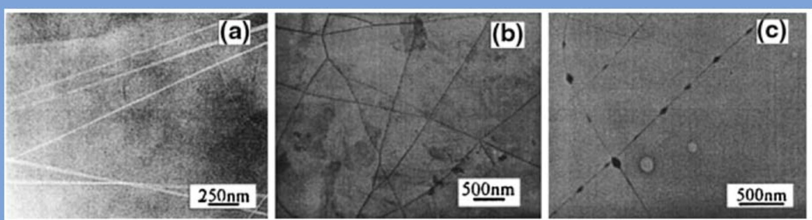
FACTORS AFFECTING THE PREPARATION OF ELECTROSPUN NANOFIBERS

A. Solution Paramètres

- The surface tension and solution viscosity can been adjusted by changing the mass ratio of solvents mix and fiber morphologies.
- Basically, surface tension determines the upper and lower boundaries of the electrospinning window if all other conditions are fixed.



a) 65/35, b) 50/50, c) 35/65,
TEM images of PVP (4 wt. %) nanofibers electrospun from ethanol/DMF solution with different mass ratios:

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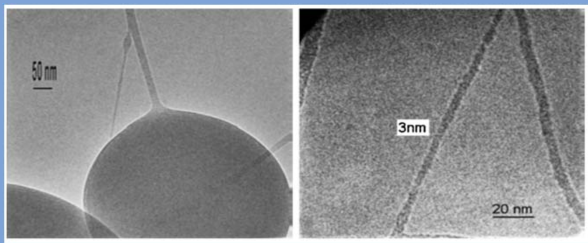
Factors affecting the preparation of Electrospun nanofibers

A. Solution Parametres

5. Conductivity/Surface Charge Density

- Solution conductivity is mainly determined by the polymer type, solvent sort, and the salt.
- Additionally, the electrical conductivity of the solution can be tuned by adding the ionic salts like KH_2PO_4, NaCl, and so on.
- **With the aid of ionic salts, nanofibers with small diameter can be obtained.**



Beaded nanofibers — Bead-free nanofiber by adding 0.44 % pyridine

SEM images of the electrospun products from 2 wt. % nylon-4, 6/formic acid solution.

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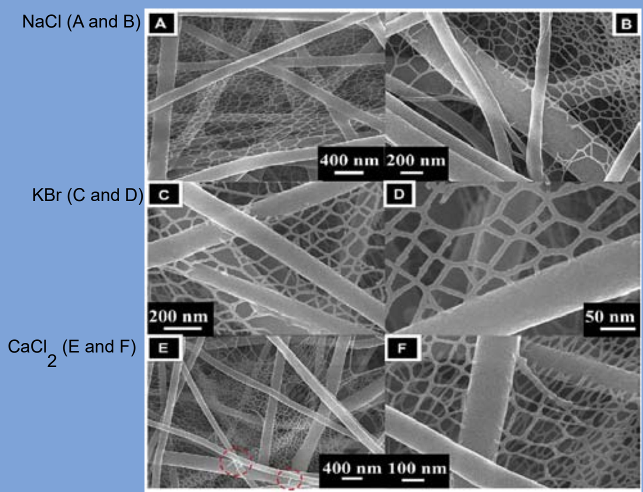
Factors affecting the preparation of Electrospun nanofibers

- Effect of ionic salts



- NaCl, KBr, and $CaCl_2$ are strong ionic salts.
- have high dissociation rates especially in the aqueous solutions.

FE-SEM images showing the spider-net in the electrospun nanofiber mats of Nylon-6 in formic/acetic acid, containing 1.5 wt% salt.

Nasser A.M. Barakat, Muzafar A. Kanjwal, Faheem A. Sheikh, Hak Yong Kim. Polymer 50 (2009) 4389–4396

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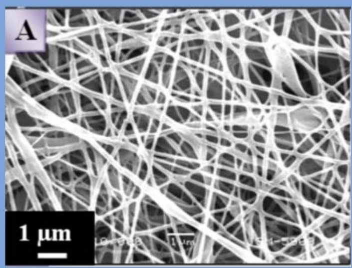
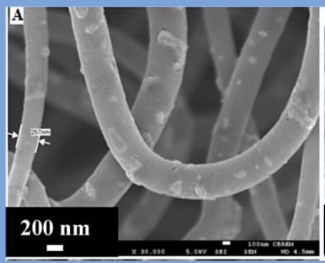
Factors affecting the preparation of Electrospun nanofibers

- **Impact of the salt nature**
  - **- Metallic salts of some organic acids have tendency to form sol–gel (e.g. nickel acetate and cobalt acetate**



Before calcination



After calcination in Ar atmosphere

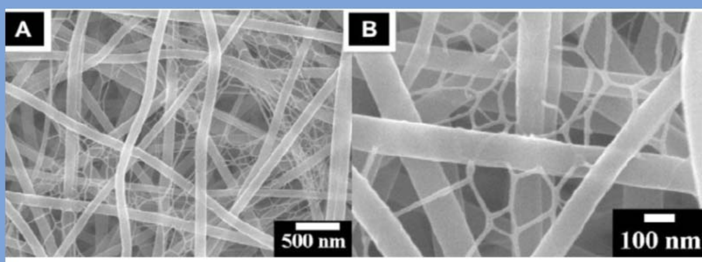
SEM images for the PVA/NiAc nanofibers mats

B.M.. Thamer, M.H. El-Newehya, N. A.M. Barakat, M.A. Abdelkareemd, S.S. Al-Deyab, and H.Y. Kim. Electrochimica Acta 142 (2014) 228–239 KSU

Factors affecting the preparation of Electrospun nanofibers

- **Impact of the salt nature**
  - Weak metallic acid was used; hydrogen hexacholorplatinate solution (H_2PtCl_6), It cannot form a sol–gel in the polymeric solution.

    The synthesized spider-nets are trivial compared with those obtained in the case of using the inorganic salts

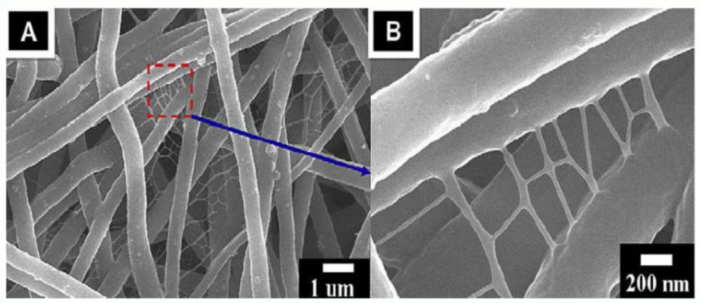


FE-SEM images showing the spider-net in the electrospun nanofiber mats of Nylon-6 in formic/acetic acid, containing 1.5 wt% salt, H_2PtCl_6.

Nasser A.M. Barakat, Muzafar A. Kanjwal, Faheem A. Sheikh, Hak Yong Kim. Polymer 50 (2009) 4389–4396 KSU

Factors affecting the preparation of Electrospun nanofibers

- Effect of polymer solution
  - PU solution in THF/DMF.
  - THF/DMF have very low polarity compared to water and do not react with the inorganic salts.
  - Small parts of spider-net were formed due to low ionization of the used salts in the PU solution.



FE-SEM images of electrospun polyurethane nanofiber mat containing 1.5 wt% salt, NaCl.

Nasser A.M. Barakat, Muzafar A. Kanjwal, Faheem A. Sheikh, Hak Yong Kim. Polymer 50 (2009) 4389–4396

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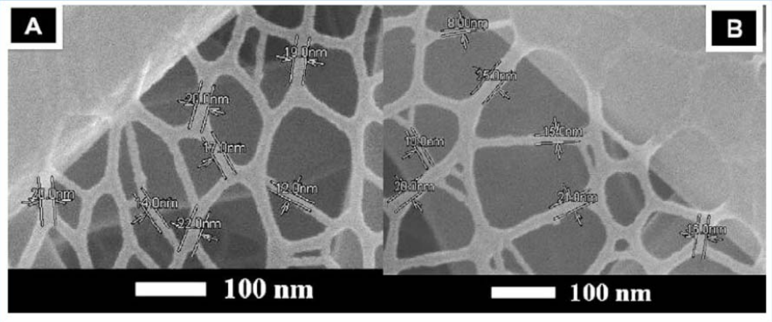
Factors affecting the preparation of Electrospun nanofibers

- Effect of salt kind and concentration on fiber diameter

The average diameter of the nanofiber in the spider-net synthesized is almost independent on both of salt kind and concentration.



Diameters of some fibers in the synthesized spider-net in case of 1.5 wt% salt, NaCl (A) and CaCl2 (B) of Nylon-6.

Nasser A.M. Barakat, Muzafar A. Kanjwal, Faheem A. Sheikh, Hak Yong Kim. Polymer 50 (2009) 4389–4396

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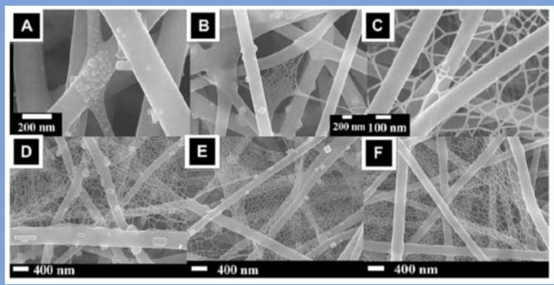
Factors affecting the preparation of Electrospun nanofibers

- **Effect of stirring time**

At 0.5 h; there is no spider-nets can be observed and salt nanoparticles are apparent attaching to the nanofibers. (stirring time was not enough to liberate ions on the solution).
At 3 h; spider-net starts to appear.
At 24 h (long time stirring); much spider-net was formed and no salt nanoparticles could be observed.

At 0.5 h; some salt nanoparticles are apparent and also spider-net is formed (fast dissociation of the salt in acid medium).
At 3h; decrease the amount of the salt nanoparticles.
At 24 h; completely dissolve the salt.



FE-SEM images after mixing times: 0.5, 3 and 24 h for PVA/NaCl (A, B and C)and for nylon-6/NaCl (D, E and F). Salt concentration is 1.5 wt.%.

Nasser A.M. Barakat, Muzafar A. Kanjwal, Faheem A. Sheikh, Hak Yong Kim. Polymer 50 (2009) 4389–4396

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Factors affecting the preparation of Electrospun nanofibers

B. Processing Parametres

1. Voltage

- Only the applied voltage higher than the threshold voltage, charged jets ejected from Taylor Cone, can occur.
- However, the effect of the applied voltages on the diameter of electrospun fibers is a little controversial.
- **For example;**
  Reneker and Chun have demonstrated that *there is not much effect of electric field on the diameter of electrospun polyethylene oxide (PEO) nanofibers.*

Reneker DH, Chun I (1996) Nanometre diameter fibres of polymer, produced by electrospinning. Nanotechnology 7(3):216–223.

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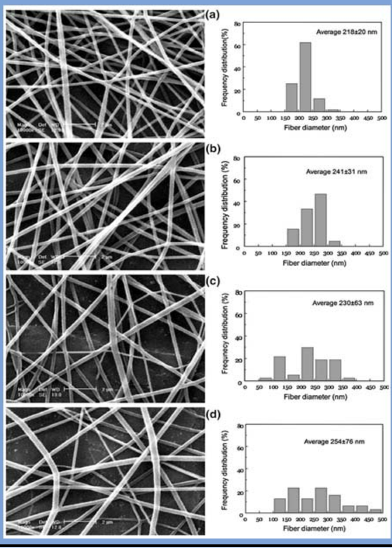
FACTORS AFFECTING THE PREPARATION OF ELECTROSPUN NANOFIBERS

B. Processing Parametres



Several groups suggested that higher voltages facilitated the formation of large diameter fiber.

For example;

Zhang *et al.* investigated the effect of voltage on morphologies and fiber diameters distribution with poly(vinyl alcohol) (PVA)/water solution as model.

Effect of voltage on morphology and fiber diameter distribution from a 7.4 wt. % PVA/water solution (DH = 98 %, tip–target distance = 15 cm, flow rate = 0.2 mL/h). Voltages: a) 5; b) 8; c) 10; d) 13 kV.

Zhang C, Yuan X, Wu L, Han Y, Sheng J (2005). Eur Polym J 41(3):423–432.

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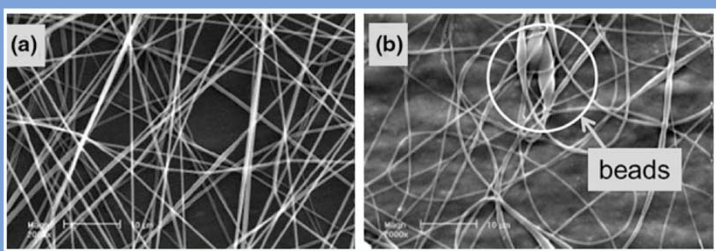
FACTORS AFFECTING THE PREPARATION OF ELECTROSPUN NANOFIBERS

B. Processing Parametres

2. Flow Rate

- Generally, lower flow rate is more recommended as the polymer solution will get enough time for polarization.
- If the flow rate is very high, bead fibers with thick diameter will form rather than the smooth fiber with thin diameter owing to the short drying time prior to reaching the collector and low stretching forces.



SEM images of the effect of the flow rate on the morphologies of the PSF fibers from 20 % PSF/DMAC solution at 10 kV. Flow rates of A and B are 0.40 and 0.66 ml/h,

Buchko CJ, Chen LC, Shen Y, Martin DC (1999) Processing and microstructural characterization of porous biocompatible protein polymer thin films. Polymer 40(26):7397–7407.

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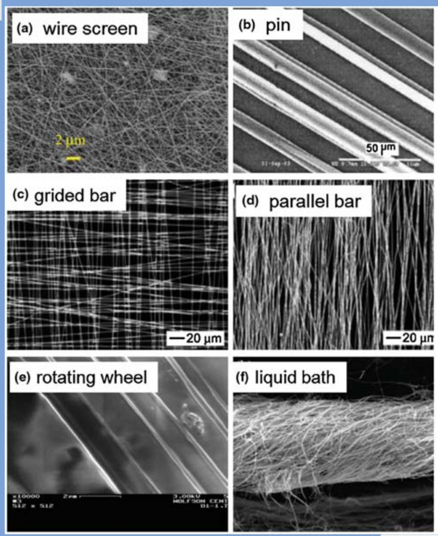
Factors affecting the preparation of Electrospun nanofibers

B. Processing Parametres

3. Collectors

- Collectors usually acted as the conductive substrate to collect the charged fibers.



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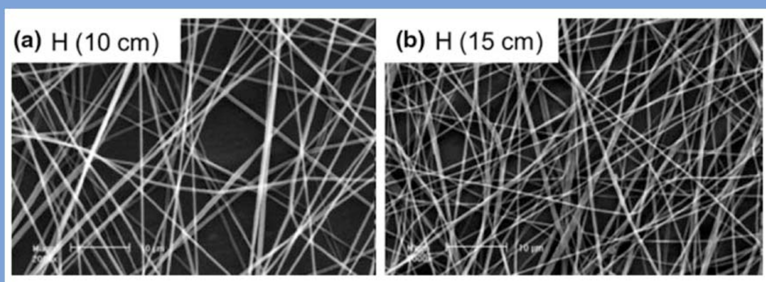
Factors affecting the preparation of Electrospun nanofibers

B. Processing Parametres

4. Tip-to-Collector Distance (TCD)

- If the distance is too short, the fiber will not have enough time to solidify before reaching the collector.

- If the distance is too long, bead fiber can be obtained.



SEM images of the electrospun PSF fibers from 20 wt. % PSF/DMAC solution at 10 kV with different distances. The distances of A and B are 10 and 15 cm, respectively. The diameters of A and B are 438 ± 72 and 368 ± 59 nm,

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Factors affecting the preparation of Electrospun nanofibers

C. Ambient Parametres

Ambient parameters can affect the fiber diameters and morphologies.

1. Humidity

- **Low humidity** may dry the solvent totally and increase the velocity of the solvent evaporation.
- **High humidity** will lead to the thick fiber diameter owing to the charges on the jet can be neutralized and the stretching forces become small.
- The variety of humidity can also affect the surface morphologies of electrospun nanofibers.

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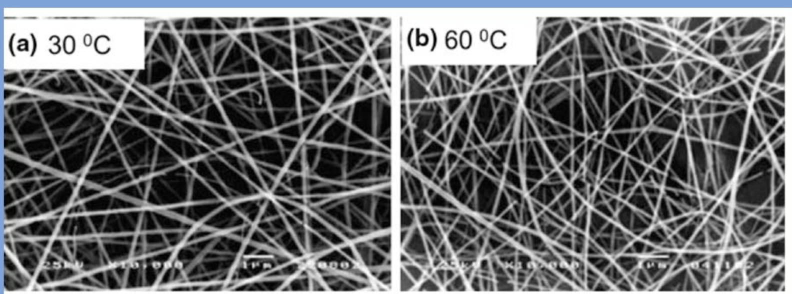
Factors affecting the preparation of Electrospun nanofibers

C. Ambient Parametres

2. Temperature

- Increasing temperature favors the thinner fiber diameter.



SEM images of the electrospun PA-6-32 fibers under different temperatures. The temperatures of A and B are 30 and 60 °C, respectively. The diameters of A and B are 98 and 90 nm

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Workshop Outlines

- ❖ Historical Background.
- ❖ Electrospinning Technique.
- ❖ Electrospun Nanofibers Architectures & Control of Various Morphologies
- ❖ Factors Affecting the Preparation of Electrospun Nanofibers
- ❖ Nanofibers Made From Polymers And Metal Oxides.
- ❖ Large Scale Production of The Electrospun Nanofibers
- ❖ Applications of Electrospun Nanofibers.
- ❖ Electrospinning at KSU; Petrochemical Research Chair.

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Nanofibers made from polymers and metal oxides

Electrospinning of polymer + solvent system

Sl. No.	Polymers	Suitable solvents
1.	Polyvinyl alcohol (PVA)	Water
2.	Polyvinyl acetate (PVAc)	Acetone, water
3.	Polyethylene oxide (PEO)	Water/chloroform, Iso-propyl alcohol
4.	Polyvinyl chloride (PVC)	Tetra hydro furan (THF), Di-methyl formamide (DMF)
5.	Polyurethane (PU)	DMF
6.	Polycarbonates (PC)	DMF, THF
7.	Polyvinyl pyrrolidone (PVP) Polyvinylcarbazole	Water, ethyl alcohol, isoproponal Dichlormethane
8.	Cellulose acetate	Acetone
9.	Polyacrylonitrile (PAN)	DMF
10.	Polystyrene (PS)	DMF, Diethyl formamide (DEF), toluene
11.	Poly ether amide (PEA)	Hexa fluoro 2-propanol
12.	Polyethylene terephthalate	Dichloromethane + tri-fluoro acetic acid
13.	Polyaniline	Chloroform
14.	Polyimides Polyamides (PA)	Phenol Dimethyl acetamide
15.	Polysulfone	N, N-dimethylformamide
16.	Nylon 6	1,1,1,3,3,3-hexa fluoro-2-propanol (HFIP), DMF, Formic acid
17.	Polycaprolactone	Acetone
18.	Poly (Methyl methacrylate) PMMA	Toluene + DMF, THF, acetone, chloroform
19.	Polyethylene terephtalate, (PET)	Dichlormethane and trifluoracetic acid
20.	Collagen	Hexafluoro-2-propanol

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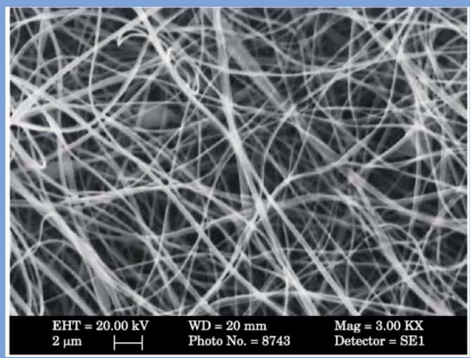
NANOFIBERS MADE FROM POLYMERS AND METAL OXIDES

o PAN Fibers

- Polyacrylonitrile (PAN) polymer nanofibers in Dimethyl Formamide (DMF) were prepared by electrospinning technique (V = 9kV, TCD = 7 cm).
- The diameters of the fibers are in the range of 50–320 nm.



SEM images of PAN nanofibers

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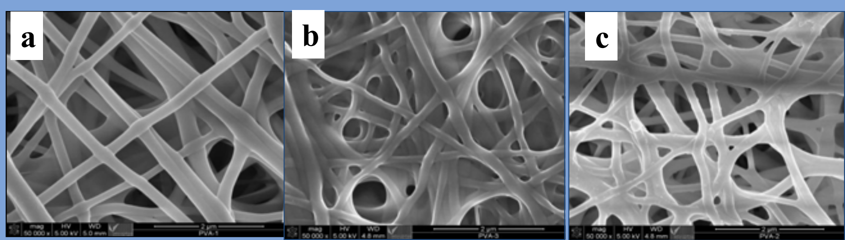
NANOFIBERS MADE FROM POLYMERS AND METAL OXIDES

o PVA/PEO Fibers

- Fabrication of electrospun nanofibers based on PVA/PEO blend.
- Stabilization of electrospun PVA/PEO nanofibers against disintegration in water by heating in oven at 110ºC, or by soaking in isopropyl alcohol for 6 h.



SEM images of electrospun nanofibers containing MTZ; (a) electrospun mat; (b) electrospun mat-alc; (c) electrospun mat-h.

M. El-Newehy, S. Al-Deyab, E.-R. Kenawy, and A. Abdel-Megeed, *Fibers and Polymers*, 13(6), 709-717, 2012.

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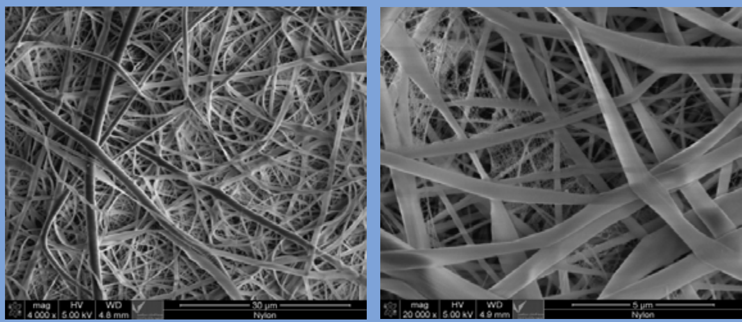
NANOFIBERS MADE FROM POLYMERS AND METAL OXIDES

o Nylon-6 Fibers

- Nanospider technology for the production of Nylon-6 nanofibers from formic acid



SEM images of electrospun nylon-6 nanofiber containing.

M. El-Newehy*, S. Al-Deyab, E.-R. Kenawy, and A. Abdel-Megeed. *Journal of Nanomaterials*, Vol. 2011, Article ID 626589, 8 pages, 2011.

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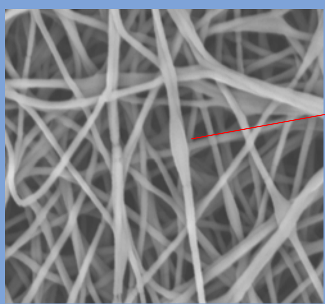
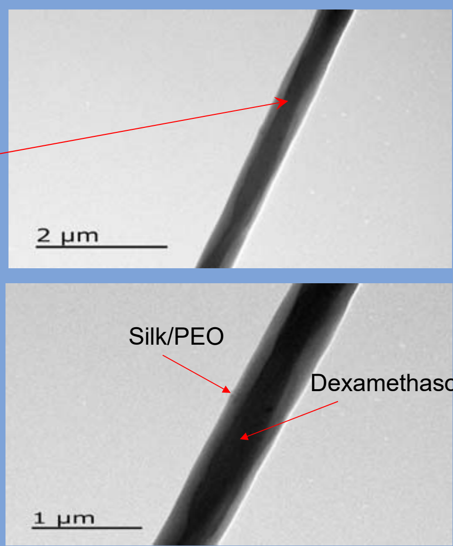
NANOFIBERS MADE FROM POLYMERS AND METAL OXIDES

o Silk /PEO





TEM images of Silk/PEO nanofibers with dexamethasone

W. Chen, D. Li, A. El-Shanshory, M. El-Newehy, H.A. El-Hamshary, S.S. Al-Deyab, C. He, X. Mo. *Colloids and Surfaces B: Biointerfaces*, 126, 561-568, 2015

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Nanofibers made from polymers and metal oxides

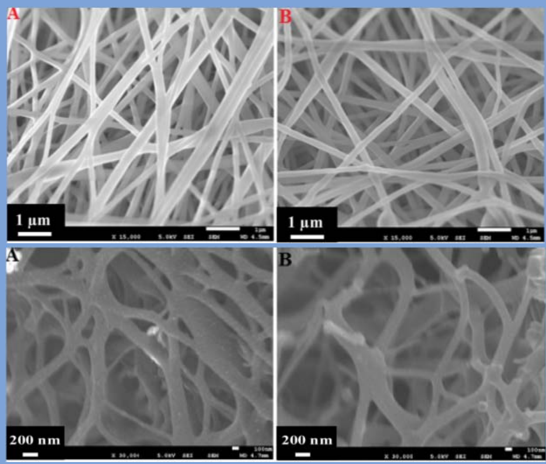
o **PVA/CoAc**

Urea content

(A) 0.0% (B) 1.0%.

Before calcination

After calcination in Ar atmosphere at 850°C



SEM images for the PVA/CoAc nanofibers mats.

B.M. Thamer, M.H. El-Newehy, S.S. Al-Deyab, M.A. Abdelkareem, H.Y. Kim, N.A.M. Barakat. Applied Catalysis A: General 498 (2015) 230–240

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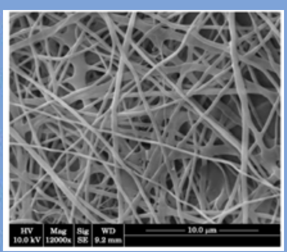
Nanofibers made from polymers and metal oxides

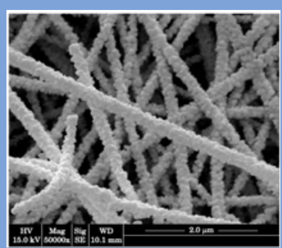
o **Alumina Nanofibers**

- Alumina nanofibers were prepared using PVA as polymer precursor and aluminium acetate as alumina precursor.
- The prepared nanofibers were heat treated at 900°C and 1300°C in order to remove the organics to generate pure alumina nanofibers.



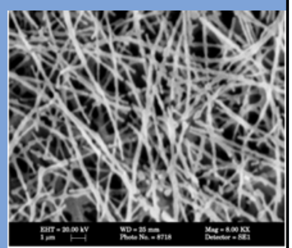
SEM images of PVA/Al acetate nanofibers

Electrospinning (TCD = 10 cm, flow rate = 1.3 mL/h, humidity 50–60



SEM images of Alumina nanofibers heat treated at 900°C.

beaded structure due to loss of organics leaving the unsintered alumina phase)



SEM images of Alumina nanofibers heat treated at 1300°C.

the diameters of the fibers are further reduced due to sintering

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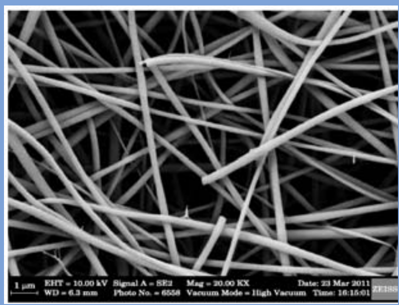
Nanofibers made from polymers and metal oxides

o Barium Titanate ($BaTiO_3$) Nanofibers

- Applications as dielectric capacitors, non-volatile ferroelectric random access memories, transducers, sensors and actuators, solid oxide fuel cells etc
- $BaTiO_3$ nanofibers were prepared from a homogeneous viscous solution of barium acetate + titanium isopropoxide + polyvinylpyrolidone (PVP) solutions by electrospinning technique (V = 9 kV, TCD = 7cm).



SEM images of electrospun Barium titanate nanofibers

Fibers cylindrical, smooth with diameters in the range of 50–400 nm

SEM images of heat treated electrospun Barium titanate nanofibers

The calcined BaTiO3 nanofibers are found to be coarse, brittle and diameter reduced by 12 %

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- ❖ Electrospinning at KSU; Petrochemical Research Chair.

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Large scale production

- The major challenge associated with electrospinning is its production rate, compared with that of conventional fiber spinning.
- Solvent recovery in large-scale electrospinning is a crucial issue, which has limited the industrialization of this technology.
- Although melt electrospinning can eliminate solvent recycle problems, the majority of fibers produced by melt electrospinning have relatively large diameters.

  To date there have been no reports on the mass production of nanofibers from melt polymers.

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Large scale production

- However, the understanding of the scale-up possibility of the electrospinning process is still in its infancy.
- Here we summarize recent advances regarding the enhancement of electrospinning throughput with special emphasis on multiple jets from multi-needles and the free surface of polymer solutions.

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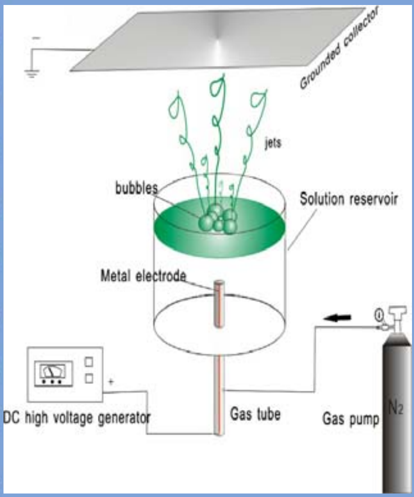
Large scale production

BUBBLE ELECTROSPINNING FOR MASS PRODUCTION OF NANOFIBERS



The experimental setup of the aerated solution electrospinning

- The polymer solution was added into the reservoir.
- Open the gas pump carefully until multiple bubbles were formed on the liquid surface.
- Then turn on the DC high voltage generator.
- When the applied voltage was increased to the threshold voltage, there were multiple jets towards the collector from the bubbles.
- The experiment was carried out at room temperature.

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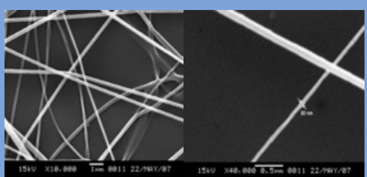
Large scale production

BUBBLE ELECTROSPINNING FOR MASS PRODUCTION OF NANOFIBERS

New bottom-up electro spinning

Bubble Electro spinning



The minimum diameter of nanofibers was 50nm.

Advantages

- More bubbles can produce more jets.
- Production rate could be higher than that in the ordinary e-spin process
- One nozzle produce several bubbles
  - easy manufacture,
  - easy operation,
  - low cost,
  - high throughput, etc

Disadvantages

- The arrangement of the electrospun fibers was in disorder.
- Trajectory ejecting jets were so thick that the mixture solvent had no time to volatilize completely because of water in the solvent

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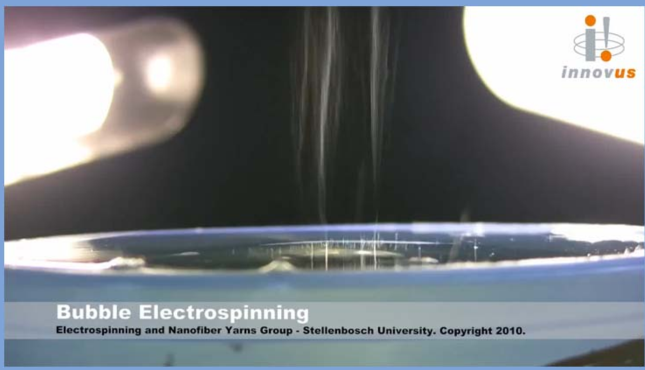
Large scale production

BUBBLE ELECTROSPINNING FOR MASS PRODUCTION OF NANOFIBERS



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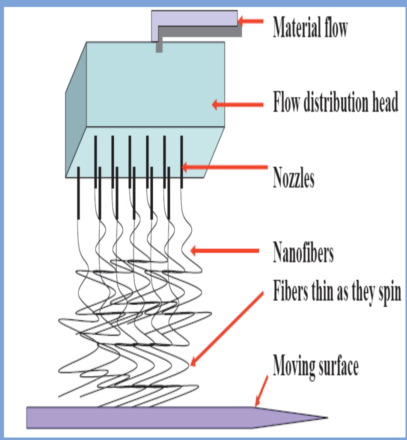
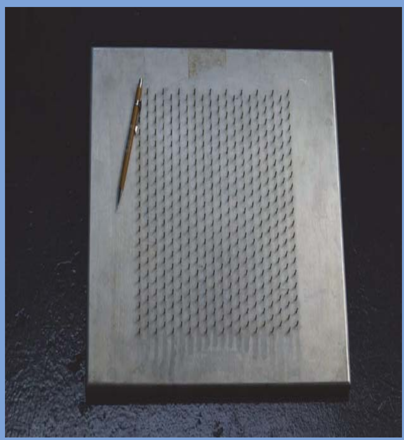
Large scale production

MULTI-NOZZLE CONSTRUCTIONS





Schematic (a) and photograph (b) of a multi-nozzle spinning head by NanoStatics

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Large scale production

MULTI-NOZZLE CONSTRUCTIONS

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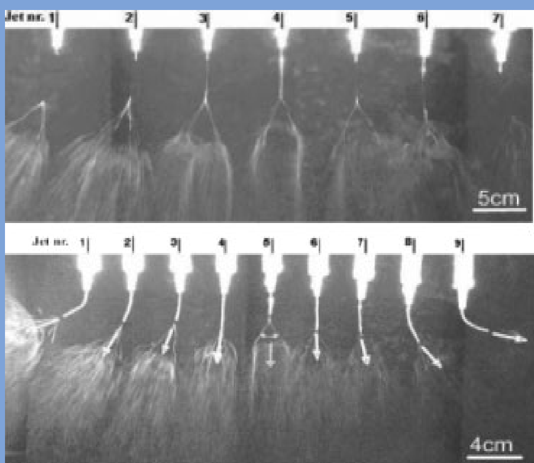
Large scale production

MULTI-NOZZLE CONSTRUCTIONS

SEVEN- AND NINE- NEEDLEs WITH LINEAR ARRAY



Advantage

Stable electro spinning process from each Needle

Disadvantage

Interference between jets, non-uniform Nano fibers deposition

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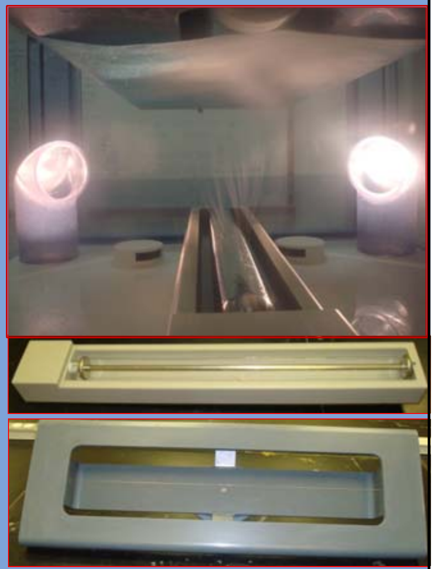
Large scale production

FREE LIQUID SURFACE ELECTROSPINNING

NANOSPIDER TM

Nanospider; NS LAB 500S
Elmarco, CZECH REPUBLIC



Advantage

- No clogging
- Production rate
  1.5 g min^{-1} m^{-1}

Disadvantage

- Loose control of solution feeding

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Large scale production

FREE LIQUID SURFACE ELECTROSPINNING

NANOSPIDER TM

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Large scale production

NOZZLE-LESS ELECTROSPINNING UNIT

The nozzle-less principle using rotating electrodes has been developed into a commercially available industrial scale

Nozzle-less production electrospinning line (NanospiderTM)

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Large scale production

COMPARISON OF NOZZLE VS NOZZLE-LESS ELECTROSPINNING

Production variable	Nozzle	Nozzle-Less
Mechanism	Needle forces polymer downwards. Drips and issues deposited in web.	Polymer is held in bath, even distribution is maintained on electrode via rotation.
Hydrostatic pressure	Production variable – required to be kept level across all needles in process.	None.
Voltage	5 – 20 kV	30 – 120 kV
Taylor cone separation	Defined mechanically by needle distances.	Nature self-optimizes distance between Taylor cones (Eq. (6)).
Polymer concentration	Often 10% of solution.	Often 20% or more of solution.
Fiber diameters	80, 100, 150, 200, 250 and higher. Standard deviation likely to vary over fiber length.	80, 100, 150, 200, 250 and higher. Standard deviation of +/- 30%.

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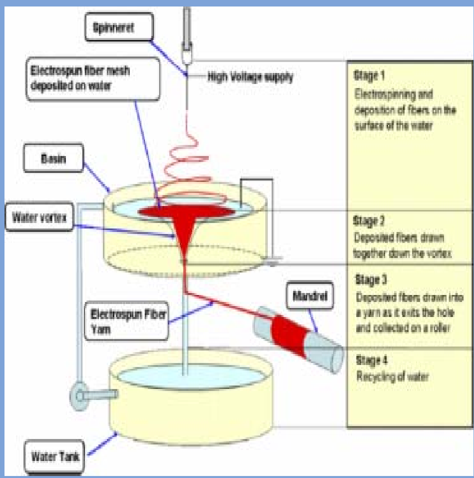
Large scale production

ELECTROSPINNING SETUP WITH A DYNAMINC LIQUID COLLECTOR



Advantage

- **Twists imparted on nanofibre bundle liquid recycling**
- **Production rate**

  57–76 m min^{-1}

Disadvantage

- **Polymers to be electrospun should not be soluble in the liquid bath**
- **No drying device**

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Applications of Nanofibers

- ❖ **Electrospun nanofibers are potential for many applications**
- ❖ **Properties of electrospun nanofibers**
  - o **Electrospun ceramic nanofibers are micro-nano porous in nature**

    These properties of electrospun nanofiber membranes make them suitable as filters in environment science.
  - o **The other properties of nanofibers such as**
    - **high porosity**
    - **large surface area**

    make them use in a variety of applications including fabrication of electric and optical devices, optical waveguides, optoelectronic components, fluidic devices, gas storage units, tissue engineering scaffolds, bioreactors etc.

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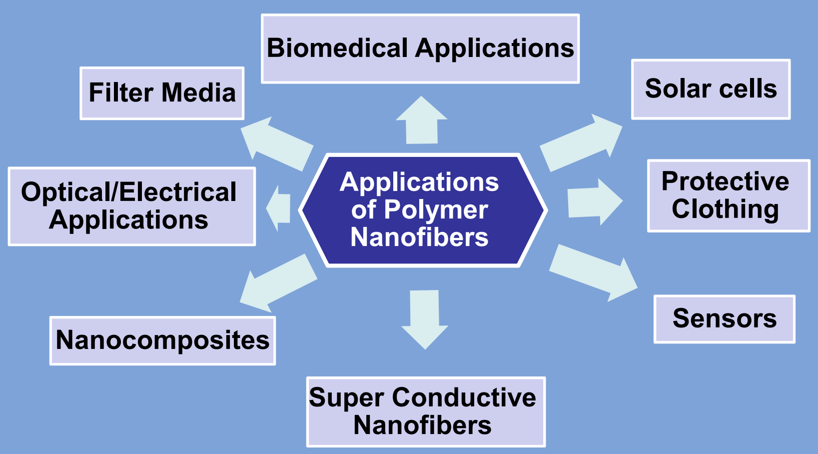
Applications of Nanofibers



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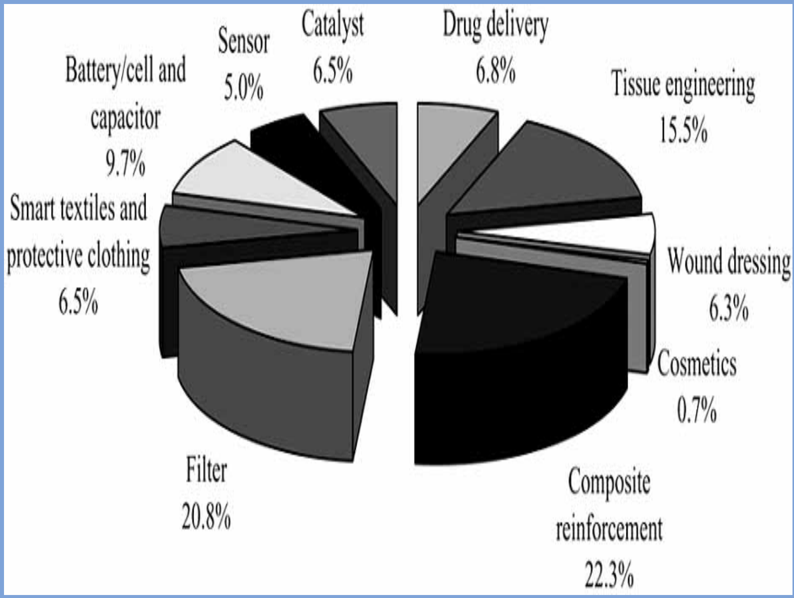
Applications of Nanofibers



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Applications of Nanofibers

Applications of polymer and ceramic nanofibers

Nanofibers	*Applications*
Cellulose	As a novel filtration membrane
Polysulfone	Removal of micro-particles from waste-water, Improve the life of ultrafiltration or nanofiltration membranes
Nylon-6	Pre-filters for the removal of micro-particles form water above the membrane average pore-size without severe fouling
poly (L-lactide-co-ε-caprolactone) (PLLA) nanofibers]	3D scaffold for blood vessel tissue engineering
Collagen	For culturing smooth muscle cell
Polyester/urethane	Skeletal muscle tissue engineering
Polyurethane	Wound dressing material to effectively exuded fluid from the wound
PCL/gelatin	Scaffold for wound healing and layereddermal reconstitution
Gelatin/PVA	Controlled release of drug
Polybenzimidazole (PBI)	Used as fillers to have higher fracture toughness and modulus of epoxy and rubber material
PAN	Hydrogen Storage, PAN membrane as lithium battery separator because of high ion conductivity and electrochemical stability, photo voltaic cells
PANi/PVP	NO_2 Gas Sensor
PVP-iodine	antibacterial, antimycotic and antiviral applications
Polyimides	Proton exchange membrane for fuel cell
PVA	Bioseparators for negatively charged nanoparticles in microfluidic systems
WO_3 nanofibers	Ammonia gas sensor
TiO_2	Photocatalytic activities toward decomposition of methylene blue and gaseous formaldehyde, NO_2 and H_2 gas sensor
MgO	Electrodes in lithium ion batteries
MoO_3	Ammonia gas sensor
Fe_2O_3	CO_2 sensor, ethanol sensor
ZnO	CO_2 sensor
Al_2O_3	High temperature application
ZrO_2	Oxygen sensors, fuel cells, electrochemical capacitor electrode
$BaTiO_3$	Nano scale capacitor, dynamic random access memory, ferroelectric random access memory

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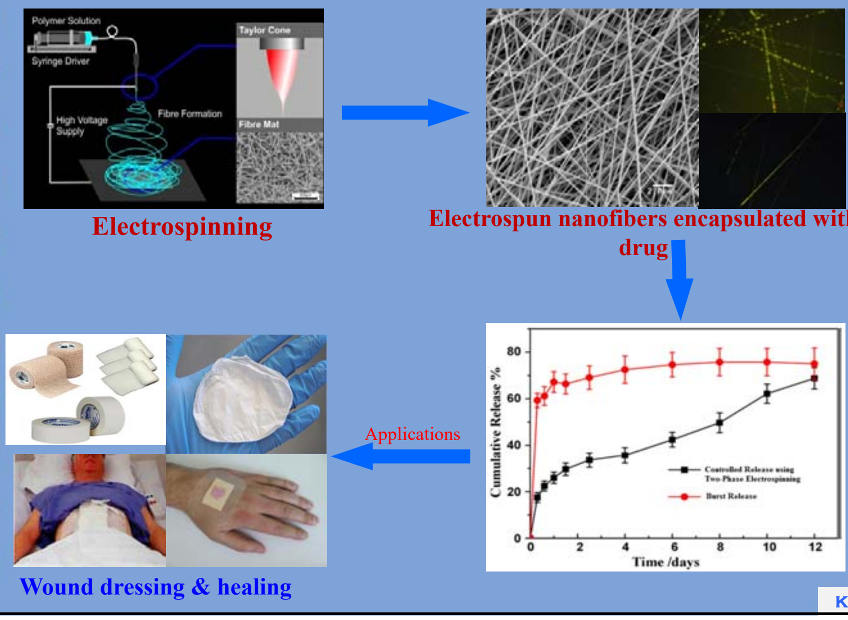
Biomedical Applications



Biomedical Applications

Drug delivery

- ❖ **Controlled release is an efficient process of delivering drugs in medical therapy.**
- ❖ **It can balance the delivery kinetics, minimize the toxicity and side effects, and improve patient convenience**

❖ In a controlled release system;

- **The active substance is loaded into a carrier or device first**
- **and then releases at a predictable rate *in vivo* when administered by an injected or non-injected route.**

Biomedical Applications

Drug delivery

- **Electrospun nanofibers have exhibited many advantages;**
  - **The drug loading is very easy to implement via electrospinning process (*More than one drug can be encapsulated and the high applied voltage used in the electrospinning process had little influence on the drug activity*).**
  - **The high specific surface area**
  - **Short diffusion passage length give the nanofiber drug system higher overall release rate than the bulk material (e.g. film).**
- **The release profile can be finely controlled by modulation of nanofiber morphology, porosity and composition.**

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Biomedical Applications

Drug delivery

- **Nanofibers for drug release systems mainly come from**
  - **biodegradable polymers, such as PLA, PCL, poly(D-lactide)(PDLA), PLLA, PLGA**
  - **hydrophilic polymers, such as PVA, PEG and PEO.**
  - **Non-biodegradable polymers, such as PEU.**
- **Model drugs that have been studied include;**
  - **Water soluble**
  - **poor-water soluble**
  - **water insoluble drugs.**
- **The release of macro-molecules, such as DNA and bioactive proteins, from nanofibers was also investigated.**

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Biomedical Applications

Drug delivery

- Many factors may influence the release performance, such as
  - Type of polymers used
  - Hydrophility and hydrophobicity of drugs and polymers,
  - solubility,
  - drug polymer comparability,
  - additives, and the existence of enzyme in the buffer solution.
- In most cases, water soluble drugs, including DNA and proteins, exhibited an early-stage burst.

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Biomedical Applications

Drug delivery

- The early burst release can also be lowered via
  - The polymer shell can also be directly applied, via a coaxial co-electrospinning process, and the nanofibers produced are normally named "core-shell".
  - Water-in-oil emulsion can be electrospun into uniform nanofibers, and drug molecules are trapped by hydrophilic chains.
  - Encapsulating water soluble drugs into nanoparticles, followed by incorporating the drug-loaded nanoparticles into nanofibers.
- In addition, the rate of releasing a water soluble drug could be slowed down when nanofiber matrix was crosslinked.

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Biomedical Applications

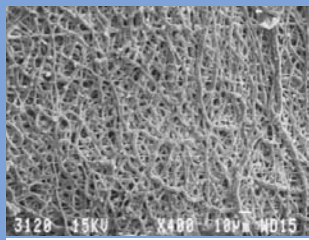
Drug delivery

❖ **The use of electrospun fibers as drug carriers may be attributed to the work of Kenawy *et al.* in 2002.**

- They investigated delivery of tetracycline hydrochloride based on the fibrous delivery matrices of poly(ethylene-*co*-vinyl acetate) (PEVA), poly(lactic acid) (PLA) and their mixtures.
- Electrospun PEVA showed the highest releasing rate which was 65% of its drug content within 100 h

and the electrospun PEVA/PLA (50/50) released about 40% over the same time period,

whereas electrospun PLA fibers exhibited negligible release over 50 h.



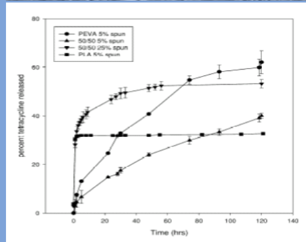


Fig. 5. Percentage release of tetracycline HCl from electrospun mats vs. time.

Kenawy, E.-R., Bowlin, G.L., Mansfield, K., Layman, J., Simpson, D.G., Sanders, E.H., and Wnek, G.E., *Journal of Controlled Release*, 2002. 81(1-2): p. 57-64.

Biomedical Applications

Drug delivery

❖ **The first issued patent on drug delivery system using electrospun nanofibers is attributed to the work of *Belenkaya in 2003*.**

- **Silver sulfadiazine, which is useful for the treatment of burns, was added to the poly(D,L-lactide-coglycolide) (PLG) and poly(*N*-vinyl pyrrolidone) (PVP) blend (PLG/PVP: 20/80 w/w).**
- **The drug-containing blend was fabricated into nanofibers by electrospinning to yield a 1% silver sulfadiazine concentration in the final matrix.**
- **The prepared nanofibrous membrane with drug possessed a thickness around 1.5-2.0 μm and a surface density around 5 mg/cm^2.**
- **The biodegradation of PLG/PVP electrospun nanofibers *in vivo took 3-8 days.***

Belenkaya, B.G., Sakharova, V.I., Polevov, V.N.: US2003069369 (2003).

Biomedical Applications

Wound Dressing

- Polymer nanofibers can also be used for the treatment of wounds or burns of a human skin, as well as designed for haemostatic devices with some unique characteristics.

- With the aid of electric field, fine fibers of biodegradable polymers can be directly sprayed/spun onto the injured location of skin to form a fibrous mat dressing.

Nanofibers for wound dressing (www.electrosols.com).

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Biomedical Applications

Why Electrospun Nanofibers For Wound Dressing?

- High porosity of electrospun nanofibers
  Which allows gas exchange
- Fibrous structure
  That protects wounds from infection and dehydration.
- Non-woven electrospun nanofiberous membranes for wound dressing usually have pore sizes in the range of 500-1000 nm.
  Which is small enough to protect the wound from bacterial penetration.
- High surface area of electrospun nanofibers
  Is extremely efficient for fluid absorption and dermal delivery.

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Biomedical Applications

Why Electrospun Nanofibers For Wound Dressing?

❖ For example

Lee *et al* prepared a chitosan-containing non-woven web.

- The chitosan was first electrospun into nanofibers with average diameter less than 1,000 nm and the non-woven web was then treated in hyaluronic acid.
- The formed web was
  biocompatible and biodegradable
  and it also showed quick antibacterial capability,
  excellent air permeability,
  and fast moisturizing performance.
- A multilayered anti-adhesion barrier was constructed by coating a hydrophilic, biooriginated polymer including PLA and hyaluronic acid on the electrospun nanofibrous base layer.
- The multi-layered anti-adhesion barrier solved the disadvantages of the conventional gel, sponge, film or nonwoven anti-adhesion systems, such as adhesion to tissues or organs, poor flexibility, low physical strength, etc.

Lee, Y.H., Noh, H.G., Lee, S.Y.: KR118730 (2007).

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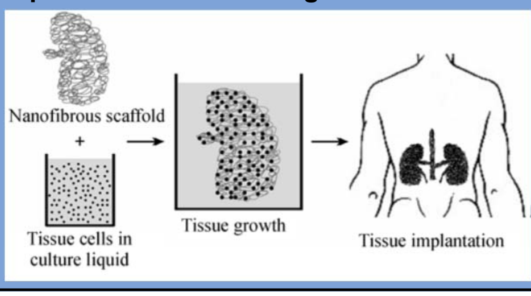
Biomedical Applications

Tissue Engineering Scaffold

❖ One of the challenges to the field of tissue engineering/ biomaterials is the design of ideal scaffolds/synthetic matrices that can mimic the structure and biological functions of the natural extracellurlar matrix (ECM).

❖ The purpose is to repair, replace, maintain, or enhance the function of a particular tissue or organ



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Biomedical Applications

Tissue Engineering Scaffold

- The core technologies intrinsic to this effort can be organized into three areas:
  - cell technology
  - scaffold construct technology
  - technologies for in vivo integration.
- The scaffold construct technology focuses on designing, manufacturing and characterizing three-dimensional scaffolds for cell seeding and in vitro or *in vivo* culturing.

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Biomedical Applications

Tissue Engineering Scaffold

- There are a few basic requirements that have been widely accepted for designing polymer:
  - a scaffold should possess a high porosity, with an appropriate pore size distribution.
  - a high surface area is needed.
  - biodegradability is often required, with the degradation rate matching the rate of neo-tissue formation.
  - the scaffold must possess the required structural integrity to prevent the pores of the scaffold from collapsing during neo-tissue formation, with the appropriate mechanical properties.
  - the scaffold should be non-toxic to cells and biocompatible, positively interacting with the cells to promote cell adhesion, proliferation, migration, and differentiated cell function.

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Biomedical Applications

Biohybrid Electrospun Nanofibers:
Encapsulation of Cells into Electrospun Fibers

- Biohybrid materials: containing or composed of both biological and non-biological components.

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Biomedical Applications

Biohybrid Electrospun Nanofibers:
Encapsulation of Cells into Electrospun Fibers

- Generally, biological material has been encapsulated in electrospun fibers.
- For example;
  - DNA has been encapsulated for potential therapeutic applications in gene therapy.
  - Some proteins, enzymes and small molecules have also been embedded in electrospun nanofibers.
  - Filamentous bacterial viruses suspended in a polymer solution were electrospun and found to remain viable when examined immediately after electrospinning

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Biomedical Applications

Biohybrid Electrospun Nanofibers:
Encapsulation of Cells into Electrospun Fibers

- The encapsulation of biological material while preserving its activity is important for many applications.
- Recently, there has been a greatly increased interest in using bacterial viruses as an alternative to bacterial antibiotics and as vectors for gene delivery (viral and non-viral vectors)

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Biomedical Applications

Biohybrid Electrospun Nanofibers:
Encapsulation of Cells into Electrospun Fibers

- Challenge:
  - The conditions of the electrospinning process that allow the encapsulation of intact bacteria and bacterial viruses while maintaining their viability.
  - However, the longevity of functional bacteria is limited once they have been isolated from their native environment.

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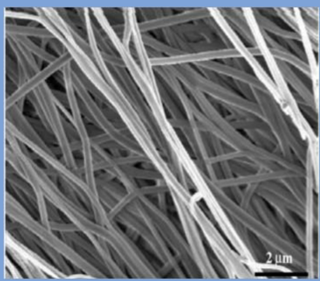
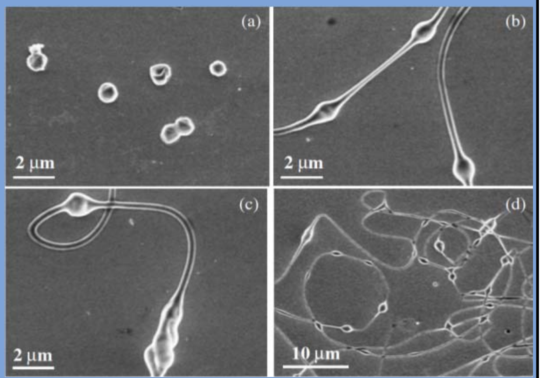
Biomedical Applications

Biohybrid Electrospun Nanofibers:
Encapsulation of Cells into Electrospun Fibers



HRSEM micrograph of a mat formed by electrospun PVA nanofibres.



HRSEM micrographs of (a) individual *S. albus* cells, and ((b)–(d)) embedded *S. albus* cells in electrospun PVA nanofibres.
(c) Shows the embedding of what looks to be an aggregate of several bacterial cells. (d) A lower magnification of these fibres.

WSalalha1, J Kuhn2, Y Dror1 and E Zussman. "Encapsulation of bacteria and viruses in electrospun nanofibers", Nanotechnology 17 (2006) 4675–4681

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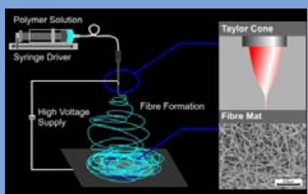
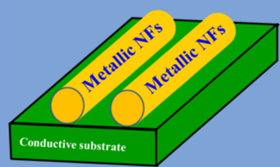
Energy Applications



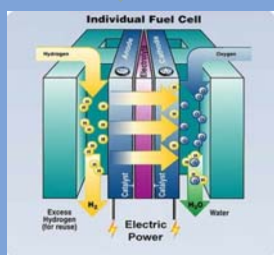
Electrospinning

Calcination



Novel Electrode

Applications



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Energy Applications;
As Electrode Support for Fuel Cells

Problem Description and Challenges

Difficulties in DMFC and Solutions

Poor anode kinetics
- Development novel catalyst
- Enhancing active catalyst area

High cost
- Decrease noble metals loading
- Used non-precious metals (Ni, Co, Pd, Fe,…etc)

Methanol crossover
- Development membrane

Objectives

The main objectives of this study are:

- To fabricate of polymeric electrospun nanofibers containing transition metals as a new class of materials used as anode electrode in DMFCs
- To study the influence of nitrogen doping on the electrocatalytic activity of introduced catalysts toward methanol oxidation

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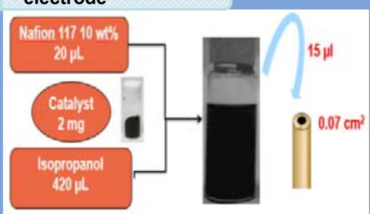
Energy Applications;
As Electrode Support for Fuel Cells

Method

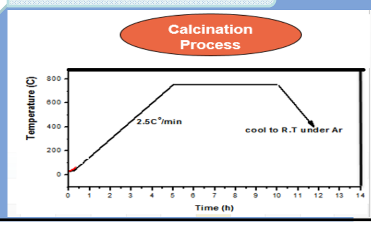
Step 1 • Preparation of blend polymer and metals (sol-gel)

Step 2 • Electrospinning process

Step 4 • Preparation of working electrode



Step 3 • Calcination process



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Aerogels

- **Aerogels** are a diverse *class* of porous, dry gel, solid materials, extreme low densities (which range from 0.0011 to ~0.5 g cm^{-3}) (about 15 times heavier than air).
- **Aerogels** are open-porous (that is, the gas in the aerogel is not trapped inside solid pockets).

An aerogel is an open-celled, mesoporous (contains pores ranging from 2 to 50 nm in diameter), solid foam that is composed of a network of interconnected nanostructures and that exhibits a porosity (non-solid volume) of no less than 50%.

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AEROGELS

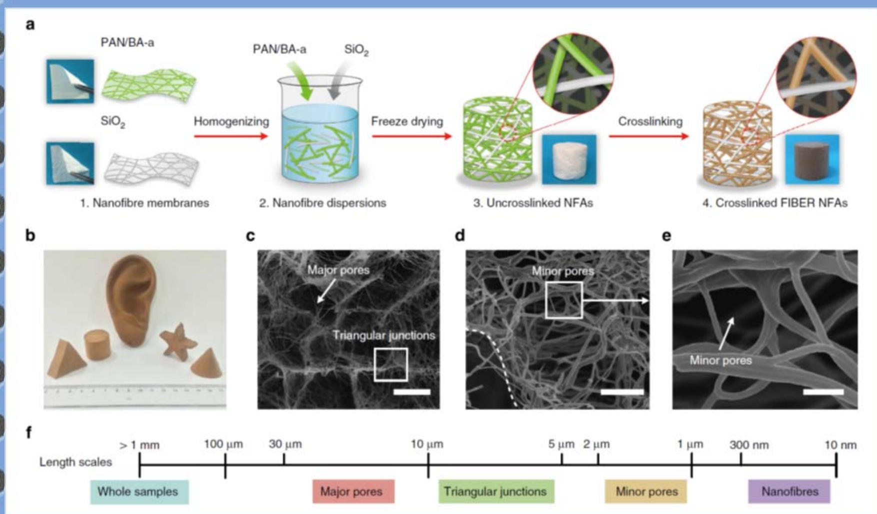

Figure 1 | Design, processing and cellular architectures of FIBER NFAs (q¼9.6mgcm3). (a) Schematic showing the synthetic steps. (1) Flexible PAN/BA-a and SiO2 nanofibre membranes are produced by electrospinning. (2) Homogeneous nanofibre dispersions are fabricated via high-speed homogenization. (3) Uncrosslinked NFAs are prepared by freeze drying nanofibre dispersions. (4) The resultant FIBER NFAs are prepared by the crosslinking treatment. (b) An optical photograph of FIBER NFAs with diverse shapes. (c–e) Microscopic architecture of FIBER NFAs at various magnifications, showing the hierarchical cellular fibrous structure. (f) Schematic representation of the dimensions of relevant structures. Scale bars, 20 mm (c), 5 mm (d) and 1 mm (e).

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Workshop Outlines

- ❖ Historical Background.
- ❖ Electrospinning Technique.
- ❖ Electrospun Nanofibers Architectures & Control of Various Morphologies
- ❖ Factors Affecting the Preparation of Electrospun Nanofibers
- ❖ Nanofibers Made From Polymers And Metal Oxides.
- ❖ Large Scale Production of The Electrospun Nanofibers
- ❖ Applications of Electrospun Nanofibers.
- ❖ Electrospinning at KSU; Petrochemical Research Chair.

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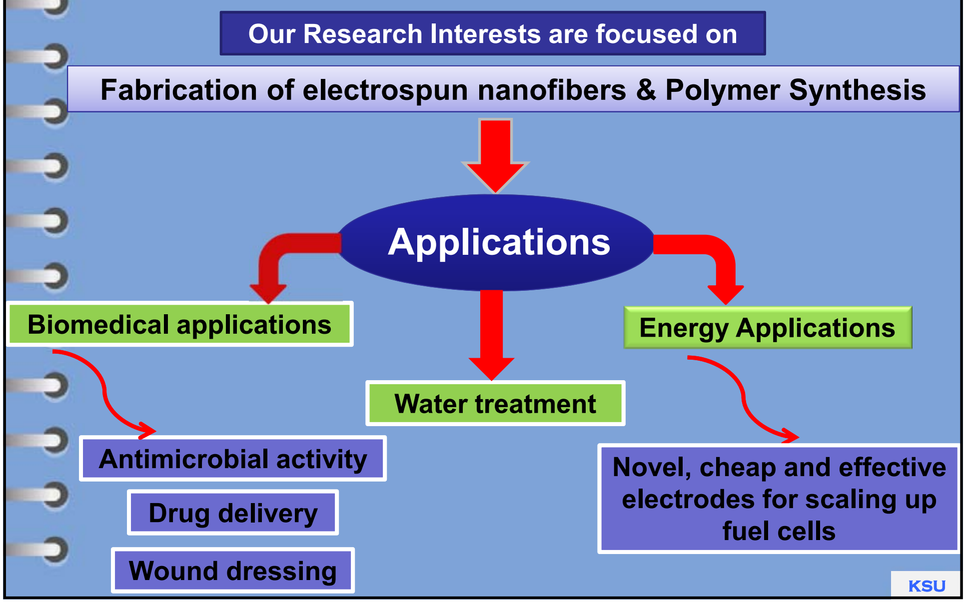
Electrospinning at KSU; Petrochemical Research Chair



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Electrospinning Setup at PRC

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Central Laboratory at PRC

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Electrospinning is an old but yet
fascinating technique.
Thank You