2.2.3 Electrospinning

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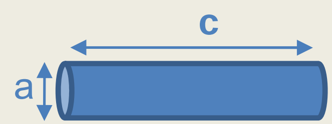
1. Introduction

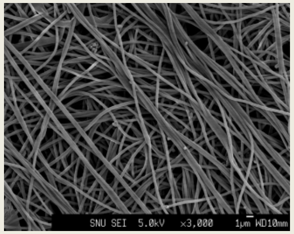
1.1 Various ways to make nanofibers

. 1D-nanostructures

- Nanofibers & Nanorods
- Classified by **aspect ratio** (c/a)

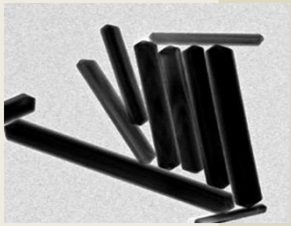


Nanofibers



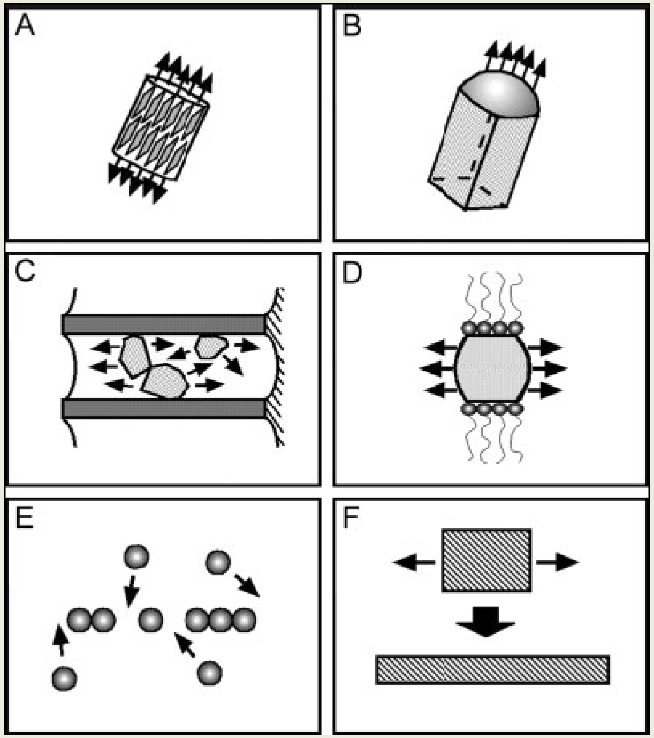
* From our lab

Nanorods



* www.seashelltech.com/nanoRods.shtml

. Various strategies for achieving nanofibers



A. Using anisotropic crystallographic structure
B. Using nanoparticles as a seed
C. Using Template
D. Using Surfactant or capping reagent
E. Self-assembly of nanoparticles
F. Size reduction

* Y. Xia, P. Yang, et al., *Adv. Mater.*, 15, 3 (2003) 353-389

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1. Introduction

1.2 System of electrospinning

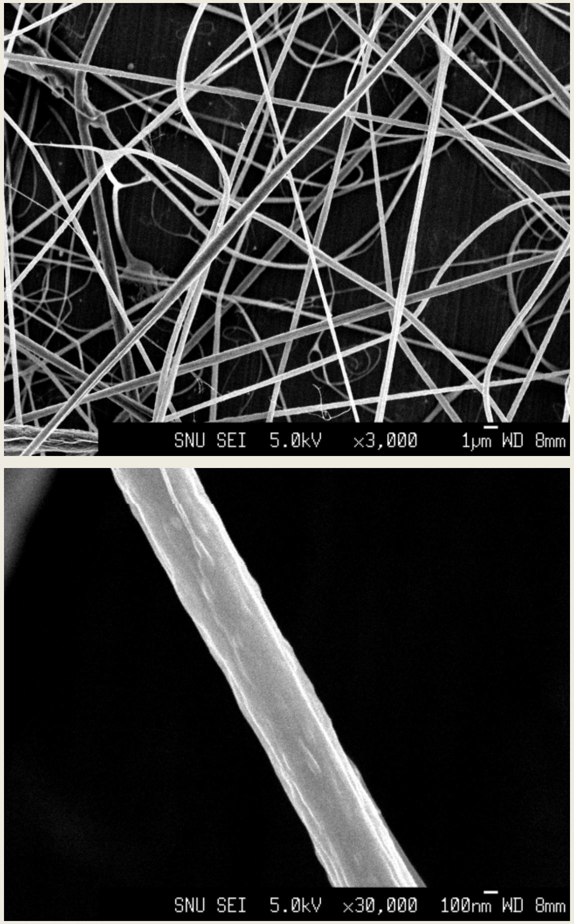
. Electrospinning

- 1D-nanostructure synthesis method using electrical field force with polymer & conducting solvent solution
- Classified by **aspect ratio** (c/a)

. Advantage of electrospinning method

- Simplest method for 1D-structure synthesis
- Easy to fabricate solid & hollow structure
- Long in length
- Uniform in diameter
- Diversified in composition

* Dan Li, Younan Xia, *Adv. Mater.*, 16, 14 (2004) 1151-1170



< Electrospun nanofibers >

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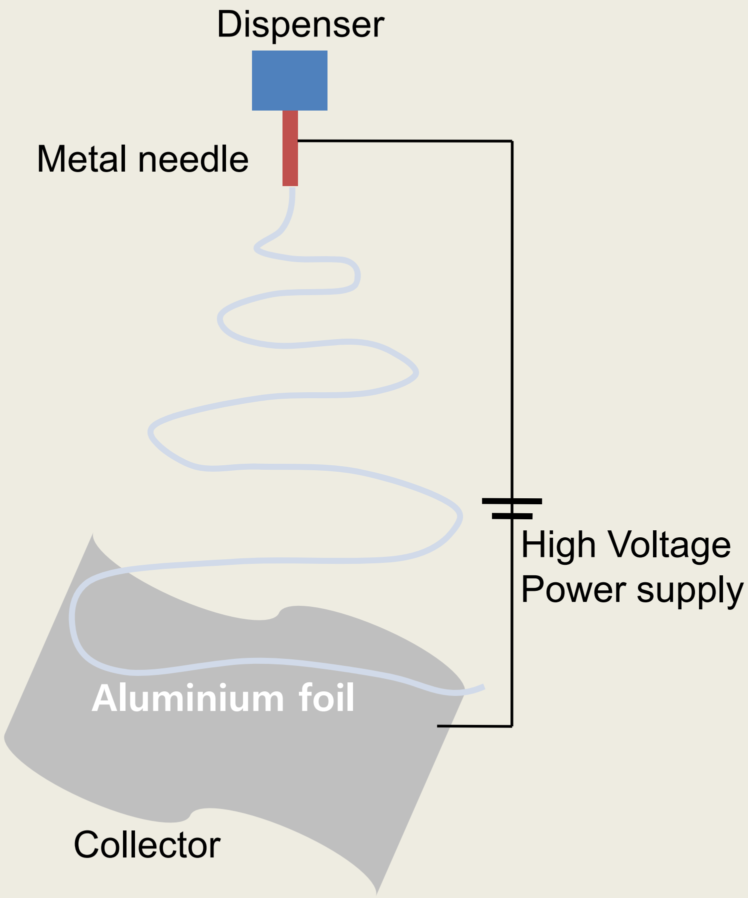
1.2 System of electrospinning



. System main components

- High voltage power supply
- Metal needle
- Collector
- Solution dispenser

. Accessories

- Robot arm
- specified needle
- multiple dispenser system

2. Controlling electrospinning process

2.1 Polymer solution parameter

(1) Molecular weight & solution viscosity

. Effect of the viscosity of the solution

- profound effect on electrospinning process
- resultant fiber morphology
  - .. **Lower** viscosity → **electrospraying** and **polymer particles**
  - .. **Higher** viscosity → **beaded** fibers

. Factors of the viscosity of the solution

- Viscosity is proportional to
  - .. M_w of the polymer
  - .. Polymer concentration
  - .. Viscosity of the solvent
- Polymer length determine the amount of entanglement of the polymer chains in the solvent

Viscometry term	Formula
Relative viscosity	$\frac{\eta_1}{\eta_2}$
Specific viscosity	$\frac{\eta_1}{\eta_2} - 1 \quad or \quad \eta_r - 1$
Reduced viscosity	$\frac{\eta_{sp}}{c}$
Intrinsic viscosity	$[\eta] = \frac{K\left(\overline{r}^2\right)^{3/2}}{M}$

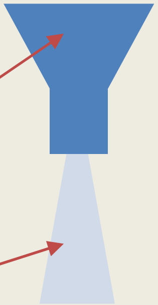
2. Controlling electrospinning process

2.1 Polymer solution parameter

(2) Surface tension

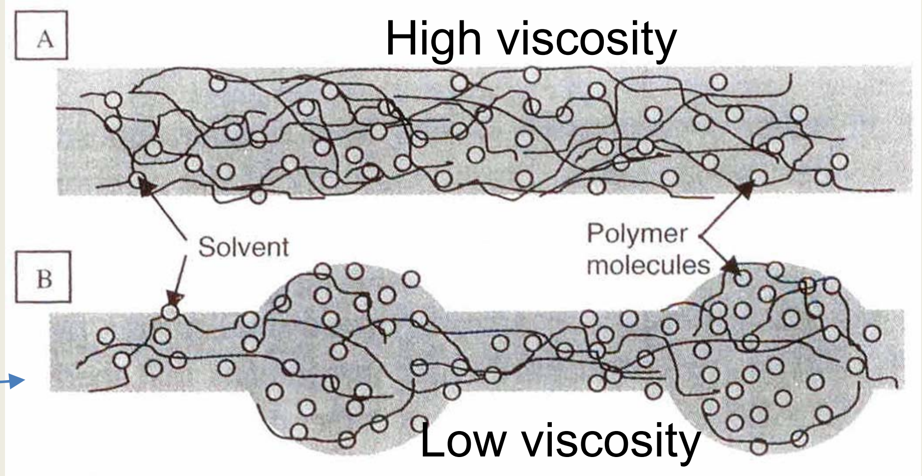
. Surface tension in electrospinning

- Initiation of the electrospinning requirement
  ← Charged solution to overcome the surface tension
- After extruded from the needle
  ← **Cause the formation of beads** along the jet



. Bead formation

- **High surface tension - decreasing the surface area per unit mass**
  → Higher congregated solvent molecules = **spherical shape**
- **Lower viscosity**
  .. Lower interaction between polymer & solvent
  .. Solvent molecules tend to aggregate **causing beads**



2. Controlling electrospinning process

2.1 Polymer solution parameter

(3) Solution conductivity

. Solution conductivity in electrospinning

- Higher conductivity of the solution = more charges are carried
- Increasing stretching of the solution → less beads
- More stretched fiber → smaller diameter

. Increasing solution conductivity

- Use higher conductivity solvent
- Addition of ions
  .. Insert the salt
- **Use the ionic surfactant**
  .. Increase the solution conductivity at the same time reducing the surface tension
- Chaging the pH of the solution

Solvent	Conductivity (mS/m)
1,2-Dichloroethane	0.034
Acetone	0.0202
Butanol	0.0036
Dichloromethane/ Dimethylformamide (40/60)	0.505
Dichloromethane/ Dimethylformamide (75/25)	0.273
Dimethylformamide	1.090
Distilled Water	0.447
Ethanol	0.0554
Ethanol (95%)	0.0624
Ethanol/Water (40/60)	0.150
Methanol	0.1207
Propanol	0.0385
Tetrahydrofuran/Ethanol (50/50)	0.037

< Conductivity of solvents >

2. Controlling electrospinning process

2.1 Polymer solution parameter

(4) Dielectric constant

Solvent	Dielectric constant
2-Propanol	18.3
Acetic acid	6.15
Acetone	20.7
Acetonitrile	35.92-37.06
Chloroform	4.8
Dichloromethane	8.93
Dimethylformamide	36.71
Ethyl acetate	6.0
Ethanol	24.55
m-Cresol	11.8
Methanol	32.6
Pyridine	12.3
Tetrahydrofuran	7.47
Toluene	2.438
Trifluoroethanol	27.0
Water	80.2

< dielectric constant of solvents >

. Dielectric constant in electrospinning

- Higher Dielectric constant
  → reducing the beads formation
  → smaller diameter
- Effect to solubility of the polymer
  .. Add of co-solvent for dielectric constant can impact to solubility of polymer
  .. Add of DMF(high DC)
  → poor solubility of PS

2.2 Processing conditions

(1) Voltage

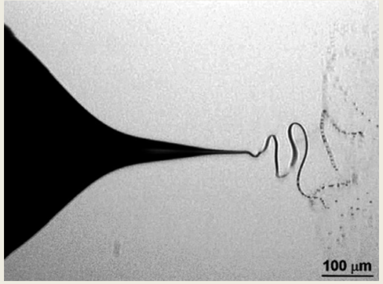
. Electric field from high voltage in electrospinning

- Induce the charges in the solution
- Overcome the surface tension of the solution

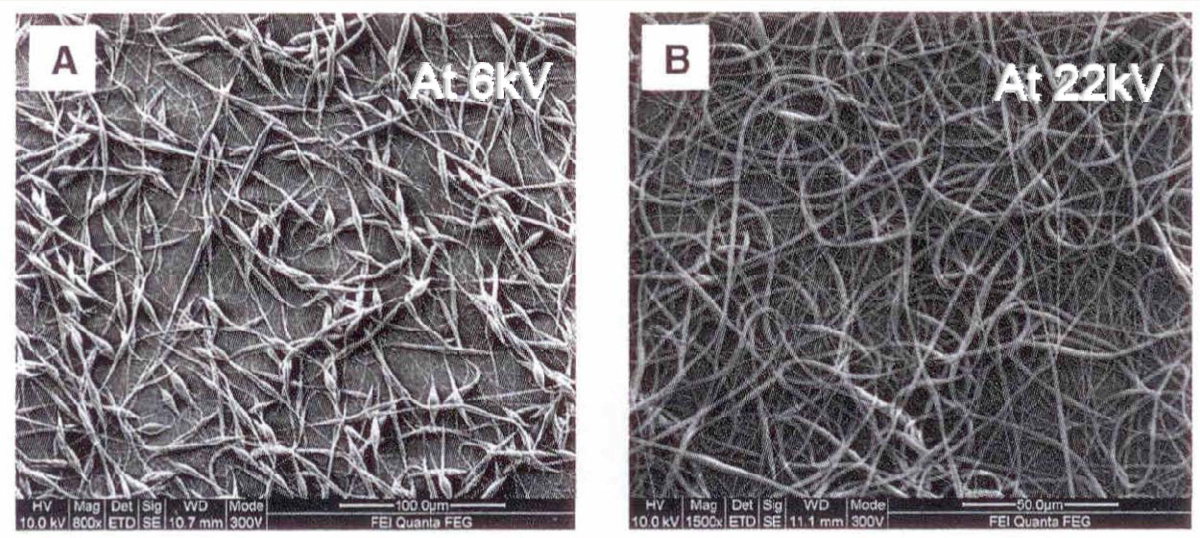
. Effect of voltage to the electrospun resultants

- Higher voltage → accelerate charges
  .. Smaller diameter
- Stabilized the Taylor Cone (Depending on the feedrate)

< Taylor cone >



http://bbs.labscn.com/upload/2008/12/14/22/a08eaf6d-164a-48cd-9324-c2ed16af96e7.jpg



* W.E. Teo and S. Ramakrishna, National University of Singapore

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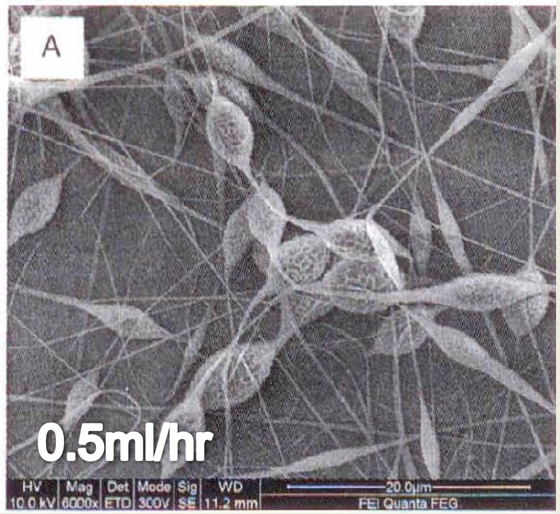
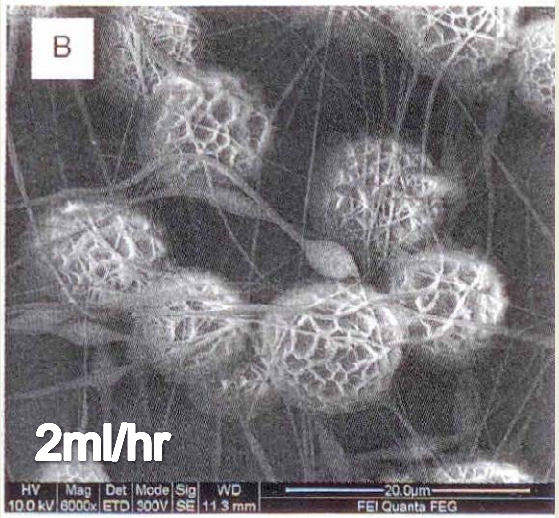
2.2 Processing conditions

(2) Feedrate

. Feedrate in electrospinning
- Determine the amount of solution
- Influence to stability of Taylor cone

. Effect of feedrate
- Higher feedrate → more solution
  .. Larger diameter
  .. Larger beads size
- Higher feedrate → more solvent
  .. Not enough time to evaporate given solvent
  .. Forming webs





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* W.E. Teo and S. Ramakrishna, National University of Singapore

2.2 Processing conditions

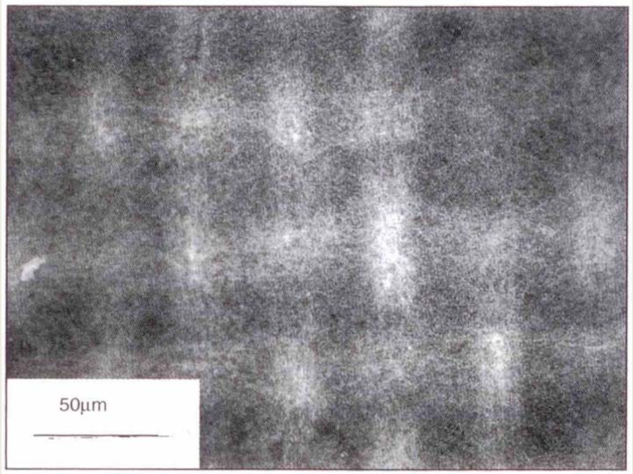
(3) Temperature

. Temperature in electrospinning
- Determine the evaporation rate
- Reduce the viscosity of the solution
- Increase the solubility of the polymer in the solution

(4) Collector

. Collector in electrospinning
- Made of conductive material such as aluminum foil
- non-conductive material
  → accumulation of the charges
  → repulsive force & less fibers on the collector

Collagen collected on braided Teflon sheet →



* W.E. Teo and S. Ramakrishna, National University of Singapore

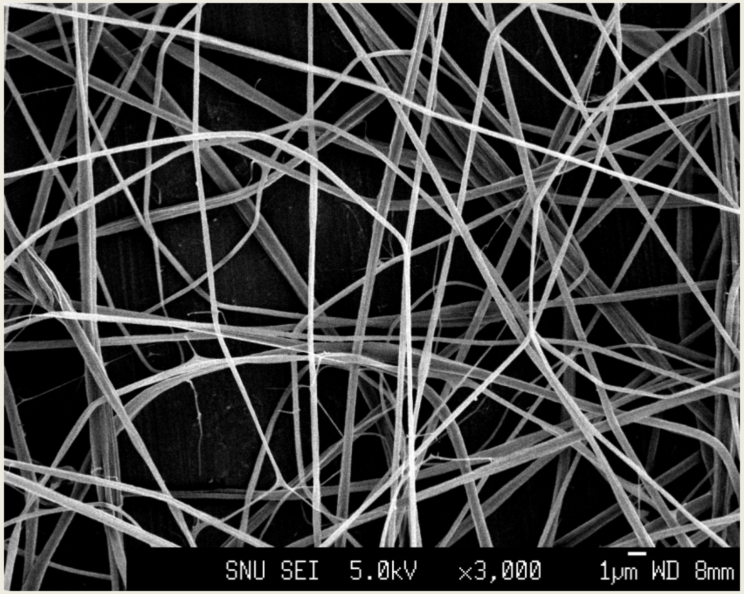
2. Controlling electrospinning process

2.2 Processing conditions

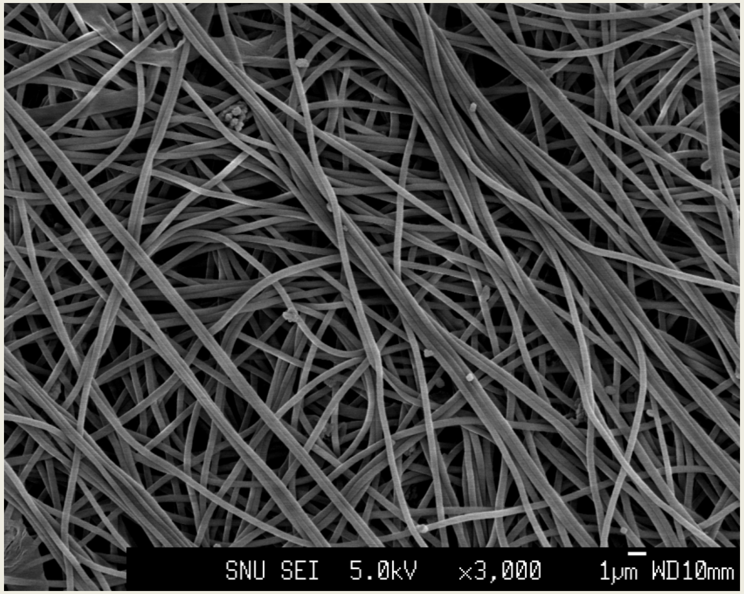
(5) Diameter of needle

. Effect of the needle diameter

- Smaller internal diameter
  → Reduce the clogging and beads
  → Reduce the diameter of electrospun fibers
- Influence of the needle diameter is not remarkable



< LTO/PAN/PMMA using 0.26mm of needle >



< LTO/PAN/PMMA using 0.61mm of needle >

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2.2 Processing conditions

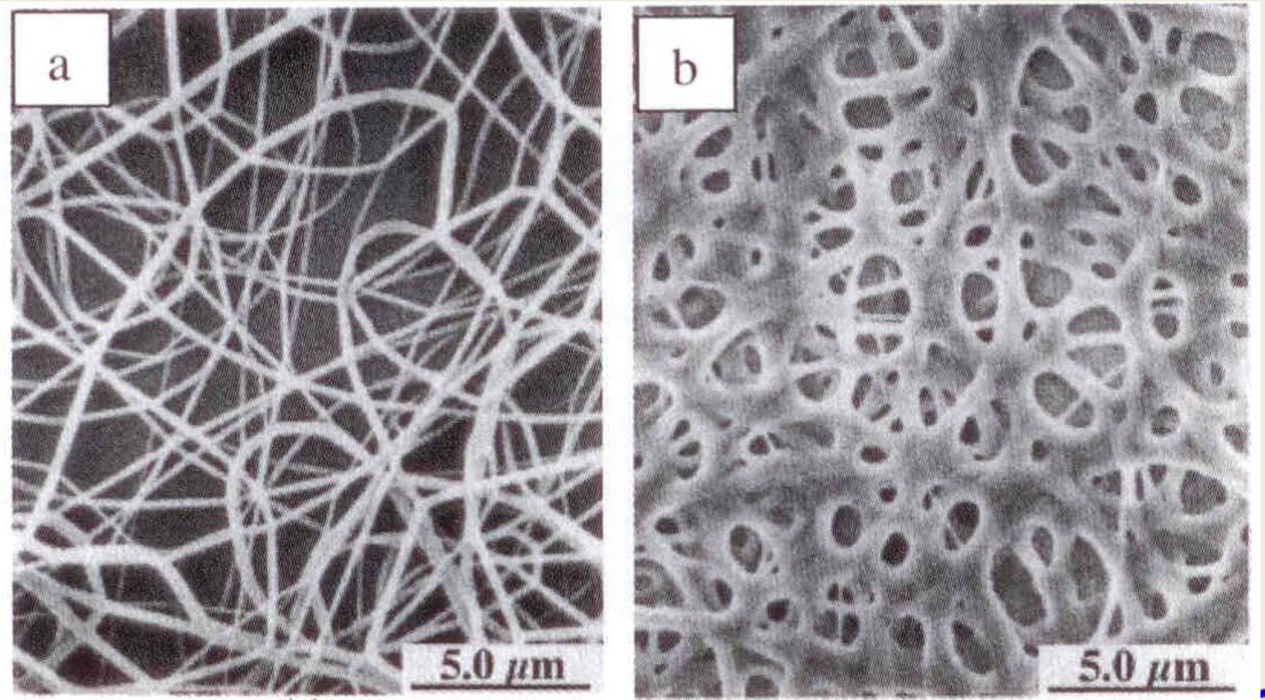
(6) Distance between Needle and Collector

. Effect of the deposition distance

- Directly influence to both the flight time and the electric field

→ Evaporation time of the solvent

→ Acceleration of the charges in the solution



< Nylon 6,6 at (a) 2 cm deposition distance and (b) 0.5cm deposition distance >

* Buchko *et. al.* (1999)

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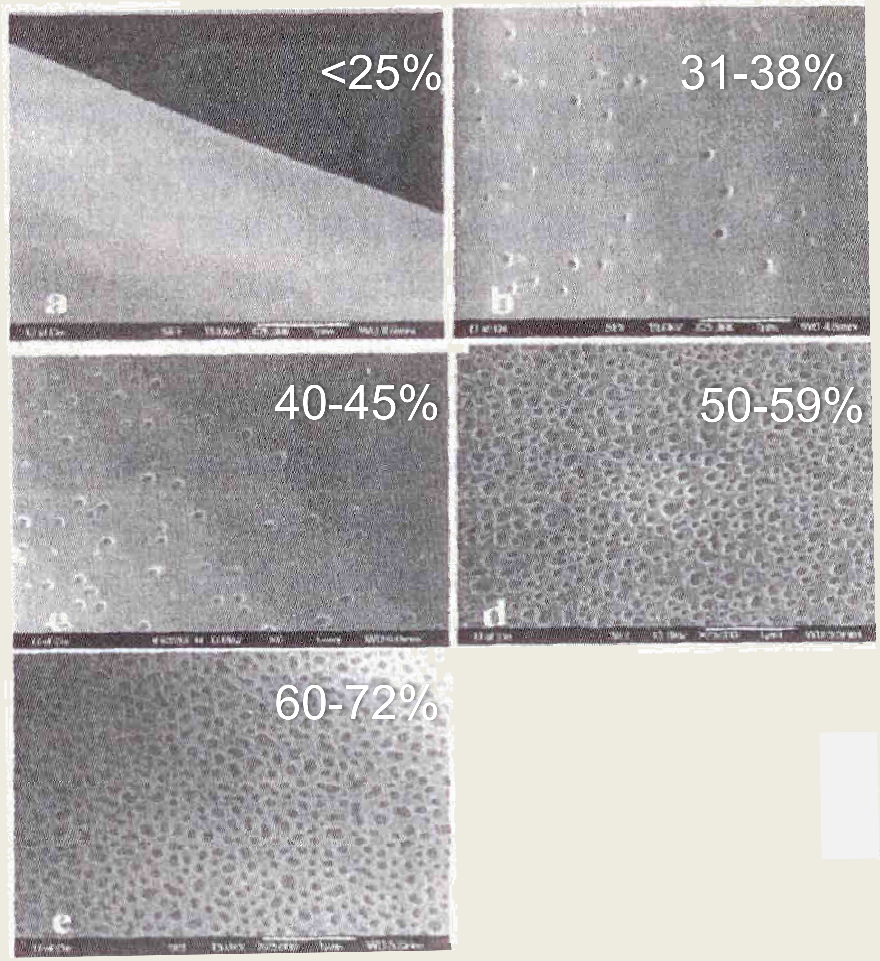
2. Controlling electrospinning process

2.2 Processing conditions

(7) Humidity



< Surface FE-SEM image of Polysulfone/Tetrahydrfuran fibers under various humidity >

. Effect of the humidity

- influence to surface morphology
- effect to evaporation time of the solvent
- very low humidity
  - → solvent dries rapidly
  - → no solvent at the needle tip
  - → few charges on the fibers

* Casper *et. al.* (2004)

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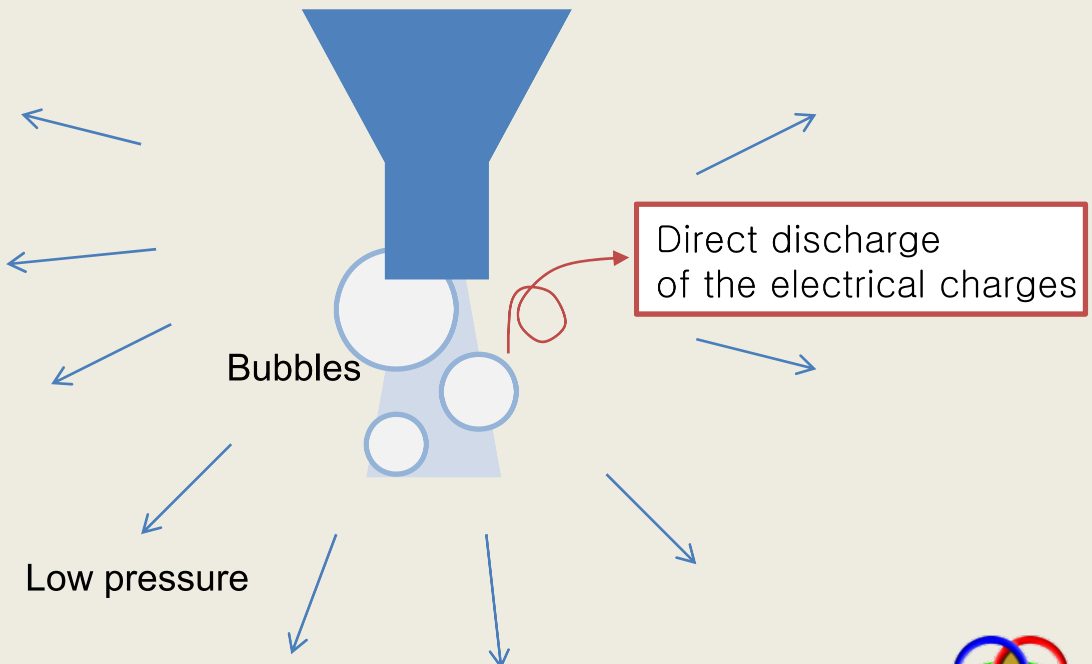
2.2 Processing conditions

(8) Pressure

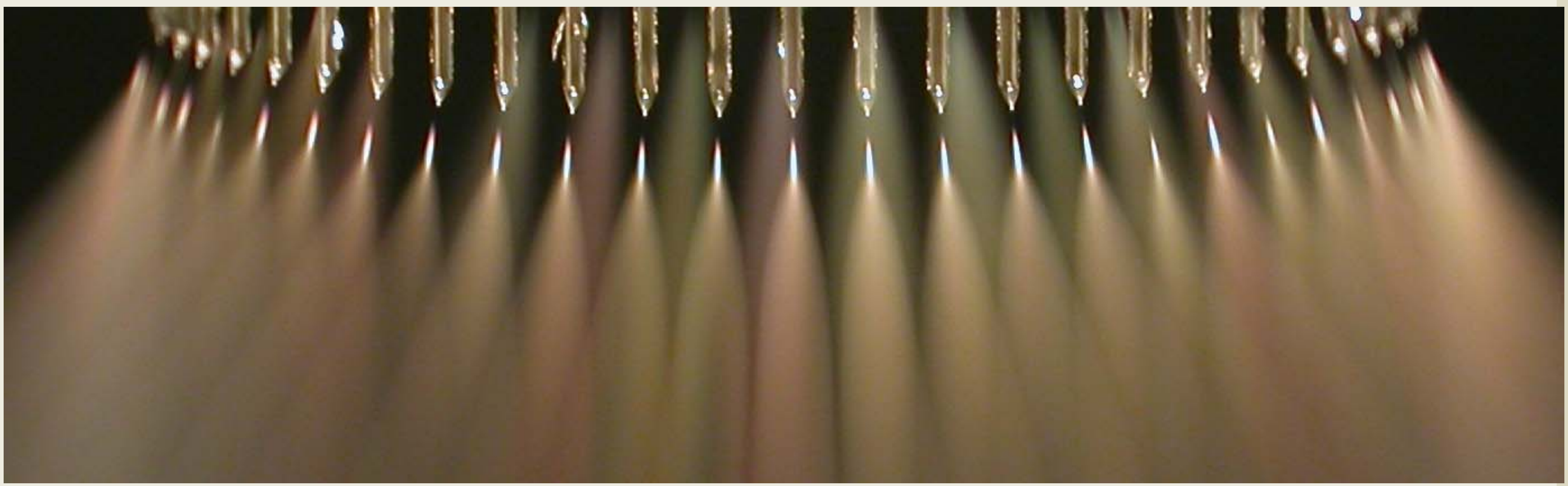
. Effect of the low pressure

- Reduction of the pressure → tendency to flow out
- unstable jet initiation
- Rapid bubbling of the solution → not possible to electrospinning



3.1 Multiple electrospinning

. Enhancing the productivity of the nanofibers
- Using multiple needles for electrospinning
- Charges in the Individual jet → influence to other jets
- Important factors : **Stability control**



* http://yflow.com/UserFiles/Image/Multi%2050%20a.JPG

< Multiple needles electrospinning system >

3.2 Melt electrospinning

. No use of the solvent

- Using polymer solution → Electrospinning of molten polymer
- Heat supply need
  .. Remaining polymer solution state
- More closer tip-collector distance
- Larger diameter of fibers

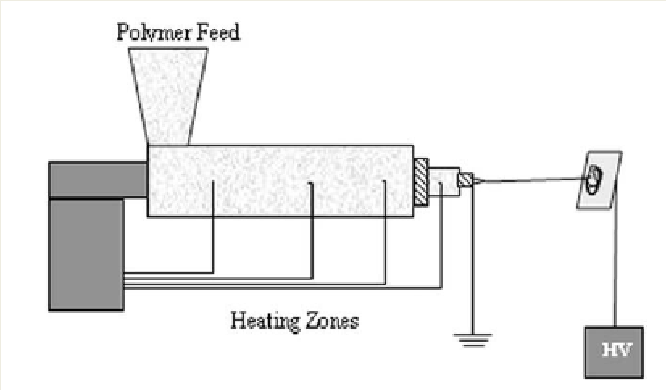
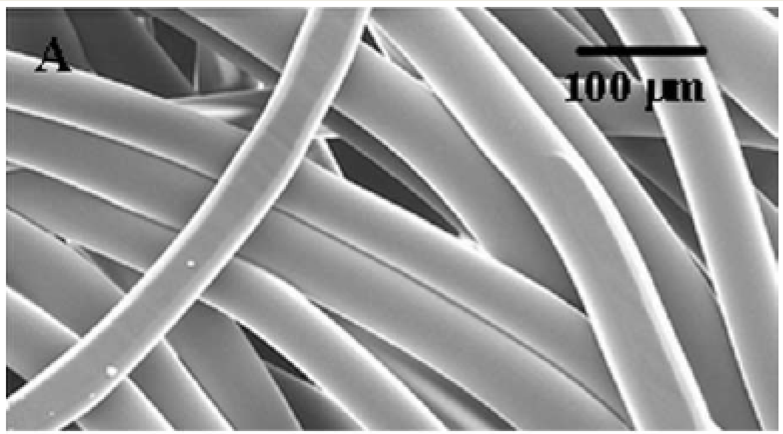


Fig. 1. A schematic diagram describing the melt-electrospinning technique.



< ESEM micrographs of 19,600Mw melt-electrospun polypropylene at an electric field strength of 10 kV cmK1 at 2 cm >

* J. Lyons et al., Polymer 45 (2004) 7597–7603

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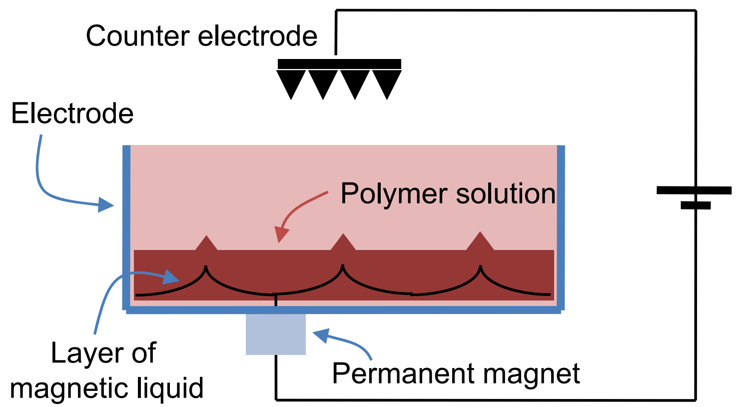
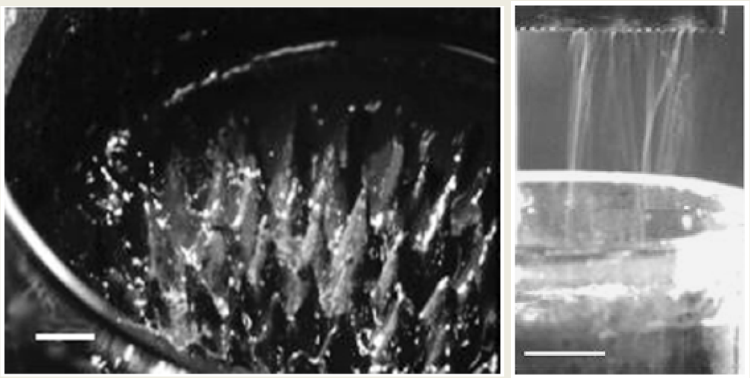
3.3 Needleless electrospinning

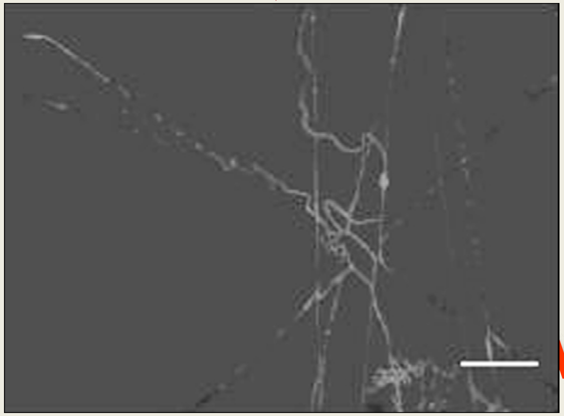
. **No use of the needle**

- Upward needleless electrospinning
- Magnetic field → Tip-shaped magnetic liquid
  .. Generating tip-shaped polymer solution from magnetic liquid
- Multiple electrospinning
  .. Multiple solution tips



< Scheme of needleless electrospinning >





* A.L. Yarin, E. Zussman, Polymer 45 (2004) 2977–2980

4.1 Core-Shell structure

. Coaxial electrospinning (Two solutions)

- Two concentrically aligned nozzles (Dual nozzle) are used for spinning.
- High throughput method compared with other synthesis methods

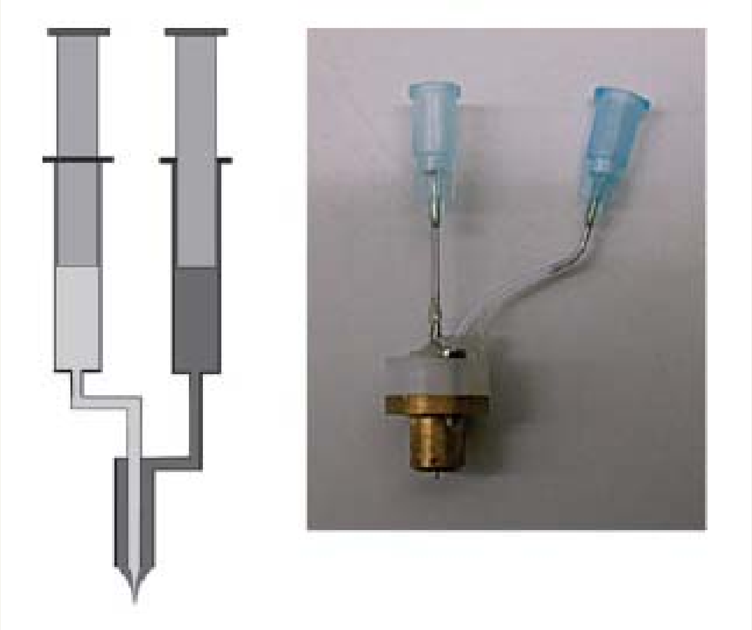


Fig. A setup for coaxial electrospinning

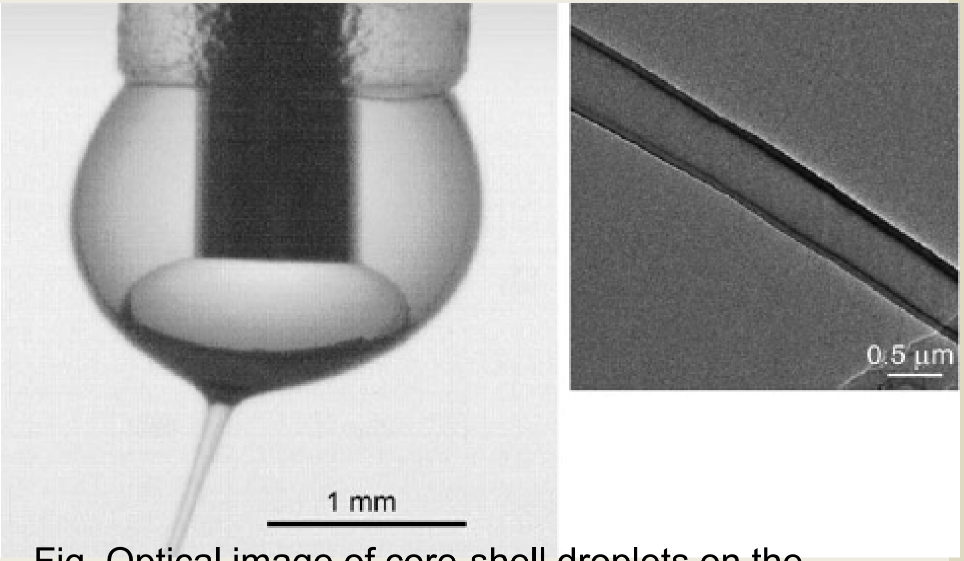


Fig. Optical image of core-shell droplets on the nozzle and PVDF(core) : PC(shell) fiber image

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4.2 Hollow nanofibers

. Two-Step method (Electrospinning and CVD)

- Template polymer nanofibers are electrospun.
- The nanofibers are coated by sheath material by CVD.
- The template nanofibers are removed via annealing.

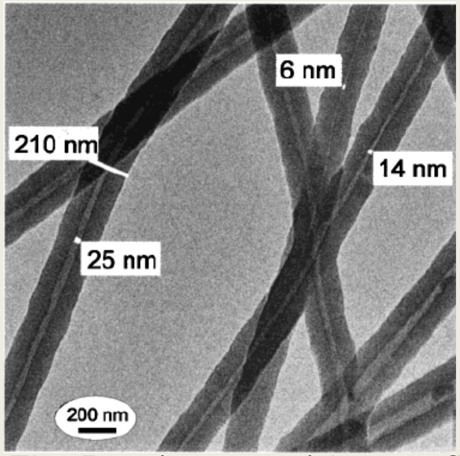

Fig. Poly(p-xylene) hollow fiber (Polyamide template)

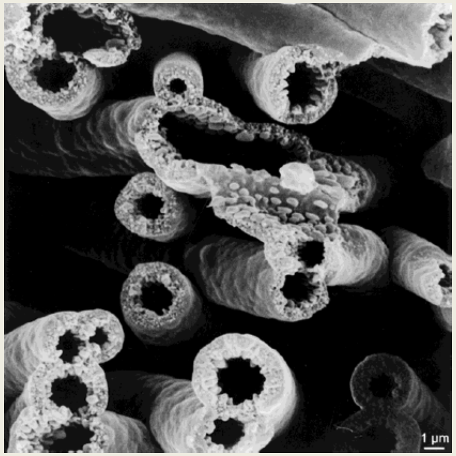

Fig. Poly(p-xylene) hollow fiber (Poly(l-lactide) template)

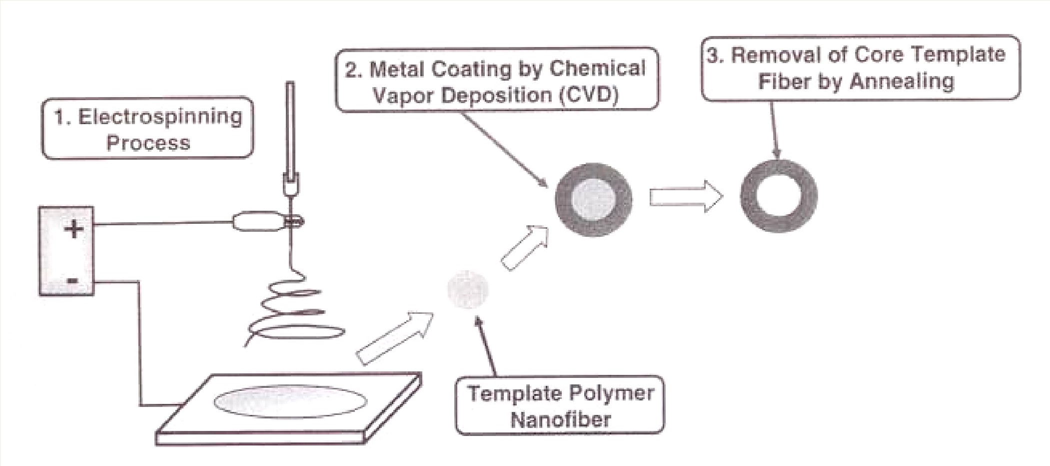

Fig. Hollow fibers made by coating of template polymer nanofibers using chemical vapor deposition method

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4. Control of structure

4.2 Hollow nanofibers

. One-Step processing by Coaxial electrospinning (Solution + Liquid)

- Dual nozzle system
- Polymer solution (and/or inorganic sol)
  → Shell material
- Immiscible liquid (such as mineral oil)
  → Core material

- Removal mineral oil (and polymer) by calcination simultaneously
  → Hollow fibers are collected

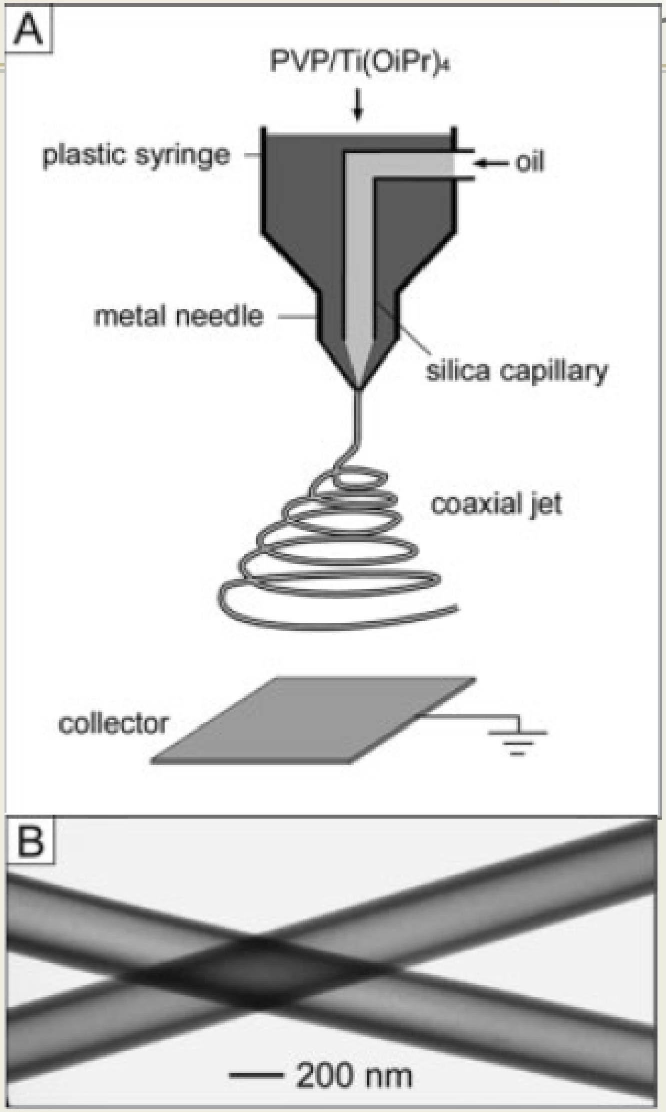

Fig. Schematic illustration of the setup and TEM image of hollow nanofiber

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4.3 Porous nanofibers

. Selective removal

- Electrospinning solution containing two polymers
  → Polymer blend nanofibers are formed
- Selective removal of a component from the nanofibers
- The fibers become highly porous when equal amounts of the two polymers were loaded

. Formed by water vapor

- Water droplets are formed due to evaporative cooling
  → Humidity of the electrospinning environment plays a part in the formation of porous nanofibers.

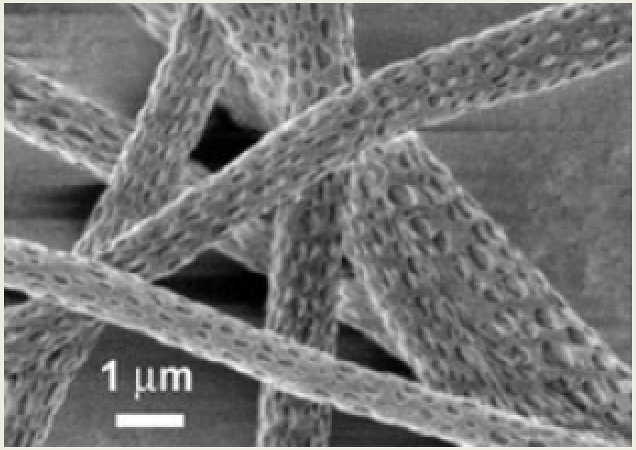

Fig. SEM image of Poly(l-lactide) fiber

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5. Application of electrospun fiber

5.1 Medical application

. Wound healing

- It is found that wounds such as burns and abrasions heal rapidly if they are covered by a thin web of nanofibers, in particular, of biodegradable polymers.

- Nanowebs have enough pores to assure the exchange of liquids and gases with the environment, but have dimensions that prevent bacteria from entering.

Fig. PEO fibers electrospun from handheld electrospinning device

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5. Application of electrospun fiber

5.1 Medical application

. Drug delivery

- Instantaneous high drug release usually causes the side effect.
- Burst drug release is preferred for the treatment that uses antibiotics
  → controlled drug release need

- Electrospun fiber can control the release amount of drug

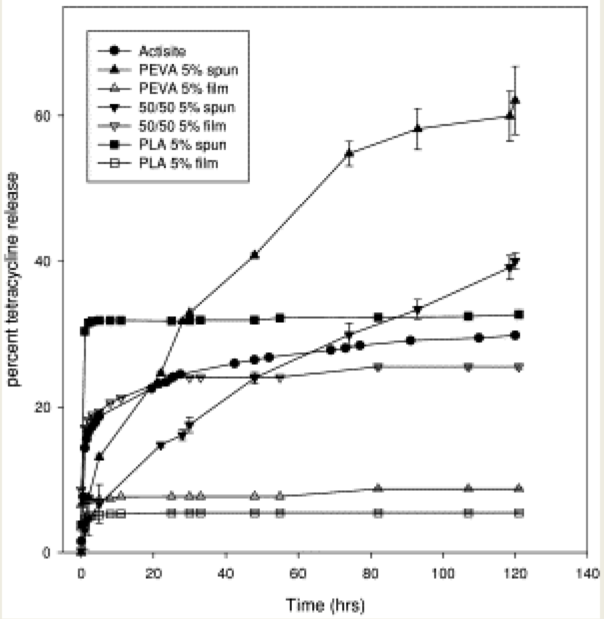

Fig. Percentage release of tetracycline HCl from films and electrospun mats vs. time

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5. Application of electrospun fiber

5.2 Catalyst

- Electrospun nanofibers have high surface area
  → Attractive class of support for catalyst

- Electrospinning polymer solution containing metal salt (such as $Pd(OAc)_2$)
- Reducing the nanofibers in the presence of a reducing agent (such as H_2 at 130℃)
  → Nanofibers containing catalyst nanoparticles are made

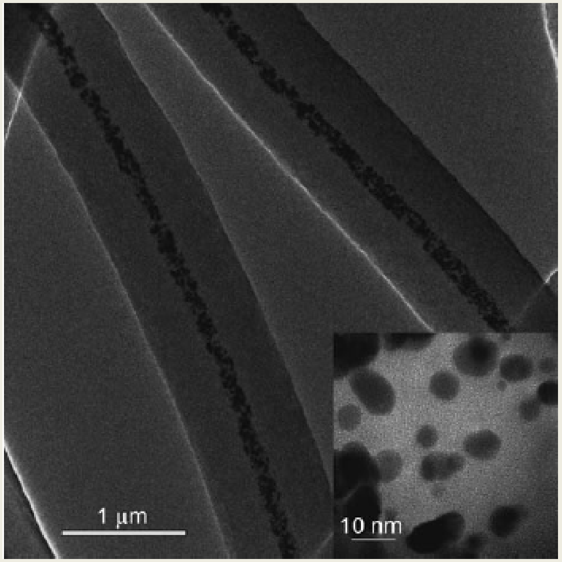

Fig. SEM image of nanofibers loaded with bimetallic nanoparticle system.

5.3 Filter

- To reach high filter efficiencies, it is necessary that the size of the channels and pores in the filter materials be adjusted to the fineness of the particles to be filtered.
  → A transition from fibers with diameters in the micrometer range to fiber with diameters in the nanometer range is required.
  → By adjusting the processing and solution conditions, the diameter of electrospun nanofiber can be tuned.

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