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A Review on Nano/Micro Fiber Fabrication Methods by Near-Field Electrospinning

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Abstract

Faculty: Nanotechnology

School of Engineering and Sciences

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keywords: nanotechnology, nano-fiber, near-field electrospinning, NFES

1 Summary

TABLE 1.1: Electrospun Polymer Solutions - Solution and Process Parameters

Polymer(s):	Poly(ethylene oxide) (PEO)
Solvent(s):	Deionized water
NFES Variant:	Low-Voltage NFES
Polymer Solution and Process Properties:	<ul style="list-style-type: none"> • PEO Concentration: 1, 2, and 3 <i>wt%</i> • Rise in solution conductivity with the increase in PEO concentration • Solution Stirring: 24 <i>h</i> of free diffusion followed by 96 <i>h</i> of stirring at 30 <i>rpm</i> • 3 <i>mL</i> syringe • 27 gauge type 304 stainless steel needle • Solution deposition rate: lower than 1 $\mu\text{L}/\text{h}$ • needle-to-collector distance: 1 <i>mm</i> • Collector substrate: Pyrolyzed SU-8 carbon and Si • NFES process initiated by an air interference with a glass microprobe tip (1 to 3 μm tip diameter) to overcome the surface tension • Time to produce a stable continuous jet: 45 <i>min</i> • Polymer jet initiated at 400-600 <i>V</i> and dispensed at 200-400 <i>V</i> • Collector linear speed: 10-40 <i>mm/s</i> • The voltage turned on when the solution formed a full-sized droplet of 500 μm diameter at the needle tip.
Fiber Characterization:	<ul style="list-style-type: none"> • Diameter: 50-425 <i>nm</i>
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TABLE 1.2: Electrospun Polymer Solutions - Solution and Process Parameters

Polymer(s):	Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) with Poly(ethylene oxide) (PEO)
Solvent(s):	acetonitrile / toluene mixture (65 / 35); acetic acid / toluene (17 / 83); pure toluene
NFES Variant:	<i>Not determined.</i>
Polymer Solution and Process Properties:	<ul style="list-style-type: none"> • Concentrations: <ul style="list-style-type: none"> – MEH-PPV solution: 10 <i>mg</i> of MEH-PPV in 2 <i>mL</i> of toluene – 500 μL of MEH-PPV solution with 250 <i>mg</i> of PEO in 3.5 <i>mL</i> of acetonitrile / toluene (65 / 35) – 500 μL of MEH-PPV solution with 250 <i>mg</i> of PEO in 3 <i>mL</i> of acetic acid / toluene (17 / 83) – The resulting MEH-PPV/PEO concentration is 1:100 • Solution Stirring: MEH-PPV solution stirred for 4 <i>h</i>; PEO solution stirred for 8 <i>h</i>; MEH-PPV/PEO solution stirred and ultrasonically agitated • Collector substrate: SiO₂/Si (oxide thickness = 800 <i>nm</i>) • needle-to-collector distance: 500 μm • μm-diameter tip Tungsten spinneret in a 26 gauge needle • Solution deposition rate: 50 $\mu\text{L}/\text{h}$ • Electrostatic voltage: around 1.3 <i>kV</i> • x-y stage velocity: 50 <i>cm/s</i>
Fiber Characterization:	<ul style="list-style-type: none"> • Distance between adjacent fibers: around 100 μm • Fiber diameter: around 100 <i>nm</i>
Ref:	[2]

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TABLE 1.3: Electrospun Polymer Solutions - Solution and Process Parameters

Polymer(s):	Poly(ethylene oxide) (PEO)
Solvent(s):	Water
NFES Variant:	Scanning Tip Electrospinning and NFES
Polymer Solution and Process Properties:	<ul style="list-style-type: none"> • 7 wt % PEO aqueous solution • Under room temperature at 1 <i>atm</i> • needle-to-collector distance: 500 μm • needle diameter: outer: 200 μm; inner: 100 μm • applied voltage for jet initiation: 1.5 <i>kV</i> • applied voltage for fiber deposition: 600 <i>V</i> • Mechanical drawing is applied by using a tungsten probe with 1 μm tip diameter to poke inside the meniscus. • The probe is then rapidly pulled away from the polymer droplet to activate the continuous electrospinning process • polymer jet diameter: 3 μm • polymer feed rate: 0.1 $\mu\text{L}/\text{h}$ • x-y stage velocity: 120 <i>mm/s</i>
Fiber Characterization:	<ul style="list-style-type: none"> • 108 <i>m</i> yield in 15 <i>min</i> with a fiber diameter of 709 ± 131 <i>nm</i> • Fiber diameter: around 49-74 <i>nm</i> when applied voltage is 800 <i>V</i>
Ref:	[3]

TABLE 1.4: Electrospun Polymer Solutions - Solution and Process Parameters

Polymer(s):	Poly(ϵ -Caprolactone) (PCL)
Solvent(s):	<i>Not applicable.</i>
NFES Variant:	Melt Electrospinning Writing (MEW)
Polymer Solution and Process Properties:	<ul style="list-style-type: none"> • Collector substrate: NCO-sP(EO-stat-PO)-coated glass slide surfaces • Accelerating voltage 2.0–10.0 <i>kV</i> • Collector distance: 1–10 <i>mm</i> • Heating temperature: 80–120 °C • Feeding air pressure 0.5–4.0 <i>bar</i> • Spinneret diameters: 21, 23, 25, 27, 30, and 33 <i>G</i> • Axis velocity: 1000–9000 <i>mm/min</i> • Fibre spacing: 100 μm
Fiber Characterization:	<ul style="list-style-type: none"> • Filament surface is smooth and homogeneous • The crystalline regions formed perpendicular to the filament • Fiber diameter: 817 ± 165 <i>nm</i>
Ref:	[4]

TABLE 1.5: Electrospun Polymer Solutions - Solution and Process Parameters

Polymer(s):	Poly(vinylidene fluoride) (PVDF)
Solvent(s):	N,N-dimethylformamide (DMF)
NFES Variant:	Helix Electrohydrodynamic Printing (HE-printing)
Polymer Solution and Process Properties:	<ul style="list-style-type: none"> • 1.8 g PVDF in 4.1 g of DMF and 4.1 g of acetone to obtain a concentration of 18% • Solution kept at 35 °C for about 6 h until the solution was homogeneous. • Collector substrate: Poly(dimethylsiloxane) (PDMS) on Ecoflex • Solution feed rate: 400 nL/min • Needle diameter: inner 260 μm; external 510 μm • Applied voltage: 1.5–3 kV • Nozzle-to-collector distance: 10–50 mm • x-y stage velocity: 0–400 mm/min • At room temperature and 35–45% humidity
Fiber Characterization:	<ul style="list-style-type: none"> • Stretchable serpentine structures with specific wavelength and amplitude. • Wavelength: about 100–2000 μm • Fiber diameter: about 1.5–3 μm
Ref:	[5]

TABLE 1.6: Electrospun Polymer Solutions - Solution and Process Parameters

Polymer(s):	Polyhedral Oligomeric Silsesquioxane-Poly(Carbonate-Urea)Urethane (POSS-PCU) and Polyhedral Oligomeric Silsesquioxane-Poly(Caprolactone-Poly(Carbonate-Urea)Urethane) (POSS-PCL-PCU)
Solvent(s):	Dimethylacetamide (DMAC) and 1-Butanol
NFES Variant:	Electrohydrodynamic 3D Print-patterning or Electrohydrodynamic Jetting
Polymer Solution and Process Properties:	<ul style="list-style-type: none"> • Solution concentration: POSS-PCU and POSS-PCL-PCU used in 20% w/w concentration in DMAC • Needle diameter: 750 μm • Applied voltage: 8.0-10.0 kV • Solution flow rate: less than 1 $\mu L/min$ • Needle-to-collector distance: about between 500 μm to 2 mm • x-y stage velocity: 10 mm/s • Ethanol-coated substrate
Fiber Characterization:	<ul style="list-style-type: none"> • Distance between adjacent fibers: 250 μm • Fiber diameter: 5-50 μm
Ref:	[6]

TABLE 1.7: Electrospun Polymer Solutions - Solution and Process Parameters

Polymer(s):	Poly(ethylene oxide) (PEO)
Solvent(s):	Distilled water
NFES Variant:	Electrohydrodynamic Writing or Mechano-electrospinning (MES)
Polymer Solution and Process Properties:	<ul style="list-style-type: none"> • Polymer solution weight concentration: 6 wt% PEO • Needle-to-collector distance: 7.5 mm • Applied voltage to initiate the jet: 2 kV • Applied voltage during deposition: 0.8-1 kV • Under the room temperature and relative humidity of about 25%. • x-y stage velocity: around 400 mm/s • Solution flow rate: 1200 nL/min
Fiber Characterization:	<ul style="list-style-type: none"> • Distance between adjacent fibers: 5 μm • Fiber diameter: 200-350 nm
Ref:	[7]

TABLE 1.8: Electrospun Polymer Solutions - Solution and Process Parameters

Polymer(s):	Poly(ethylene oxide) (PEO)
Solvent(s):	Deionized water and the ethanol with a volume ratio of 3:1
NFES Variant:	Airflow-assisted Electrohydrodynamic Direct-writing (EDW)
Polymer Solution and Process Properties:	<ul style="list-style-type: none"> • Concentration: 8 <i>wt%</i> PEO • Outer airflow passage diameter: 1 <i>mm</i> • Airflow gas pump pressure: 25 <i>kPa</i> • Inner liquid passage diameter: 0.21 <i>mm</i> • Silicon substrate • Needle-to-collector distance: 2 <i>mm</i> • Solution flow rate: 30 $\mu\text{L}/\text{h}$ • Applied voltage: about 2 <i>kV</i> • x-y stage velocity: between 1-20 <i>mm/s</i>
Fiber Characterization:	<ul style="list-style-type: none"> • Fiber deposition position accuracy: $5.13 \pm 6.67 \mu\text{m}$ • Fiber diameter: $3.73 \pm 1.37 \mu\text{m}$
Ref:	[8]

TABLE 1.9: Electrospun Polymer Solutions - Solution and Process Parameters

Polymer(s):	
Solvent(s):	
NFES Variant:	
Polymer Solution and Process Properties:	<ul style="list-style-type: none"> • 1
Fiber Characterization:	<ul style="list-style-type: none"> • a
Ref:	[1]

References

- [1] Gobind S. Bisht et al. "Controlled Continuous Patterning of Polymeric Nanofibers on Three-Dimensional Substrates Using Low-Voltage Near-Field Electrospinning". In: *Nano Letters* 11.4 (Apr. 2011), pp. 1831–1837. ISSN: 1530-6984. DOI: [10.1021/nl2006164](https://doi.org/10.1021/nl2006164). URL: <https://pubs.acs.org/doi/10.1021/nl2006164>.
- [2] Daniela Di Camillo et al. "Near-field electrospinning of conjugated polymer light-emitting nanofibers". In: *Nanoscale* 5 (2013), pp. 11637–11642. DOI: [10.1039/C3NR03094F](https://doi.org/10.1039/C3NR03094F). URL: <https://arxiv.org/ftp/arxiv/papers/1310/1310.5101.pdf>.
- [3] Chieh Chang, Kevin Limkralassiri, and Liwei Lin. "Continuous near-field electrospinning for large area deposition of orderly nanofiber patterns". In: *Appl Phys Lett* (2008), p. 3. DOI: [10.1063/1.2975834](https://doi.org/10.1063/1.2975834). URL: http://www-bsac.eecs.berkeley.edu/publications/search/send%7B%5C_%7Dpublication%7B%5C_%7Dpdf2client.php?pubID=1217995664.
- [4] Paul D Dalton, T Joergensen, and Juergen Groll. "Additive manufacturing of scaffolds with sub-micron filaments via melt electrospinning writing Related content Patterned melt electrospun substrates for tissue engineering". In: (2015). DOI: [10.1088/1758-5090/7/3/035002](https://doi.org/10.1088/1758-5090/7/3/035002). URL: <https://iopscience.iop.org/article/10.1088/1758-5090/7/3/035002/pdf>.
- [5] Yongqing Duan et al. "Helix Electrohydrodynamic Printing of Highly Aligned Serpentine Micro/Nanofibers." In: *Polymers* 9.9 (Sept. 2017). ISSN: 2073-4360. DOI: [10.3390/polym9090434](https://doi.org/10.3390/polym9090434). URL: <http://www.ncbi.nlm.nih.gov/pubmed/30965737> <http://www.pubmedcentral.nih.gov/articlerender.fcgi?artid=PMC6418525>.
- [6] Ashish Gupta et al. "Novel Electrohydrodynamic Printing of Nanocomposite Biopolymer Scaffolds". In: *Journal of BIOACTIVE AND COMPATIBLE POLYMERS* 22 (2007). DOI: [10.1177/0883911507078268](https://doi.org/10.1177/0883911507078268). URL: <https://journals.sagepub.com/doi/pdf/10.1177/0883911507078268>.
- [7] YongAn Huang et al. "Versatile, kinetically controlled, high precision electrohydrodynamic writing of micro/nanofibers". In: *Scientific Reports* 4.1 (May 2015), p. 5949. ISSN: 2045-2322. DOI: [10.1038/srep05949](https://doi.org/10.1038/srep05949). URL: <http://www.nature.com/articles/srep05949>.

- [8] Jiaxin Jiang et al. "Electrohydrodynamic Direct-Writing Micropatterns with Assisted Airflow". In: *Micromachines* 9.9 (Sept. 2018), p. 456. ISSN: 2072-666X. DOI: 10.3390/mi9090456. URL: <http://www.mdpi.com/2072-666X/9/9/456>.
- [9] Jinseong Kim, Bohee Maeng, and Jungyul Park. "Characterization of 3D electrospinning on inkjet printed conductive pattern on paper". In: *Micro and Nano Systems Letters* 6.1 (Dec. 2018), p. 12. ISSN: 2213-9621. DOI: 10.1186/s40486-018-0074-1. URL: <https://mns-l-journal.springeropen.com/articles/10.1186/s40486-018-0074-1>.
- [10] Jongwan Lee et al. "Fabrication of Patterned Nanofibrous Mats Using Direct-Write Electrospinning". In: *Langmuir* 28.18 (May 2012), pp. 7267–7275. ISSN: 0743-7463. DOI: 10.1021/la3009249. URL: <http://pubs.acs.org/doi/10.1021/la3009249>.
- [11] Z H Liu et al. "Direct-write PVDF nonwoven fiber fabric energy harvesters via the hollow cylindrical near-field electrospinning process". In: (2014), pp. 25003–25014. DOI: 10.1088/0964-1726/23/2/025003. URL: <http://iopscience.iop.org/0964-1726/23/2/025003>.
- [12] Sung-Yong Min et al. "Large-scale organic nanowire lithography and electronics". In: *Nature Communications* 4.1 (June 2013), p. 1773. ISSN: 2041-1723. DOI: 10.1038/ncomms2785. URL: <http://www.nature.com/articles/ncomms2785>.
- [13] Cheng-Tang Pan et al. "Near-field electrospinning enhances the energy harvesting of hollow PVDF piezoelectric fibers". In: *RSC Advances* 5.103 (2015), pp. 85073–85081. ISSN: 2046-2069. DOI: 10.1039/C5RA16604G. URL: <http://xlink.rsc.org/?DOI=C5RA16604G>.
- [14] Cheng-Tang Pan et al. *Poly(γ -benzyl α , l-glutamate) in Cylindrical Near-Field Electrospinning Fabrication and Analysis of Piezoelectric Fibers*. Tech. rep. 2. 2014, pp. 63–73. URL: https://myukk.org/SM2017/sm%7B%5C_%7Dpdf/SM971.pdf.
- [15] Chiho Song et al. "Patterned polydiacetylene-embedded polystyrene nanofibers based on electrohydrodynamic jet printing". In: *Macromolecular Research* 23.1 (Jan. 2015), pp. 118–123. ISSN: 1598-5032. DOI: 10.1007/s13233-015-3024-2. URL: <http://link.springer.com/10.1007/s13233-015-3024-2>.
- [16] Daoheng Sun et al. "Near-Field Electrospinning". In: (2006). DOI: 10.1021/nl0602701. URL: <https://pubs.acs.org/doi/10.1021/nl0602701>.
- [17] Han Wang et al. "Research on Multinozzle Near-Field Electrospinning Patterned Deposition". In: *Journal of Nanomaterials* 2015 (July 2015), pp. 1–8. ISSN: 1687-4110. DOI: 10.1155/2015/529138. URL: <http://www.hindawi.com/journals/jnm/2015/529138/>.
- [18] Zhifeng Wang et al. "Controllable deposition distance of aligned pattern via dual-nozzle near-field electrospinning". In: *AIP Advances* 7.3 (Mar. 2017), p. 035310. ISSN: 2158-3226. DOI: 10.1063/1.4974936. URL: <http://aip.scitation.org/doi/10.1063/1.4974936>.
- [19] Zhifeng Wang et al. "Fabrication and evaluation of controllable deposition distance for aligned pattern by multi-nozzle near-field electrospinning". In: *AIP*

- Advances* 8.7 (July 2018), p. 075111. ISSN: 2158-3226. DOI: [10.1063/1.5032082](https://doi.org/10.1063/1.5032082). URL: <http://aip.scitation.org/doi/10.1063/1.5032082>.
- [20] Jiachen Xu et al. "Accuracy Improvement of Nano-fiber Deposition by Near-Field Electrospinning". In: *International Workshop on Microfactories IWMF2014.9th* (2014). URL: <http://conf.papercept.net/images/temp/IWMF/media/files/0041.pdf>.
- [21] Niannan Xue et al. "Rapid Patterning of 1-D Collagenous Topography as an ECM Protein Fibril Platform for Image Cytometry". In: *PLoS ONE* 9.4 (Apr. 2014). Ed. by Wei-Chun Chin, e93590. ISSN: 1932-6203. DOI: [10.1371/journal.pone.0093590](https://doi.org/10.1371/journal.pone.0093590). URL: <https://dx.plos.org/10.1371/journal.pone.0093590>.
- [22] Gaofeng Zheng et al. "Precision deposition of a nanofibre by near-field electrospinning". In: *Journal of Physics D: Applied Physics* 43.41 (Oct. 2010), p. 415501. ISSN: 0022-3727. DOI: [10.1088/0022-3727/43/41/415501](https://doi.org/10.1088/0022-3727/43/41/415501). URL: <http://stacks.iop.org/0022-3727/43/i=41/a=415501?key=crossref.304f8be16661d1ca2c851060187b28>.
- [23] Jiang-Yi Zheng et al. "Electrohydrodynamic Direct-Write Orderly Micro/Nanofibrous Structure on Flexible Insulating Substrate". In: *Journal of Nanomaterials* 2014 (May 2014), pp. 1–7. ISSN: 1687-4110. DOI: [10.1155/2014/708186](https://doi.org/10.1155/2014/708186). URL: <http://www.hindawi.com/journals/jnm/2014/708186/>.
- [24] Jie Zheng et al. "Polymer nanofibers prepared by low-voltage near-field electrospinning". In: *Chinese Physics B* 21.4 (2012), pp. 1–6. ISSN: 16741056. DOI: [10.1088/1674-1056/21/4/048102](https://doi.org/10.1088/1674-1056/21/4/048102).