INSTITUTO TECNONÓLOGICO Y DE ESTUDIOS
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School of Engineering and Sciences

Fabrication of Suspended Nanowires Through Mechano-Near-Field Electrospinning of Polymers in Solution for the Production of Glass-like Carbon

A thesis presented by:
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in

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Declaration of Authorship

I, Antonio Osamu Katagiri Tanaka, declare that this thesis titled, "Fabrication of Suspended Nanowires Through Mechano-Near-Field Electrospinning of Polymers in Solution for the Production of Glass-like Carbon" and the work presented in it are my own. I confirm that:

- This work was done wholly or mainly while in candidature for a research degree at this University.
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Antonio Osamu Katagiri Tanaka
Estado de México, Atizapan de Zaragoza, December 02, 2020

"Carbon is a simple element but .....

One branch of chemistry is devoted to its compounds!

One branch of science is devoted to the many forms of the element as a solid material.

The best of this is that although most carbon materials are grey or black to the naked eye and the uninitiated, a closer examination reveals the form, beauty and even color of carbon science."

Marsh, Harry
Universitat d'Alacant, Alicante, Spain
scopus.com

Dedication

Thanks for all your unconditional confidence, support, patience, and encouragement. You were my main motivation for pushing through this work.

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There are a number of people without whom this thesis might not have been written, and to whom I am greatly indebted.

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Fabrication of Suspended Nanowires Through Mechano-Near-Field Electrospinning of Polymers in Solution for the Production of Glass-like Carbon

by Antonio Osamu Katagiri Tanaka

Abstract

Carbon nano-wires are versatile materials composed of carbon chains with a wide range of applications due to their high conductivity. Regardless of the high interest in the implementation of carbon nano-wires in several applications and devices, no feasible processes have been developed to fabricate carbon nano-wires with spatial control at a reasonable cost. Carbon nano-wires have been fabricated with the use of a photoresist, but little is known about polymers that can produce more conductive carbon nano-wires after pyrolysis. Various polymer solutions have been tested in near field electrospinning (NFES) and photopolymerization separately, however, few have been tested for nano-wire fabrication purposes through pyrolysis. The intention behind the thesis proposal is to implement rheology analyses of different polymer solutions to determine if they can be easily electrospun at low voltages and then fabricate nano-wires with them. This thesis work arises from the need to test a greater variety of polymers with the goal to design a polymer solution to fabricate carbon nano-wires with better conductivity than the current SU-8 polymeric nano-fibers. The research process will include the design of polymer solutions that can be electrospun, photopolymerized, and then pyrolyzed into conducting carbon nanowires. On the other hand, it is intended to engineer a newly designed polymer solution to achieve mass scale manufacturing of conductive carbon nano-wires in an inexpensive, continuous, simple and reproducible manner as central components for nano-sensors.

keywords: nanotechnology, carbon, nano-wires, Near-Field Electrospinning, NFES

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Chapter 1

Introduction

Carbon nano-materials are subjected to great interest for research purposes due to their various potential applications in diverse areas that take advantage of the nano-scale properties. Carbon nano-materials are suitable for catalysis, adsorption, carbon capture, energy and hydrogen storage, drug delivery, bio-sensing, and cancer detection. Some matchless properties that allow carbon nano-materials to be utilized within multiple functionalities include high porosity, distinguished structures, uniform morphologies, high stability, high magnetic properties, and high conductivity. [1–8]

This document bestows a thesis project to perform research to engineer a polymer solution to achieve mass scale manufacturing of high conductive carbon nano-wires with a reduced diameter in an inexpensive, continuous, simple and reproducible manner. The research intends to involve several manufacturing processes such as near field electrospinning, photo-polymerization, pyrolization, and carbonization, as they have shown to be promising methods for the fabrication of carbon nano-materials. [9] See Figure 1.1. A number of processes have been developed for specific purposes of polymeric nano-fibres, some include surface deposition, composites, and chemical adjustments. Polymeric nano-fibers must be also pyrolyzed to generate carbon nano-wires with conductive capabilities [10] for electrochemical sensing and energy storage purposes.

Nanotechnology has led to the study of different polymer patterning techniques to integrate carbon nano-wires structures. One technique is known as far-field electrospinning (FFES), a process in which electrified jets of polymer solution are dispensed to synthesize nano-fibres which are then pyrolyzed at high temperatures. One sub-technique derived from

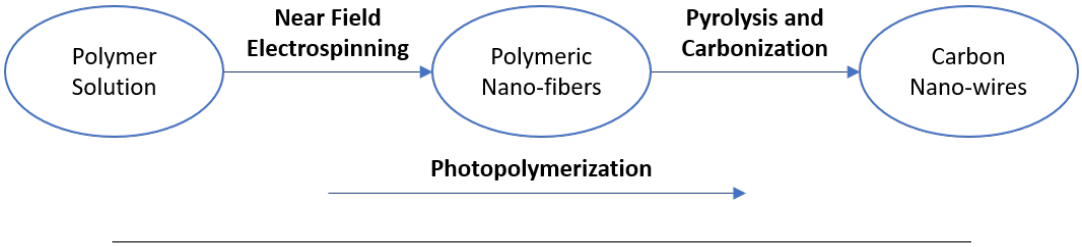


FIGURE 1.1: Fabrication process and characterization techniques of conductive carbon nano-wires to achieve through the dissertation.

electrospinning is near-field electromechanical spinning or NFEMS. Unlike FFES, NFEMS has proved to deliver high control in patterning polymeric nano-fibres. [9]

The proposal is to continue the previous work done in regards to the synthesis of carbon nano-wires. Previous work includes the fabrication of suspended carbon nano-wires by two methods: electro-mechanical spinning and multiple-photon polymerization with a photoresist. [9, 11] This work is intended to focus on electro-mechanical spinning processes only, to bring off polymer solutions that can be electrospun by NFEMS, photo-polymerized and pyrolyzed into conducting carbon nano-wires. The polymer solutions described by Cárdenas and Flores [9, 11] are to be amended to achieve the goal mentioned in the previous statement.

Traditional near-field electrospinning or NFES allows large scale manufacturability combined with spatial control of material deposition. [10] However, the reported efforts required the use of electric fields in excess of 200 kV/m for continuous operation, resulting in limited control for nano-fiber patterning in traditional NFES processes. Madou et al. [10] conclude that the current state-of-the-art synthesis processes for polymer nano-fibers lack to yield precise, inexpensive, fast, and continuous manufacturing properties.

1.1 Carbon Nanowires Research Developments in Terms of Published Papers, Synthesis and Fabrication

Nanotechnology ability to control and piece together materials at the nano-scale has enabled the development of various carbon nano-materials and carbon nano-structures, such as nano-dots, nano-fibres, nano-tubes and nano-wires. [12–15] This chapter bestows on the applications at

the micro-scale and nano-scale levels, as well as the current research of carbon-based nano-materials (CBNs).

1.1.1 Carbon and carbon-based nanomaterials

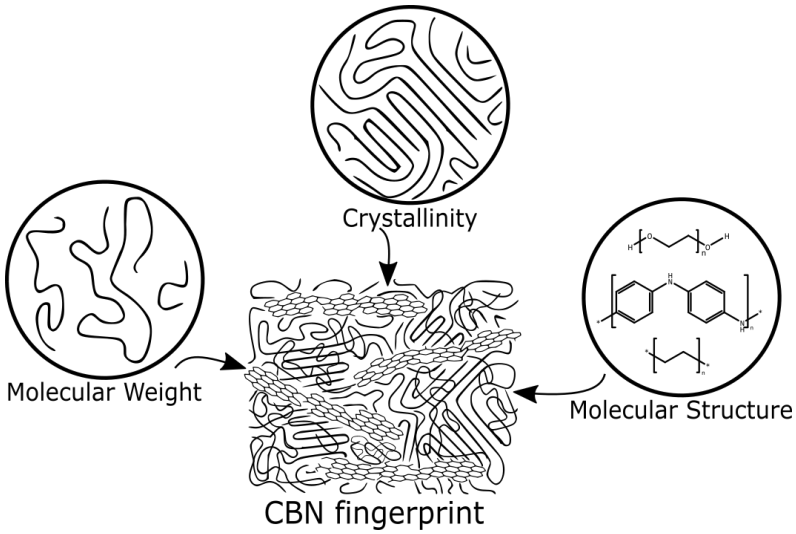


FIGURE 1.2: Molecular to meso-scale structural features of synthetic polymers influence the emergence of specific micro-structural features in polymer-derived carbon materials after pyrolysis.

Carbon is a versatile element capable to form a number of bonds with other elements or with itself. Cabon-based nano-materials (CBNs) exist in diverse forms, depending on the precise values of each degree of freedom that specify the material proclivity at multiple scales. Hybridization, crystallization, percolation, anisotropy, porosity, impurities and imperfections are some of the relevant features that determine the CBN set of properties. The combination of these features at the micro- and meso-scale burst a variety of macro-scale properties that comprise the CBN fingerprint (1.2). The interminable collection of possible CBN fingerprints range from soft, conductive lubricants to very hard, low conductivity solids; and from black colour, bulks to transparent, disordered thin films. [1] Figures 1.3 and 1.4 shows the existence of different types of allotrope as carbon orbitals have the ability to hybridize in sp1, sp2 and sp3 configurations, assembling different types of allotropes.

In terms of porosity, CBNs exhibit different properties according to the degree of 'open' and 'closed' pores. A 'closed pore' is a void or empty space in solid materials where a discontinuity is present within the array of atoms and molecules. On the other hand, an 'open pore' refers to a void which is connected to the outer surface of the solid, in other words a 'open pore' is a

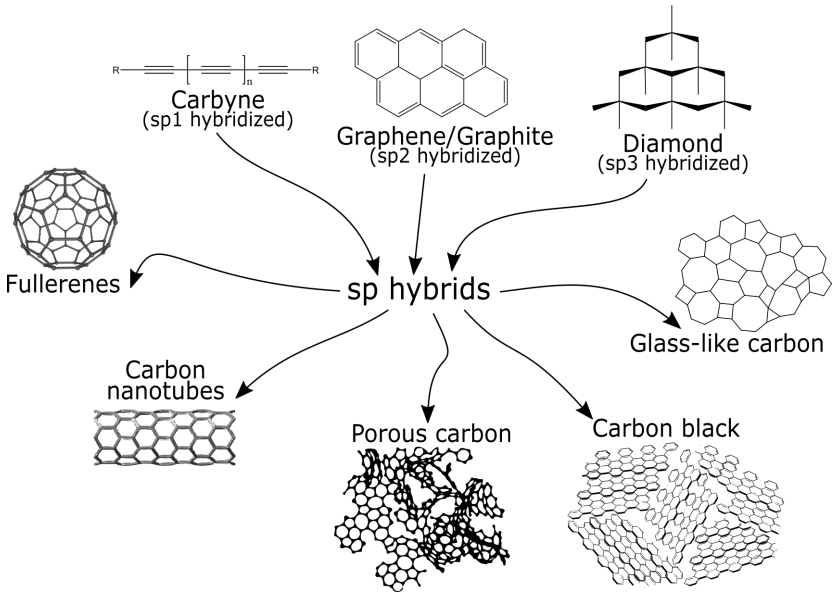


FIGURE 1.3: Three carbon allotropes (diamond, carbyne and graphene) are the building blocks of additional deriving carbon types such as fullerenes, porous carbon and glass-like carbon.

'closed pore' with an opening to the external surface. [23] Figure 1.5 shows a classification of carbon allotropes according to their porous content.

Thermal conductivity and electrical conductivity decrease with increasing porosity due to the reduced amount of material to conduct electrons and energy. Furthermore, porosity negatively affects the mechanical properties like strength and elastic modulus as it reduces the volume in which stresses are distributed. Moreover, stresses are concentrated at the pores which makes the material prone to mechanical failure. [23, 24]

Due to the versatility and variety of CBNs, CBNs have been fabricated and implemented for various purposes. [2, 4–8]. For instance, field effect transistors (FET) have been studied by Novoselov [25] and Heersche et. al. [16]. Carbon FET devices have reported field-effect mobility one order of magnitude higher than that of silicon FETs. Other literature suggests CBNs to be favorable to detect a variety of gases and bio-molecules. [26, 27] As molecules are absorbed by the CBN, the carrier density and electrical resistivity of the carbon material changes. Moreover, CBNs have showed good performance in applications in energy (prevent wastage of energy), water (purification) and diagnostics (lab-on-chip systems and nano-sensors). [15, 28] As mentioned above, the morphology of CBNs has an impact on the electrochemical and mechanical properties. [23, 24, 29] In this regard, carbon

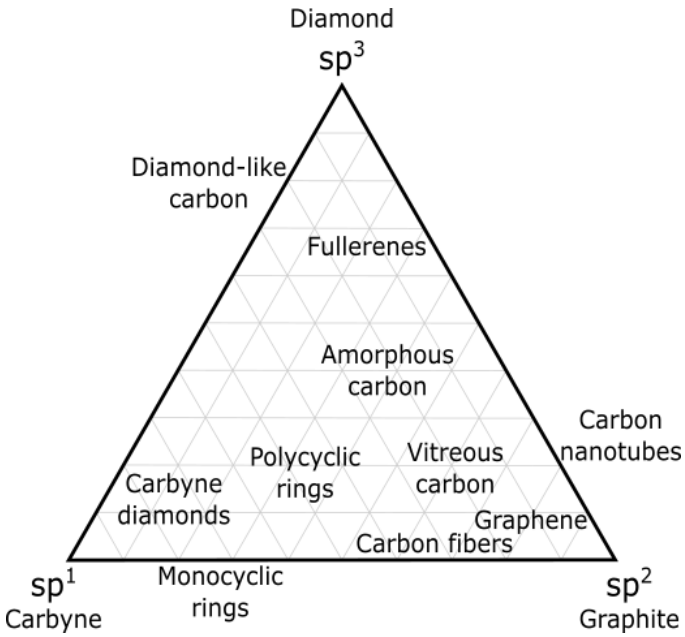


FIGURE 1.4: Ternary phase diagram of amorphous carbon regions based on hybridization degree. Adapted from [16–22].

nano-structures, such as nano-wires [30, 31], have been fabricated to achieve improved electrochemical characteristics.

1.1.2 Carbon Nano-wires

As depicted in Figure 1.4, carbon nano-fibers (CNFs) have been classified as linear, sp2-based structures. [16–22] Nano-fibers own good electrical, optical and mechanical characteristics, however those properties are highly dependent on the morphology of the fibers. [32] The material properties of 1D nano-structures depend on fiber diameter, porosity, crystallization degree and crystallization orientation. Consequently, the fabrication parameters and environment conditions have an impact on the reproducibility of high quality fibers. [32] Carbon nano-fibers (CNFs) have diameters of several micrometers (Figure 1.7) and are different from carbon nano-tubes (CNT). [33–37] Unlike carbon nano-tubes with hollow cores, carbon nano-fibers can be represented as stacked layers along the thread length. [37–39] The stacked geometry of carbon nano-fibers results in unique electrical, chemical and mechanical properties. [40–42] Unlike CNFs, carbon nano-tubes inherent problems such as high cost and low effective surface area, which limit their practical use. [22]

sp2 carbon nano-wires have been used for the improvement of power

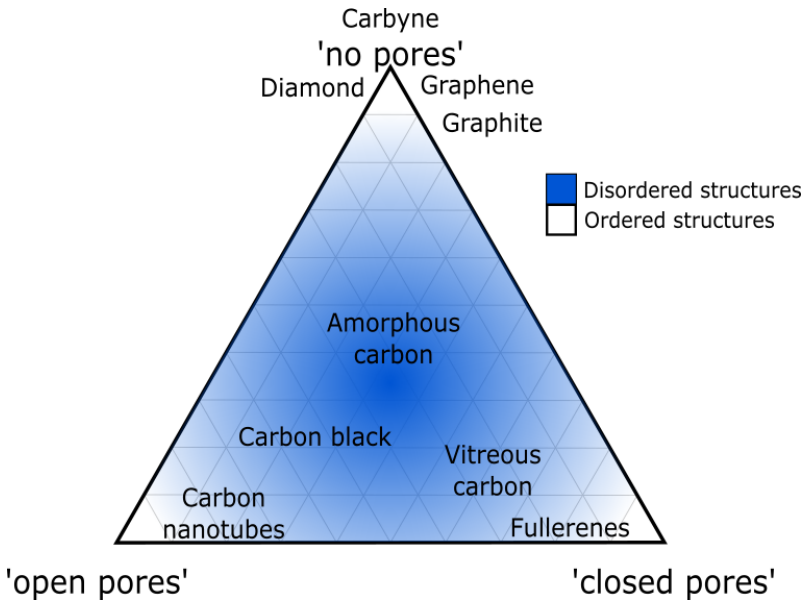


FIGURE 1.5: Ternary phase diagram of amorphous carbon regions based on structure order and porosity. Regions are colored by the degree of crystalline order within the carbon structure. White represents highly ordered structures, whereas white represents disordered structures. [23, 24]

density and specific energy in lithium-ion batteries. [43–45] Authors posit that the performance and capacity of Li-ion batteries depend on the CNF structure and texture. Through the right combination of electrospinning and carbonization parameters, electrically conductive, mechanically tough and with thin diameter fibers have been achieved by Yoon et al. [39]. Yoon reported 431 mili-ampere-hour per gram batteries with vitreous carbon nanofibers. Yoon states that the battery capacity highly depends on the pyrolysis process parameters as the morphology of the fiber develops pores and hence different surface properties. CNFs supercapacitors have been investigated as energy storage devices due to their high power bearability and long lifecycles. [46–49] The studies' authors posit that carbon nano-fibers can be implemented as high-power supercapacitors due to their large surface area and high electrical conductivity.

On the other hand, the low reactivity and unique morphology of CNFs make them promising catalyst supports for metal nano-particles. [50–52] It is well known that the morphology and nano-structure of the supporting material are the main factors that prevent agglomerations of nano-particles. [53, 54] Moreover, in bone tissue scaffold applications, collagen is the most popular scaffold. However, collagen scaffolds bring xenogenicity issues which

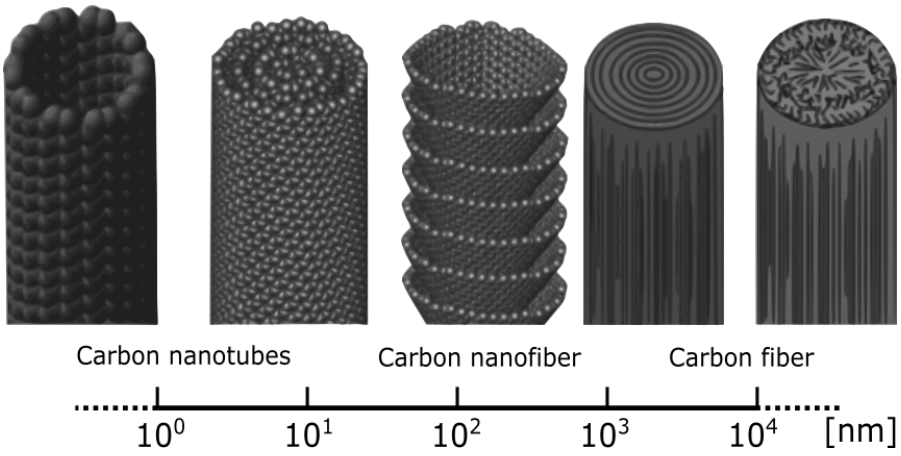


FIGURE 1.6: Various types of fibrous carbon materials bear different characteristics according to their molecular structure. Adapted from [22]

leads to disease transfer or immunogenic reactions, besides its inhability to preserve its shape once placed in the body. [55–62] Currently, carbon fibers have been studied for bone tissue scaffold, however early attempts yield too thick fibers for cell cultivation and tissue regeneration. [63, 64] As depicted in previous research of CNFs for different applications, fiber morphology seems to have a significant impact on their performance.

Typically, carbon nano-fibers (CNFs) are synthesized by a combination of a patterning process and a pyrolysis process. CNFs fabricated by electrospinning of polymer solutions with electrostatic forces. Electrospun CNFs have characteristics such as high surface area, thin morphology with nano-scale diameters. The properties of electrospun fibers allow CNFs to be implemented in nano-sensing devices, energy storage applications, and tissue scafflods. [28, 65–70] Several patterning techniques have been attempted to achieve the desired fiber morphology. In addition to electrospinning, CNFs have been also fabricated by two-photon polymerization (TPP) and photo-lithography techniques. [71] Cardenas et al. implemented TPP and conventional UV lithography to study the fabrication of CNFs within carbon micro-electromechanical systems.

1.2 Problem definition and motivation

The role of carbon nano-fibers in nano-sensor devices play an important role, as portable instruments require light-weight and small-sized components. [28] Table 1.1 lists some advantages of nano-sensors that can be accomplished

by the fabrication of CNFs via near-field electrospinning and a thermal treatment in an inert environment.

TABLE 1.1: Advantages of Nano-sensors. Adapted from [28]

Advantage	**Description**
High sensitivity	More accuracy, single molecule detection
Small size	Light-weight, portability, low-power consumption, small sample size, reduced sample preparation, and ease of use
Low response time	High-frequency, real time analysis
Low cost	Disposable devices

Sensors of small size require less time to output a stable signal as signals require less time to travel shorter lengths, hence signal noise is also reduced. Nano-sized sensors allow data collection and measurements to be performed in real time at faster speeds. [28] The nano-scale also allows sensors to increase the active surface area, enabling the absorption and detection of analytes in low concentrations. [28] The integration of small-sized sensing devices lean to lower fabrication costs as large-scale production and reproducible fabrication can be achieved when producing nanosensors. [28] Moreover, conventional sensors are bulky and require higher amounts of power to operate. In gas sensing, neither a large sensing surface or a large sample is required to get a readable output signal from the sensor. Power consumption can be saved by reducing the thermal mass of the sensor. [28] Furthermore, if several gases are to be detected, an array of several gas sensors are to be assembled into an array. A multi-gas sensor array can increase the size and cost, whereas an array of gas nano-sensors (each functionalized to detect a specific analyte) can be implemented into a single device. [28] Nano-sensors can be classified by the kind of energy or physycal phenomena that is detected, as depicted in Table 1.2 for instance: biological, mechanical, thermal, chemical, and optical sensors. [28, 72]

Carbon nanowires have been fabricated with a photoresist by multiple-photon polymerization techniques. However little is known about polymers that can produce conductive carbon nano-wires after pyrolysis, as it is generally believed that most polymers do not form significant amounts of graphitic carbon when carbonized. In the past years, photopolymerization processes have been applied to the fabrication of nano-structures with the use of an epoxy based photoresist. [73] Photopolymerization techniques deliver

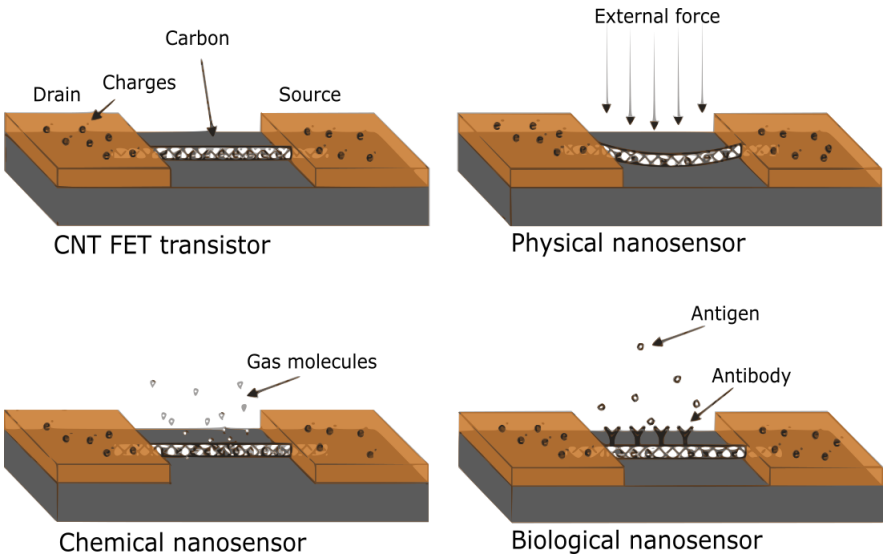


FIGURE 1.7: Diagram examples of carbon-based nano-sensors. Adapted from [72]

patterning resolutions with nano-scale tolerances through two-photon lithography for the production of highly detailed structures [74].

On the other hand, electrospinning has been acknowledged as a process with promising results at nano-structure fabrication [73], yet there is little research regarding the implementation of electrospinning for the fabrication of carbon nano-wires. Electrospinning has the potential to be a more straightforward process for the design and fabrication of nano-structures, as it can achieve mass scale manufacturing in a continuous, simple and reproducible manner. Cardenas [9] showed that electrospinning can be implemented with ease for carbon nano-wire synthesis. Mechano-electrospinning, a new variant of electrospinning shows promising results in the production of ordered carbon nano-wires. As stated in [9], mechano-electrospinning is an early technology invention and brings new challenges, such as the reproducibility of carbon nano-wire production. Furthermore, the study of a new fabrication process to produce carbon nanowires that involves mechano-electrospinning will enable spatial control of the structures' patterning.

Since electrospinning seems to be a better alternative for carbon nano-wire fabrication processes; and for that purpose of its implementation, it is required to develop polymer solutions that can be mechano-electrospun, photopolymerized and pyrolyzed into conducting carbon nano-wires. Carbon nano-materials have been subjected to research due to their various

TABLE 1.2: Classification of Nano-sensors. Adapted from [28]

Classification	**Phenomena / Energy**
Mechanical	Position, acceleration, stress, strain, force, pressure, mass, density, viscosity, moment, torque
Acoustic	Wave amplitude, phase, polarization, velocity
Optical	Absorbance, reflectance, fluorescence, luminescence, refractive index, light scattering
Thermal	Temperature, flux, thermal conductivity, specific heat
Electrical	Charge, current, potential, dielectric constant, conductivity
Magnetic	Magnetic field, flux, permeability
Chemical	Components (identities, concentrations, states)
Biological	Biomass (identities, concentrations, states)

potential applications in diverse areas that take advantage of the nano-scale properties. [8] Carbon nano-materials are suitable for the catalysis, adsorption, carbon capture, energy and hydrogen storage, drug delivery, bio-sensing and cancer detection. [8] However most applications are not currently feasible due to the lack of a continuous, simple and reproducible fabrication method with inexpensive processes. With the newly designed polymer solution, it would be possible to produce carbon nano-wires in large quantities, and therefore more applications will become feasible. On the other hand, the new technique will overcome some limitations of other methods such as lithography currently has. For instance, patterns created by lithography processes cannot be originated, only replicated, all constituent points of the pattern can only be addressed at the same time, and the process requires the pattern to be encoded into a mask. [75]

1.3 Hypothesis

The rheological properties of polymer solutions along with synthesis parameters (stage velocity, voltage, dispense rate) can be amended through rheological analyses to obtain a low voltage electrospun-able, photopolymerizable and graphitizable fibers for the fabrication conductive of carbon nano-wires with specified dimensions (diameter and length). The rheological properties of polymer solutions along with synthesis parameters are to be amended by replacing the PEO (Poly(ethylene) oxide) component within the existing polymer solutions described in Flores [11] and Cardenas

[9] work. PEO is to be replaced as its only purpose is to allow the electrospinning process to take place, but no benefit is obtained from it after pyrolysis.

1.4 Research Questions

- Is there any evidence of conductive carbon nano-wire fabrication though electrospun-able and pyrozable polymer solutions?
- What are the process parameters to consider/control for the fabrication processes of carbon nano-wires?
- What rheological properties are to be controlled/tested to deliver an electrospun-able and pyrozable polymer solution?
- Are there any efforts employed to the design of polymer solutions that can be electrospun, photopolymerized, and pyrolyzed into conducting carbon nanowires?
- What are the optimal fabrication parameters for the synthesis of carbon nano-wires through near-field electromechanical spinning?
- What materials can be used to ease the electrospinning process and favor the carbon nano-wire properties after pyrolysis?

1.5 Objectives

1.5.1 General objective

Study the practice and feasibility of a new fabrication process to achieve mass scale manufacturing of polymeric micro-wires in an inexpensive, continuous, simple and reproducible manner by the integration of near-field electromechanical spinning (NFEMS) and forward-thinking on pyrolysis processes to convert polymeric micro-wires into carbon nano-wires.

1.5.2 Specific objectives

- Design polymer solutions that can be electrospun by NFES, photopolymerized, and then pyrolyzed.

- Through rheological analyses, determine if polymer solutions can be easily employed for conducting carbon nano-wire synthesis.

- Determine and control the polymer solution rheological properties along with the process parameters of carbon nano-wire synthesis.

- Discover a PEO-similar material to allow the electrospinning process as well as input favourable properties to the carbon nano-wire yield.

1.6 Dissertation Outline

Chapter 2

Near-Field Electrospinning as an Affordable Way to Gain Spatial Control

2.1 Review of Polymer Solutions for NFES with Spatial Control

Near-field electrospinning (NFES) is identified to be a technique able to fabricate polymer nano and micro fibers with accurate placement. In the past years (2006-2020), several polymer solutions have been successfully electrospun into fibers through several variants of the conventional NFES process. Each NFES variant intents to tailor the process parameters in order to improve the fibers' properties.

Even though electrospinning is an old invention [76], it is currently a trending topic among researchers [77–79]. One of the reasons electrospinning is to be studied is its potential to fabricate polymer nano fibers from a variety of polymers. The technique allows the production of thin continuous fibers with ease, with micro and sub-micrometer diameters, which is something difficult to achieve by other techniques. Furthermore, the basic setup can be modified with ease to fabricate different fibers with diversified functionalities with different materials. The produced fibers can be aligned or unaligned. Besides, the electrospinning equipment is inexpensive and of small size, compared to the equipment of standard spinning techniques [80]. On the other hand, the understanding of the electrospinning process has improved in the last years.

Current literature dictates the typical spinning setup is comprised by three main components: a polymer reservoir, a fiber collector, and some

way to dispense the fibers onto the collector. The spinning process is an electro-hydrodynamic (EHD) technique that yields continuous polymer fibers. Other EHD techniques are spraying and atomization which produce polymer droplets and polymer particles respectively, seeFigure 2.1.

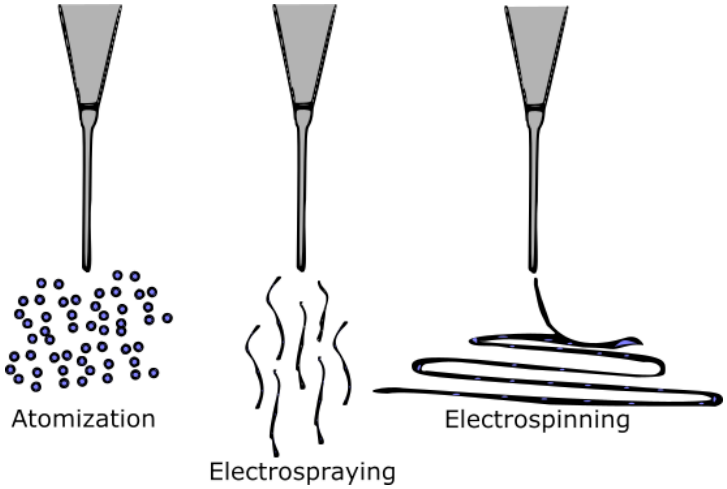


FIGURE 2.1: Electrohydro-dynamic techniques

2.1.1 Stretching forces

Electric Field

Electrospinning (electrostatic fiber spinning) is a fiber fabrication approach that implements an electric field produce fibers by an electrical potential difference between the syringe needle and the collector. With the influence of high electric fields, the fibers are prone to brake into separate layers due to the whipping instabilities as the jet travels to the substrate. The instability can be mitigated by adding additional ring electrodes between the spinneret and the grounded collector. [81]

The typical electrospinning setup applies an electrostatic charge to the polymer fluid at the tip of the needle nozzle, which results in the formation of the Taylor cone [82], from which a single polymer jet is ejected to the grounded collector. From the Taylor cone, the supplied polymer jet (typically a polymer solution) accelerates and reduces in diameter. The fiber finally develops with the complete solvent evaporation. Electrospun fibers are prone to splitting with the increase in acceleration due to high applied voltages, where multiple fibers are yield in a process known as electrospraying [83].

The electrospinning process starts with charging a polymer solution droplet. When a polymer solution is administrated with a syringe pump, solution droplets will fall under the influence of gravity. The solution dripping stops when the electric field is strong enough to break the solution's surface tension, causing the droplet to change shape forming a polymer solution jet [84].

Shin et al. [85] reported that the growth of the whipping instability is one important element within the electrospinning technique. As detailed in Shin's work, weak electric fields produce a single uniformly thinning jet, and strong electric fields the jet becomes unstable after traveling a short distance.

High voltage power supply: DC & AC - Direct current (DC) is typically used in electrospinning with the electrons flowing in one direction. Alternate current (AC) implementations are also studied as the AC creates a change in the direction of the current flow. Kessick et al. [86] demonstrated the implementation of AC power supplies in the production of polymer fibers.

The AC electrospinning setup is similar to that for the DC variant. AC electrospinning apparatus do not require a grounded collector as the current alternates. In AC, the produced fibers are prone to carry an electric charge, while those generated shortly after have an opposite charge. The difference in charges lead the fibers to discharge on each other, creating an aerogel plume of fibers [87]. The optimal AC frequency depends on the materials used and is typically within $50Hz$ and $1kHz$ [88].

The AC technique has been studied for drug loaded related applications. Balogh et al. [89] compared fibers fabricated by DC and AC spinning techniques. Their work reports that AC and DC electrospinning can produce fibers with all three polymers, where the AC process allowed the implementation of faster flow rates than in the DC setup. The DC electrospinning technique generated fibers with a maximum flow rate of 5 ml/h; on the other hand, the AC setup allowed an increase in flow rate up to 40 ml/h.

Centrifugal force

The spinning processes require the implementation of a force to break the polymer source into a polymer jet. Centrifugal spinning intends to produce

fibers by the use of a rotating polymer source. The centrifugal force generated from typical rotatory speeds above $2000rpm$, results in fiber formation. [90, 91].

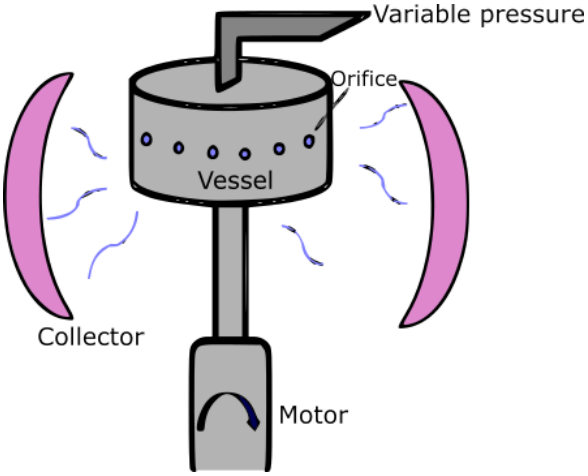


FIGURE 2.2: Typical setup used in pressurized gyration processes

The centrifugal force technique has been applied to polymer solutions and melts. This approach is used in applications were the precise deposition of the fibers is not relevant and production rate is to be maximized [92]. Efforts in centrifugal spinning are focused on drug delivery applications. Zander [93] fabricated polycaprolactone (PCL) fibers using the solution and melt variants of the centrifugal approach. Zander's fibers were produced with rotatory speed between three and 18 thousand revolutions per minute with $10\mu m$ in diameter.

On the other hand, PCL and PVP fibers were generated by Amalorpava et al. [94]. Amalorpava achieved sub micron/size fiber diameters for drug release purposes and bacteria growth inhibition properties. Literature [95] has shown that centrifugal approach has a simple setup that promises a large scale fabrication of fibers.

In some cases the centrifugal force implementations and pressurized gyration can be combined with an electric field. The implementation of two stretching forces (centrifugal and electrical forces), can help solvent evaporation [96]. Centrifugal electrospinning implements the same setup as the standard centrifugal spinning with the addition of a high voltage power supply between the rotating dispensing nozzle and the collector. The combined method has evidence to yield parallel fibers [97–100] at a higher rate [97, 98] than the standard electrospinning approach.

Blowing forces

Nano fibers can be produced with the implementation of pressurized gas with a polymer solution. The setup used for blow spinning is similar to the one used in coaxial electrospinning, where the polymer precursor is dispensed at a controlled rate. Unlike traditional electrospinning, in the solution blow spinning setup the needle nozzle applies pressurized gas to the polymer solution through an outer spinneret [101], see Figure 2.3.

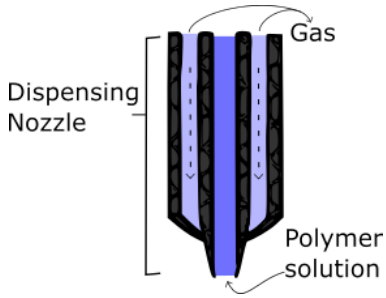


FIGURE 2.3: Dispensing nozzle used for solution blow spinning or melt blowing. [101]

Poly(lactic acid) (PLA) fibers have been produced by solution blow spinning. Oliveira et al. [102] fabricated the fibers from $6wt\%$ PLA solutions with progesterone for live stock reproductive cycle regulation applications. On the other hand, Souza et al. [101] conducted a study to compare the standard electrospinning and the solution blow spinning techniques. Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) were fabricated by both methods. The fibers produced by traditional electrospinning had thicker diameters and the size uniformity was higher in the fibers produced by solution blow spinning. The experimental setup requires a coaxial needle nozzle with a pressurized gas flow along with a potential difference between the dispensing needle and the grounded collector.

Mechanical force

Mechanical drawing comprises the simple technique to produce fibers by stretching the polymer solution with a glass pipette. [103] Nevertheless, the drawing technique is not scalable or with practical applications. [104] Touch-spinning methods have been developed to introduce a scalable technique for the production of nano fibers where the fiber is created by stretching the polymer precursor with a moving collector, as depicted in Figure 2.4. Touch-spinning is another mechanical technique that comprises a moving stage with an embedded glass rod (Figure 2.5). Where a polymer

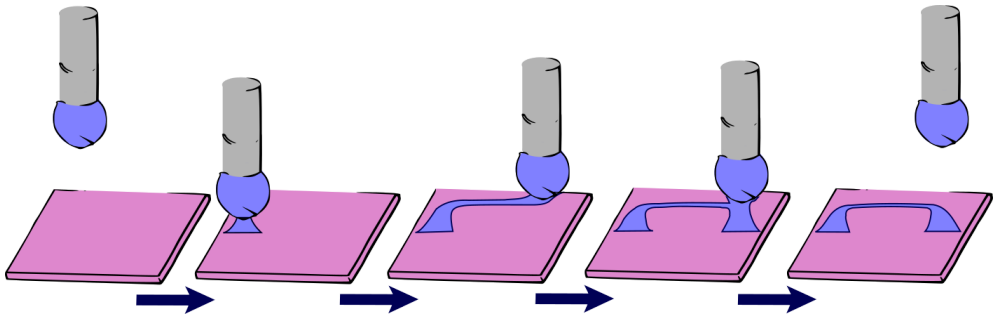


FIGURE 2.4: Typical mechanical fiber drawing process. First the needle makes contact with the substrate to break the polymer drop. Then the needle leaves the substrate and the collector moves to create and deposit the fiber. Once the fiber is written the needle makes contact witht the collector to fix the fiber deposition.

solution is supplied from a syringe needle such that the tip of the glass rod makes contact with the polymer solution as it rotates, creating fibers. The rotation stretches the fiber, causing the fiber to increase in length and decrease in diameter. The increase in length causes the fiber surface are to increase and therefore making the polymer solution solvent to volatilize, ending with a dry fiber within the collector.

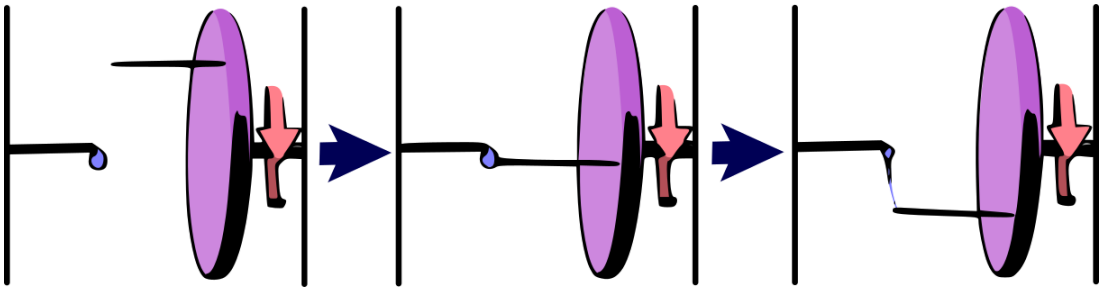


FIGURE 2.5: Touch-spinning technique. First rod is attached to a rotating stage and a polymer solution droplet is administrated through a needle. Then the rotating rod 'touches' the polymer precursor. Finally, as the rod rotates, the polymer solution is stretched and creates a fiber between the rod and the needle.

The touch spinning technique implies that the fiber diameter can be controlled by the moving collector's speed and the polymer solution concentration. The main difference relays on the fact that the touch spinning method implements mechanical control to manipulate and stretch the fibers during the fabrication process, guiding the fiber in the collector enabling better control over fiber alignment. [105]

Microfluidic forces

The microfluidic spinning technique manipulates and controls the polymer solution in networks of micrometer channels. The channel network are

typically embedded in a microfluidic chip, where the solution deposition rate is controlled by active components (pumps and valves) with a computer. Cheng et al. [106] compared and combined the microfluidic spinning and electrospinning techniques. Heterogeneous materials and cell patterning within a single microfiber can be designed by the integration microfluidic channels. Therefore, microfluidic spinning is more suitable for cell encapsulation and tissues generation [106].

On the other hand, Kang et al. [107] managed to fabricate micro fibers by imitating the "silk spinning" process of spiders. Kang's micro fibers properties were modified using a microfluidic system with a programmable flow control (See Figure 2.6). The current microfluidic spinning approach is not scalable to a large fiber production, however it enables the fabrication of high-complex fibers that are not easily achieved by other methods.

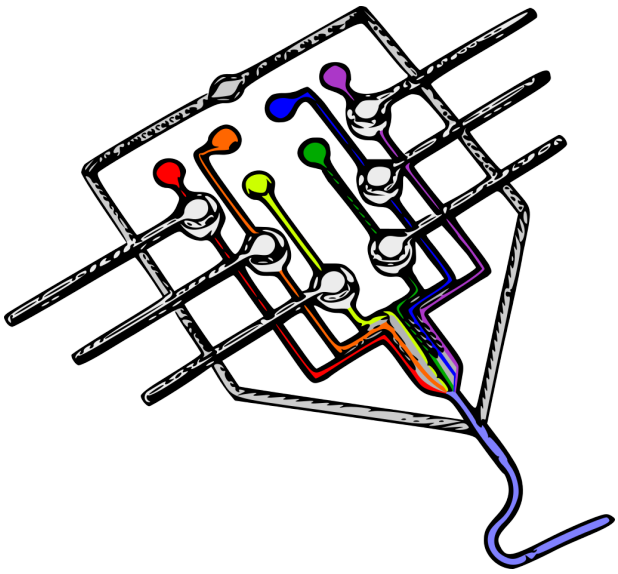


FIGURE 2.6: Microfluidic device used by Kang et al. [107]

Microfluidic techniques offer the possibility to embed several components into a single fiber, where each component can be released at different parts of the fiber.

2.1.2 Dispensing nozzle

Unlike traditional electrospinning, coaxial electrospinning (co-electrospinning) requires de implementation of a dual needle nozzle, where one needle is nested concentrically inside another needle, see Figure 2.7 [108, 109]. The purpose of the co-electrospinning setup is to produce core/shell fibers, unlike mono axial electrospinning that yields

monolithic fibers. Sun et al. [110]. Addressed electrospinning setups, where both the core and shell are comprised by PEO (poly(ethylene oxide)) and for a PEO shell with a poly(dode-cylthiophene) core. Sun et al. state that co-electrospinning has the potential to extend the range of materials that can be used for electrospinning. The shell solution can be modified to make the core solution spunable. It was also discovered that non-spunable solutions can by implemented as shell solutions in conjunction with a spunable core solution. [111]

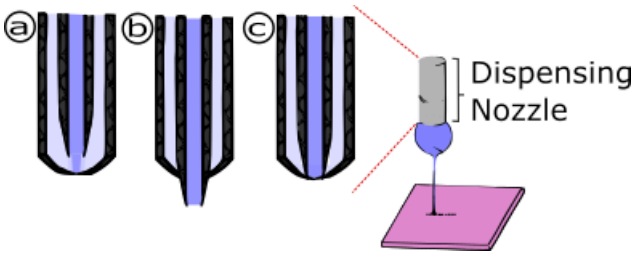


FIGURE 2.7: Needle configurations in coaxial electrospinning. (a) the outer needle encasing the inner; (b) the inner needle protruding from the outer; (c) both needles inline with each other;

Some advantages that co-electrospinning setups can break the polymer drop surface tension, initiating the jet burst from the spinneret nozzle. On the other hand, as the morphology and shape of the fibers depend on the polymer solution properties, the use of a co-axial nozzle allows the amendment of the material properties by producing bubbles, scaffolds and particles. [112, 113]. As in conventional NFES, in co-electrospinning, the needle tip is connected to a high voltage power supply with a grounded collector.

2.1.3 Polymer Reservoir (Polymer Melt & Polymer Solution)

Electrospinning processes can be classified on the polymer reservoir type. As Brown et al. [114] discussed, the polymer melt is equivalent to the polymer solution electrospinning (in place of a polymer solution a melt is used). The use of a polymer melt increases the complexity of the process, because the nozzle syringe and spinneret required to be heated to maintain the polymer in a liquid state. The fibers produced in melt spinning are typically found to have larger diameters than those from the polymer solutions due to the higher viscosity of a polymer melt than its solution. The apparatus used by Brown et al. [114] is depicted in Figure 2.8.

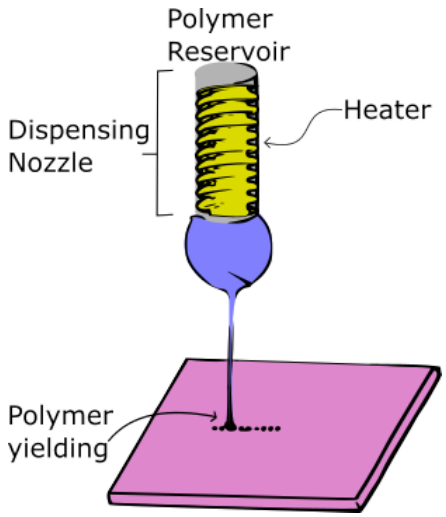


FIGURE 2.8: Typical Melt Electrospinning Setup

Despite the added complexity and thicker diameters, melt electrospinning gets around the need to handle volatile solvents, making the process safer to be performed on larger scales. Furthermore, polymer melt reservoirs get rid of any solvent contamination.

The first report of a melt electrospun drug delivery system came from Nagy et al. [115], who prepared fibers by melt electrospinning of Eudragit EPO with carvedilol. The drug and polymer were melted and mixed to form a homogeneous solid mixture prior to spinning. The melt-spun fibers reached diameters of 5–30 μm, compared to 300–1000 nm diameters produced from solution-spun fibers [115].

Balogh et al.'s work has been built on to blend plasticizes with the polymer Eudragit EPO and carvedilol active ingredient. [116] The plasticizes Triacetin, Tween 80 and Polyethylene Glycol were investigated in order to reduce the melting point of the polymer-drug mixture. The temperature drop is desirable to minimize the occurring drug degradation.

Lian and Meng [117] performed a comparison of poly(ε-caprolactone) (PCL) fibers fabricated by the melt and solution electrospinning techniques. They arrived to the conclusion that melt spinning is preferable when the polymer presents a low solubility. On the other hand the melt fibers were produced in a slower release rate. Gernot et al. [118] demonstrated that submicron-size fibers are possible through melt electrospinning. In their effort, they achieved a precise deposition of PCL fibers with diameters of $817 \pm 165nm$.

In literature, melt electrospinning has less evidence than the solution approach. However, melt electrospinning arises to be as flexible as its solution counterpart in handling multiple polymers, as reported in McCann's work [119]. Currently, the melt electrospinning setup is harder to determine and the lack of research on this technique explains its unexplored potential.

2.1.4 Polymer Solution

In electrospinning, it is typically agreed that the diameter of the fibers increased with higher concentration due to greater viscosity which withstands stretching. In near field electrospinning, similar observations have been reported where concentration increases, fiber diameter increased [120, 121], seeFigure 2.19.

TABLE 2.1: Approximation process to estimate the critical polymer concentration. Several polymer concentrations are tried and the resulting jets are observed until a continuous stream is achieved.

Observation	Concentration Adjustment
Dripping, no stream	Increase
Splitting small droplets	Increase slightly
Steady stream	No concentration adjustment
Splitting large globs	Decrease slightly
Nozzle clogging	Decrease

Polymers

The polymer selection is in function on the intended application. For example, a fast dissolving hydrophilic polymer such as poly(ethylene oxide) (PEO) is used for fast drug delivery systems. Otherwise, slow dissolving polymers such as poly(ε-caprolactone) (PCL) or poly(lactic-co-glycolic acid) (PLGA) are implemented. [122]

The polymer molecular weight along with the polymer concentration and solvent selection have a direct effect on the solution viscosity, conductivity and surface tension, hence the solution behavior in the electrospinning process. The spunable viscosity range varies with the polymer and solvent.

Solutions with low viscosity are prone to insufficient polymer chain entanglements to produce fibers. [122] On the other hand, if the solution is too viscous, then the surface tension cannot easily be overcome by the electric

field. In both cases, the result can be droplets or particles forming rather than fibers as described inTable 2.1.

Solvents

The solvent used must be capable of dissolving the polymer of interest at an appropriate concentration to form fibers, and must posses a suitable volatility. A low-volatility solvent like water may fail to evaporate completely over the distance between the spinneret and the collector. When the fibers form, they will hence contain residual water owing to this incomplete evaporation. The residue solvent will subsequently evaporate from the fibers upon storage, resulting in ribbon-like (flattened) fibers, wrinkles on the fiber surface or fused fibers. On the other hand, a high-volatility solvent may evaporate very quickly, leading to larger fiber diameters (less time for elongation before solidification) and clogging of the spinneret (due to drying of the liquid at the spinneret before jetting, or drying of the Taylor cone during jetting). Solvents commonly used for electrospinning include ethanol, chloroform, trichloroethane and hexafluoroisopropanol [78, 123, 124].

Mixtures of miscible solvents can be used to ensure that sufficient polymer can be dissolved to give a solution of appropriate viscosity and volatility with suitable dielectric constant range to allow fiber formation. However, care must be taken because using a mixture of solvents with very different volatilities can result in porous fiber structures. As reported by Katsogiannis et al. for organic solvent mixtures with dimethyl sulfoxide (DMSO). [125] DMSO evaporates much more slowly than the organic solvents used, which results in its incorporation into the fibers. The DMSO will eventually evaporate, yielding porous fibers.

It is also important to take into account the surface tension of the solution. Solvents with very high surface tensions (e.g. water) can result in instability arising during the spinning process, and a broad range of fiber diameters in the products. If necessary, a surfactant can be added to reduce the surface tension, but this will be incorporated into the fibers produced.

2.2 Properties that Improve Accuracy of Nano-Fiber Deposition

Near-field electrospinning is considered to be an outstanding technique to fabricate polymer fibers with spatial control and it has suffered several modifications to improve the precision and accuracy of the fiber deposition. This paper intents to collect the NFES variants of electrospunable polymer solutions with spatial control in recent research. Table S1 is a collection of the relevant NFES process parameters and achieved fiber morphology.

Some differences have been discovered between LV-NFES and conventional NFES. Low voltage near field electrospinning produces thinner fibers with lower voltages; as shown inFigure 2.16. Moreover, when implementing a moving stage, the fibers are affected by the mechanical stretching. Bisht et al. and Chang et al. [126, 127] reported that thinner diameters are yield with the increase of the x-y stage velocity, and larger diameters by decreasing the stage velocity.

Bisht and Chang's work [126, 127] reports a controlled technique to fabricate polymeric nano fibers in a continuous manner, using a low voltage setup. Their purpose is to find a workaround to the drawbacks of traditional NFES by using a superelastic polymer precursor, which allow continuous patterning without breaking. In low voltage near-field electrospinning (LV NFES), a visco-elastic polymer is used to allow continuous spinning at about $200V$.

Kim et al. [127] experimented with a NFES variation where the fiber deposition is guided by conductive rails, see Figure 2.9. As stated by the authors, the induced electric field is enhanced by the conductive pattern, which allows the fibers to follow the desired deposition path. As the fibers are prone to follow the conductive pattern, additional fibers can be stacked on each other. The stacking process was successfully achieved in high electric field conditions at: $750\mu m$ substrate to collector distance, and a 600 μm needle to rail (offset) distance, see Figure 2.9.

Gupta et al. [128] introduced a new technique to fabricate polymer scaffolds for tissue engineering applications and organ development. As described by Gupta et al. [128], the fiber deposition equipment is comprised by a stainless steel needle with a internal diameter of 750 μm , connected to a high voltage

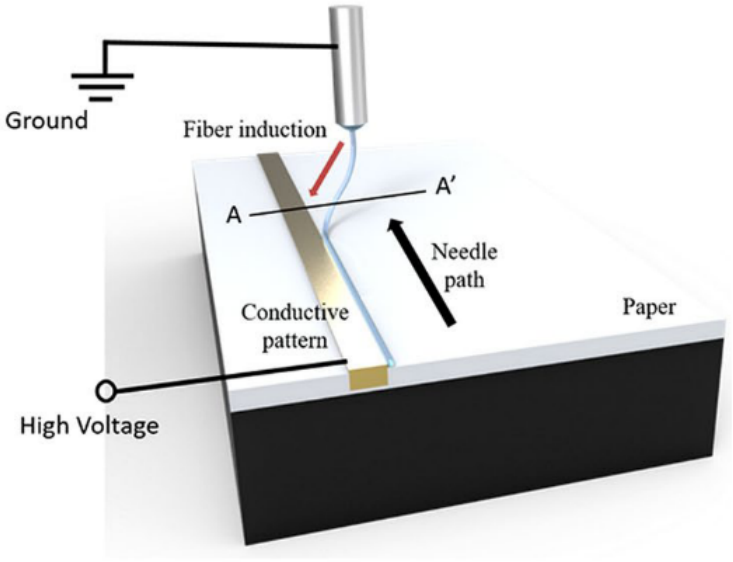


FIGURE 2.9: NFES setup for controlled fiber deposition on pre-patterned conductive electrodes. [127]

power supply of up to 30 kV with a deposition rate of about $\geq 1\mu L min^{-1}$. The setup was embedded to a motorized collector capable of controlled programmable motions, see Figure 2.10. The proposed technique was able to produce fibers of 150μm in diameter with pre-designed patterns.

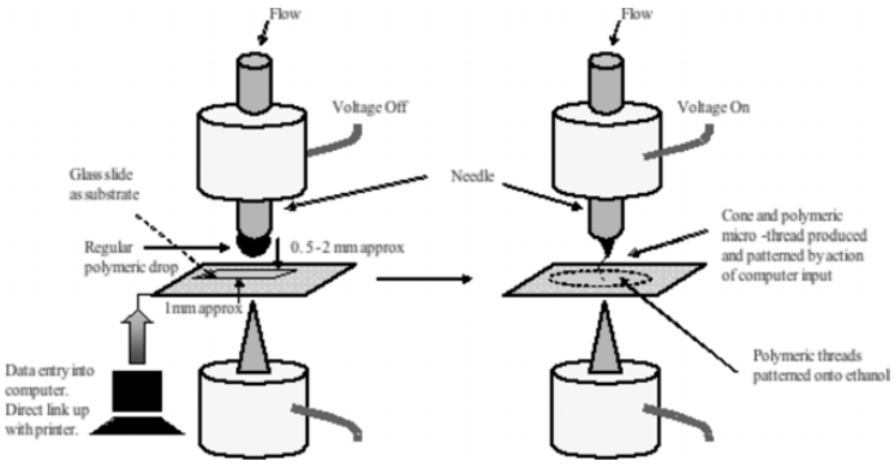


FIGURE 2.10: Schematic illustration of the electrohydrodynamic process. [128]

Wang, et al., Huang, et al., and Chen, et al. [129–131] experimented with several multi-nozzle near-field electrospinning of aligned nano fibers. The multi nozzle NFES apparatus is similar to the one used in conventional NFES with some modifications to the needle nozzle, see Figure 2.11. The authors implemented similar NFES setups where the installed linear array of nozzles is supplied with a constant flow rate of solution.

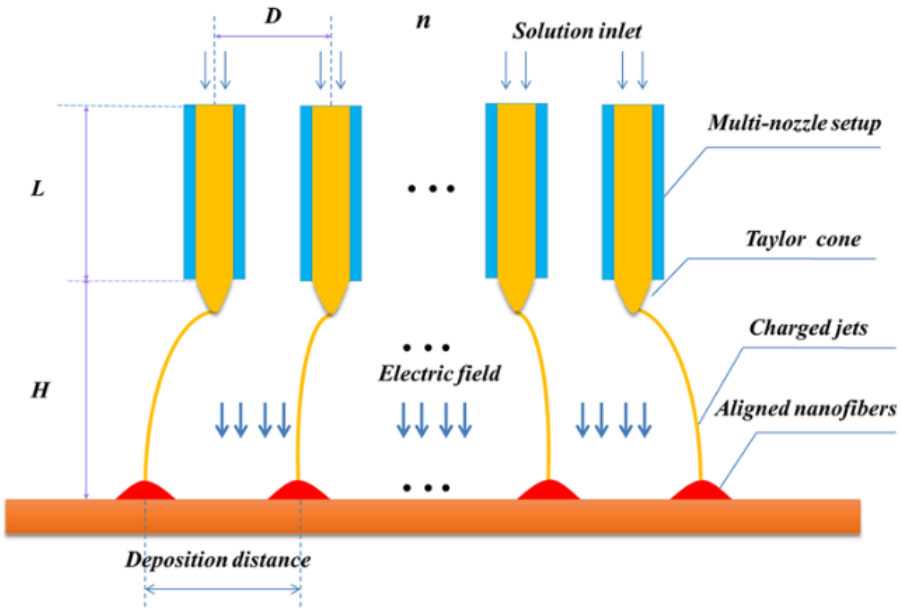


FIGURE 2.11: The geometry distribution of linear array multi-nozzle system [130]

The authors came to the conclusion that the distance between the deposited fibers increase with the increase of the needle-to-collector distance, as the influence of the applied voltage dissipates.

Huang, et al. [132] studied the mechanoelectrospinning (MES) technique for the fabrication of nano fibers. The MES technique tries to improve deposition accuracy by the introduction of a mechanical drawing force. The MES is predominantly controlled by the collector stage velocity, the nozzle-to-collector distance, and the applied voltage. The authors believe that MES can compete as a low-cost, high precision fabrication of electronics and enable the direct writing of structures for nano scale lithography. Figure 2.12 shows the polymer jet behavior when a mechanical force is implemented within the NFES process.

Micro and nano fibers have been written using AC pulse-modulated electrospinning by Bu et al. with polyehtylene terephthalate (PET) as substrate [133]. The AC electrical field influences the electrospinning jet. The alternate current tends to decrease the repulsive electrical force allowing a stable straight jet between the dispensing nozzle and the insulating PET substrate. Bu et al. varied the stage velocity; faster stage velocities enable the deposition of straighter fibers [133].

A mechano-electrospinning technique was presented by Nagle et al. [134].

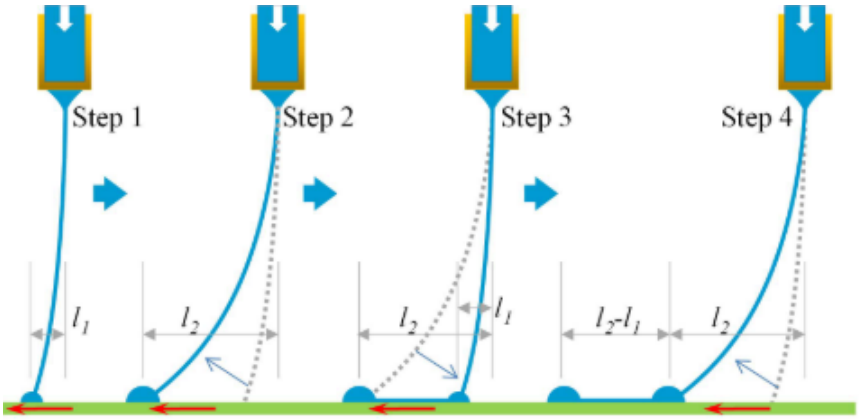


FIGURE 2.12: schematic diagram of leap direct-writing: the ink first accumulates at contact point and then gets stretched by mechanical drawing force. At a critical distance, the ink leaps to the next contact point, and gets stretched again [132]

With the implementation of a mechanical drawing force, a higher resolution nano fibrous pattern can be produced with lower voltages as the Taylor cone becomes more stable. Nagle et al. studied PEO fibers at different nozzle to collector distances. Evidence suggest that better patterning accuracy increases with increasing nozzle to collector distance as the solution is effectively dried [134]. Near field mechano-electrospinning enables the collection of non woven fibers over large areas.

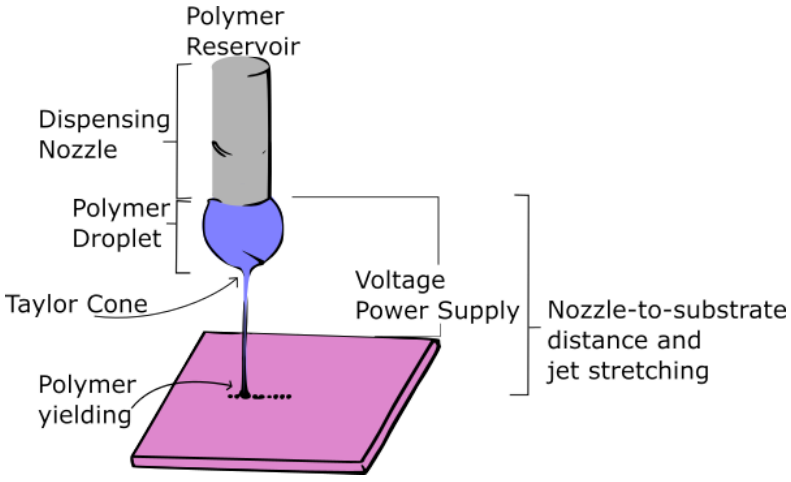


FIGURE 2.13: Near-Field ES Process Parameters

To spin nano fibers at close distances, the initial diameter of the jet is required to be as small as possible since stretching of the thread is limited. Kameoka et al. [135] demonstrated that a small initial spinning radius can be achieved using an atomic force microscope tip with a small polymer solution drop at the tip.

Near-field electrospinning, has exhibited to be capable fabricate nano fibers and nano fiber patterns [136]. Nevertheless, having a small polymer solution drop at the nozzle tip limits the length of the fibers that can be fabricated in a continuous manner. Using a spinneret with a reservoir (e.g. syringe) of solution generally produces fibers with diameter of a few micrometers [128, 137], since it creates a limit to which the nozzle inner diameter can be reduced to allow the solution to flow through. As shown inFigure 2.17, the implementation of thicker needle nozzles translate into an increase of the resulted fiber diameter

Coppola et al. [138] have showed a NFES variant that allows polymer nano fibers to be deposited directly from a polymer drop, averting the issue of nozzle clogging. The fibers are also prone soaking after deposition thus giving the fibers a semi-circular cross-section as depicted in Xue et al.'s [137] work.

2.2.1 Nozzle spinneret

The thinnest nozzles in literature so far are about $50nm$ in diameter, by Chang et al. [120] who used a $100\mu m$ inner diameter needle tip to electrospin poly(ethylene oxide) (PEO). Camillo et al. [139] used a micro-diameter tip Tungsten spinneret in a 26G needle to electrospin co-polymer, poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) with poly(ethylene oxide) (PEO). The nozzle most commonly comprises a simple narrow-bore, blunt-end metal needle. The diameter of the needle can vary, but most commonly researches work with internal diameters below 1 mm . This translates to needles of gauge 18–22. In general, this simple spinneret design can be used to achieve successful spinning. A blunt-end rather than a tapered-end for the needle exit is important as the size distribution of the products increase with an increase in needle tip angle. However, it should be noted that there will be some interactions between the solvent and polymer molecules in the solution and the metal surface of the spinneret. There will exist some attractive forces between the polar groups in the polymer and the electro-positive metal surface, which can act counter to the drawing force of the electric field and can pull the polymer solution back into the spinneret. It has been found that coating the spinneret exterior in a non-conductive and non-stick polymer such as Teflon or epoxy coating can reduce these interactions. [140, 141] As a result, the electrical energy can be more efficiently used to elongate and narrow the polymer jet, and narrower

fibers can be produced. In addition, strong attractive forces between the polymer jet and the metal spinneret can result in fibers becoming attracted to the needle, leading to lower yields and potentially to blocking of the exit orifice.

2.2.2 Applied Voltage

In recent literature, near field electrospinning has been studied to reduce the fiber diameter and to improve the fiber deposition accuracy. Madou et al. [126] and Chang et al. [120] came to the conclusion higher voltages yield thicker micro-fibers with a loss in jet stability. This relationship between the applied voltage and resulting fiber diameter is influenced by other variables such as nozzle-to-substrate distance and solution deposition rate. For instance, if a high voltage is applied at a low deposition rate then electrospraying is achieved, meaning the formation of several non-continuous fibers. The applied voltage shall be sufficient to break the surface tension and initiate the jet, but low enough to avoid multiple jets at the nozzle tip.

Madou et al. [126] achieved the fabrication of thinner fibers with spatial control by reducing the applied voltage to 200-600 V at a nozzle-to-substrate distance of 0.5-1 mm. The low voltage setting does not create enough charge to break the polymer solution surface tension to initiate the electrospinning process.

Madou et al. [126] and Chang et al. [120] initiated the electrospun fibers by mechanically pull the polymer solution at the nozzle tip using a micro-probe tip. Chang and coworkers reduced the applied voltage from 1.5 kV to 600 V with a nozzle-to-substrate distance of 500 μm to yield a fiber diameter between 3 μm and 50 nm . With an applied voltage of 200 V and a nozzle-to-substrate distance of 1 mm.

In near-field electrospinning, the applied voltage has an impact on the produced fiber morphology. For instance, a voltage higher or lower to the optimum voltage will translate into an increase in fiber diameter. Song et al. [142] demonstrated that a decrease in voltage from 400 to 500 V can reduce the fiber diameter from 160 to about 60 $nm$with a nozzle-to-substrate distance of 20 μm. A workaround to break the polymer solution surface tension is to initialize the NFES process with a higher voltage and then lower the voltage

once the jet is created. Huang et al. [132] implemented the previous and yield ordered fibers with a distance between adjacent fibers of 50 μm.

2.2.3 Nozzle-to-substrate distance

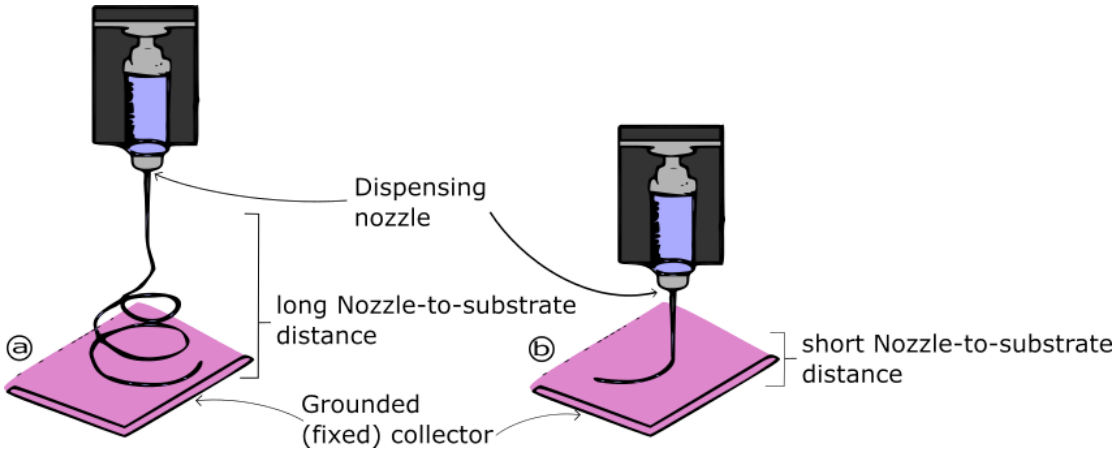


FIGURE 2.14: a) Typical Far-field Electrospinning (FFES) Setup. b) Typical Near-field Electrospinning (NFES) Setup.

Figure 2.14.a, depicts the typical setup for the conventional far-field electrospinning (FFES). As stated in previous sections, the precursor polymer droplet becomes charged with the employment of an electric field between the polymer solution and the collector [143]. When the polymer solution surface tension is overcome by the electric field potential difference a jet is formed, starting the electrospinning process. The electrospinning process can be break down into two steps: i) first the jet travels in a straight line, and ii) the jet begins to curl due to bending and whipping instabilities [86, 144]. The fiber spatial control in far-field electrospinning is limited due to the instabilities, inhibiting the precise deposition of fibers.

In the intent to achieve controlled fiber deposition, Sun et al. [136] reported an electrospinning variation known as near-field electrospinning (NFES),Figure 2.14.b, describes the near-field electrospinning setup, where the distance between the dispensing nozzle and the collector is reduced to write fibers while the jet travels in a straight line. Moreover, some mechanical influence is required to deposit fibers precisely. The mechanical force is introduced by moving collector. If the polymer solution jet speed is faster than the speed of the moving collector, the written fiber will curl; on the other hand, if the collector moves faster than the polymer jet, the fiber will gradually diminish [137, 145]. Currently, due to the lack of theoretical models, the near-field electrospinning process parameters (such

as the collector speed) are typically tuned by experience and experimentation only.

The main difference between NFES and FFES is the distance between the needle and the collector which is higher in FFES (about 10 cm) compared to NFES which ranges in the mm scale. The short distance allow the production of well aligned fibers within particular designs. In NFES, the fiber morphology can be altered by the control of the distance between the nozzle and the substrate (collector). With the decrease of the nozzle-to-substrate distance, the electric field strength increases; however it can cause incomplete solvent volatilisation and possible short circuits between the collector and the nozzle tip.

An optimal nozzle-to-substrate distance shall be defined to ensure the fabrication of dry continuous fibers. If the solvent is not well evaporated, the produced fibers are prone to defects; on the other hand if solidification happens too fast, the solids can block the spinneret which can prevent a continuous fiber yield. Furthermore, the polymer jet will discharge itself as soon as possible, therefore long distances can result in low yields.

2.2.4 Substrate

Due to the close distance between the grounded substrate and the charged spinneret in NFES, the set up is prone to electrical shorts. In NFES, when a short circuit takes place, the electrospinning process is interrupted resulting in the fabrication of discontinuous fibers. Two workarounds to avoid electrical shorts is to lower the applied voltage and to use less conductive substrates [146, 147].

Liu et al. [146] discovered that the fiber alignment is improved by using a glass-cooper foil substrate, however the well aligned fibers are spoiled after prolonged depositions due to residual charges. Additionally, the effect of residual charges is amplified with the used collector substrate contains a conductive layer and a non-conductive layer [146].

On the other hand, Choi et al. [147] implemented a hydrophilic substrate to deposit the fibers with plasma treatment to increase the conductivity of selected areas. NFES was carried put with precise deposition as the fibers were placed as per the desired design within the hydrophilic substrate.

2.3 Discussion & NFES Challenges

Helix electrodynamic printing (HE-printing) was presented by Duan et al. [148] with the intention of depositing aligned fibers. The authors fabricated a stretchable piezoelectric device using micro and nano fibers to demonstrate the possible applications of HE-printinh for electronics manufacturing. Duan et al. concluded that the fiber morphology is mainly driven by: the stage velocity, the applied voltage, and the nozzle-to-collector distance.

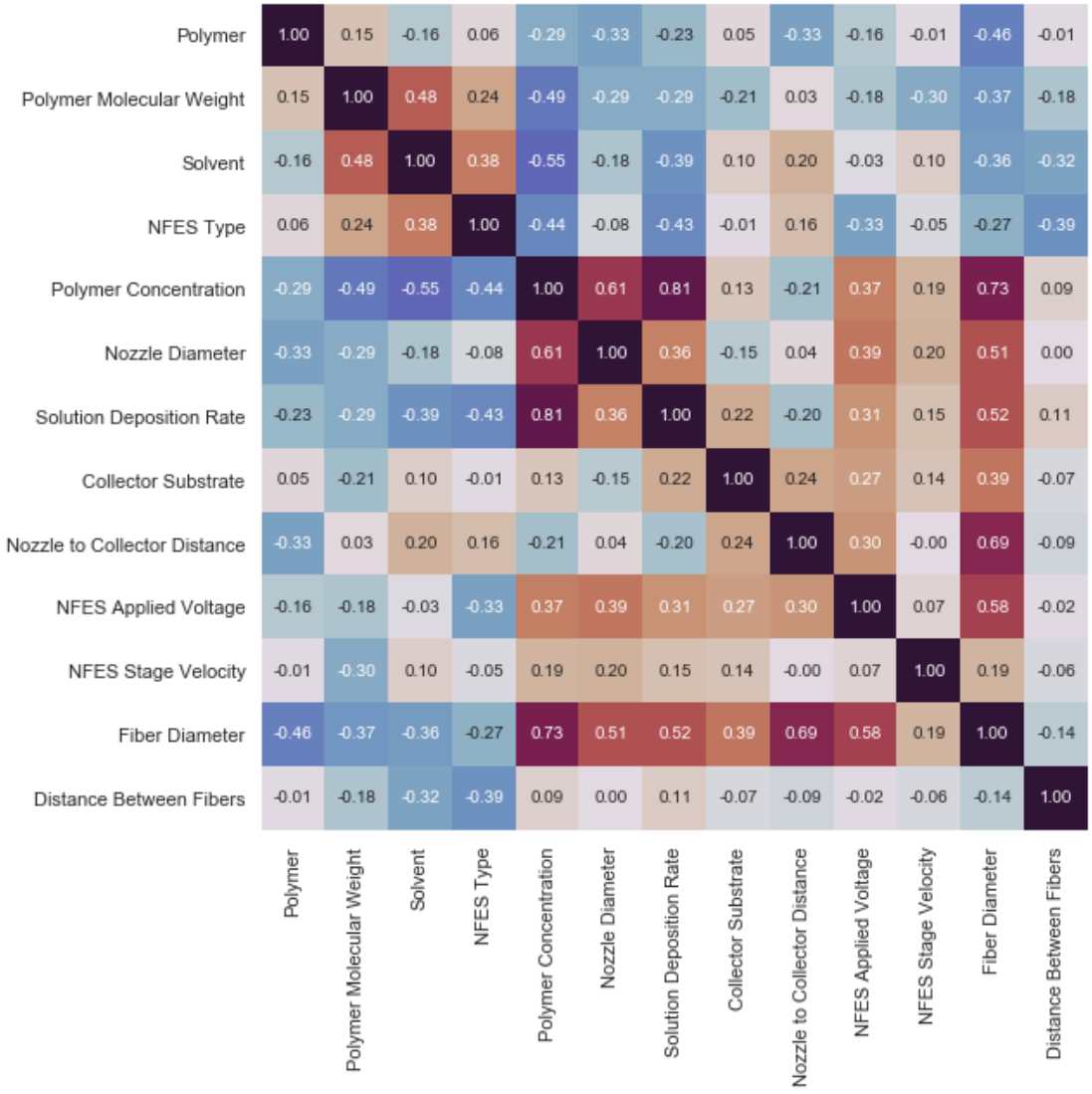
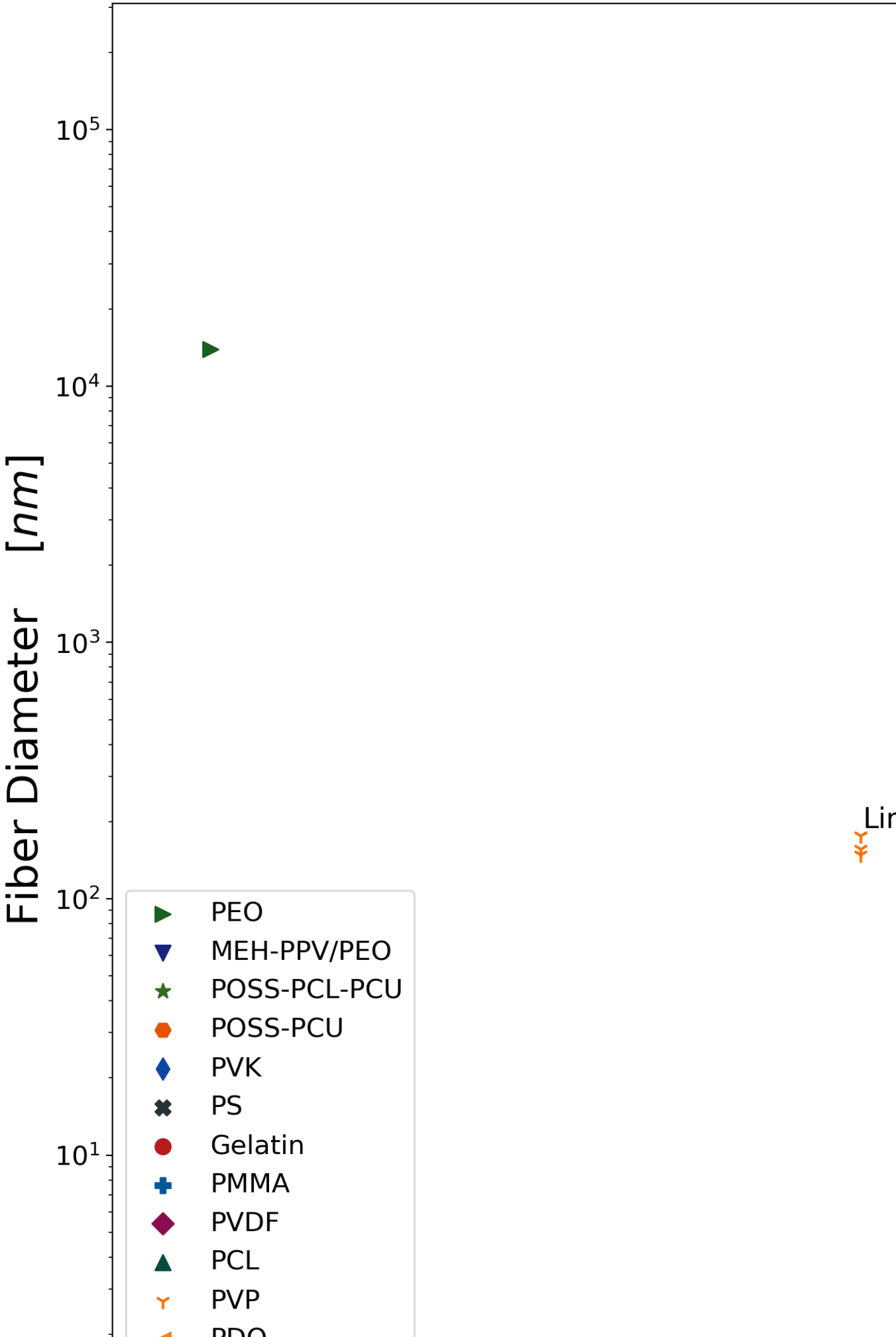
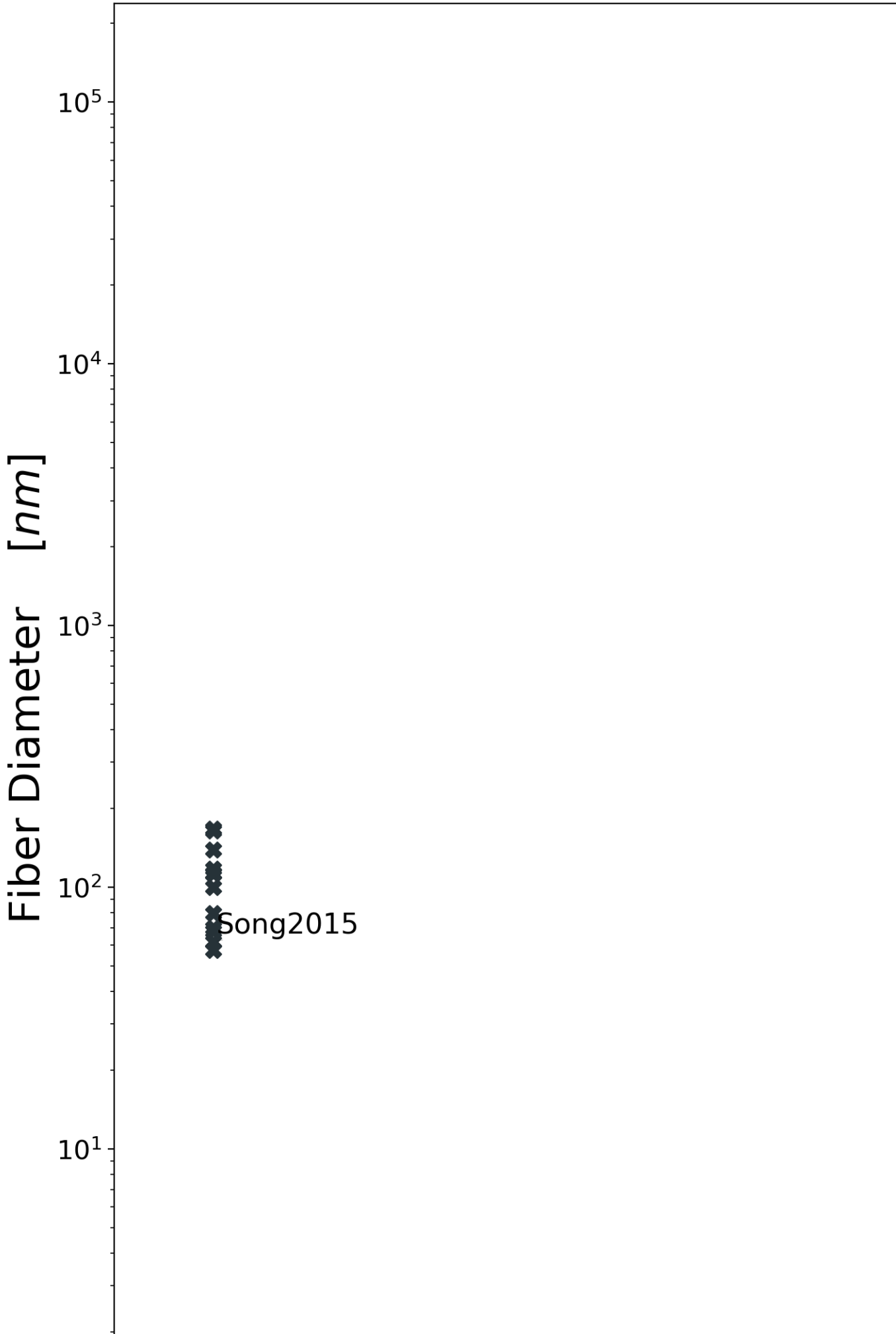
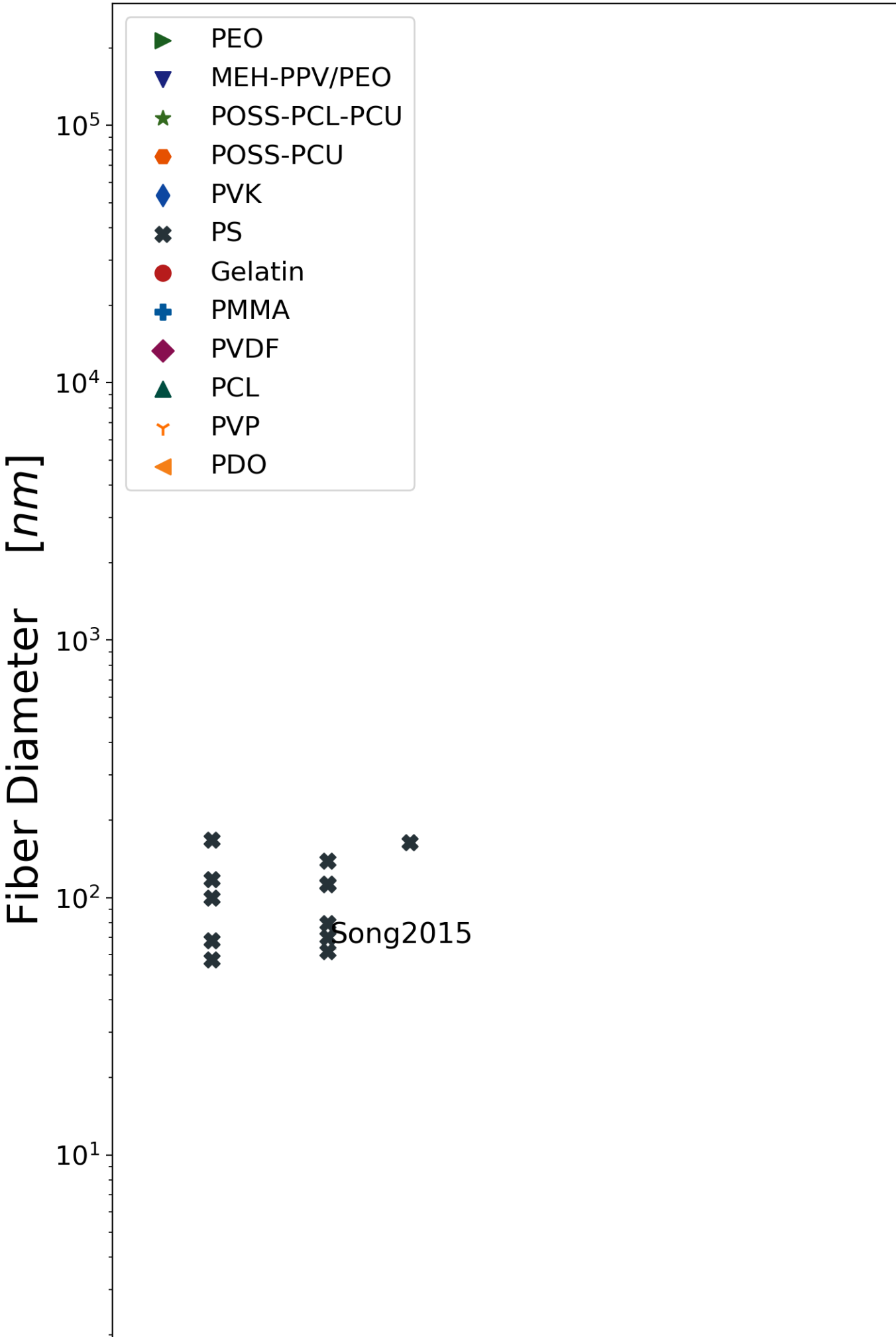


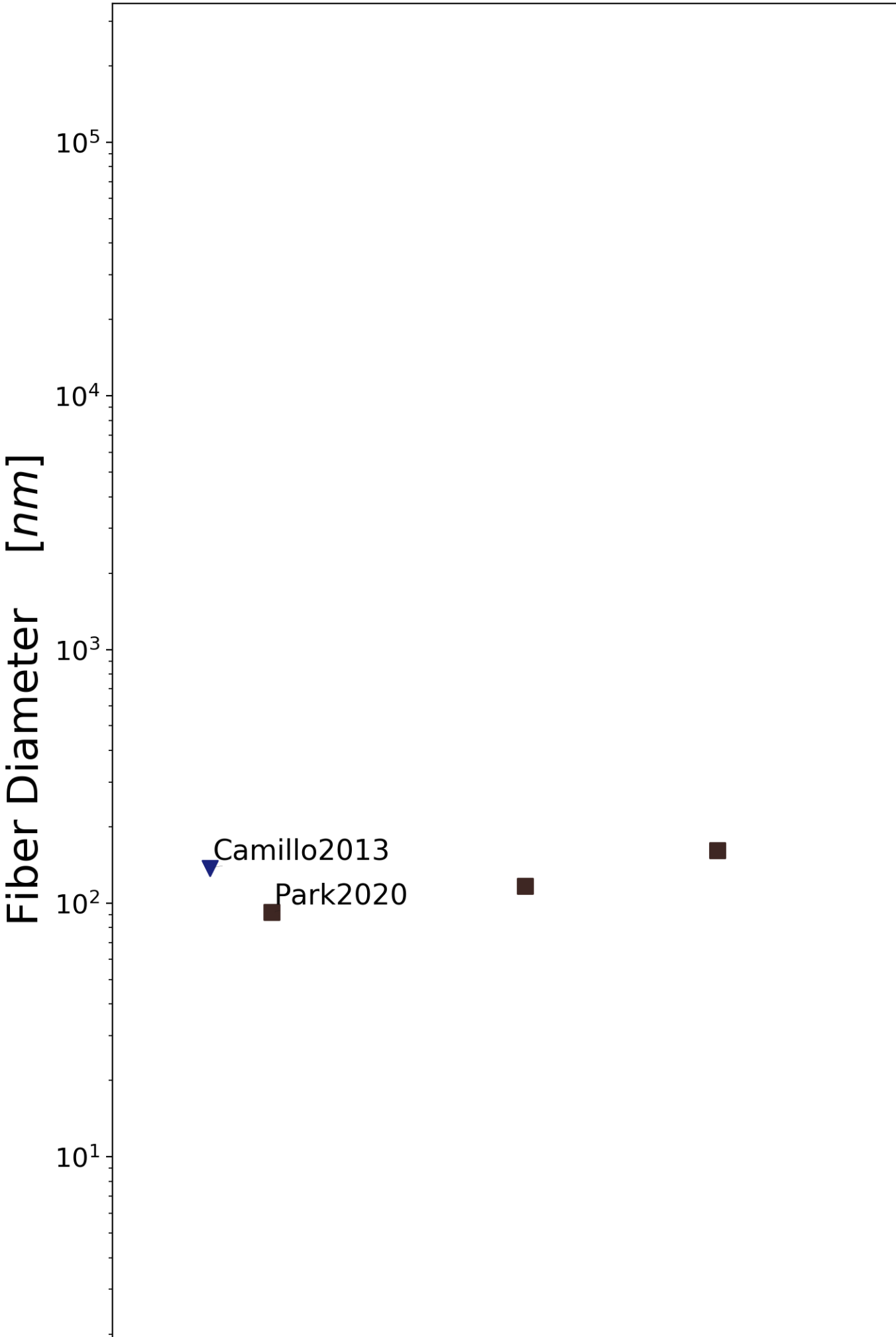
FIGURE 2.15:

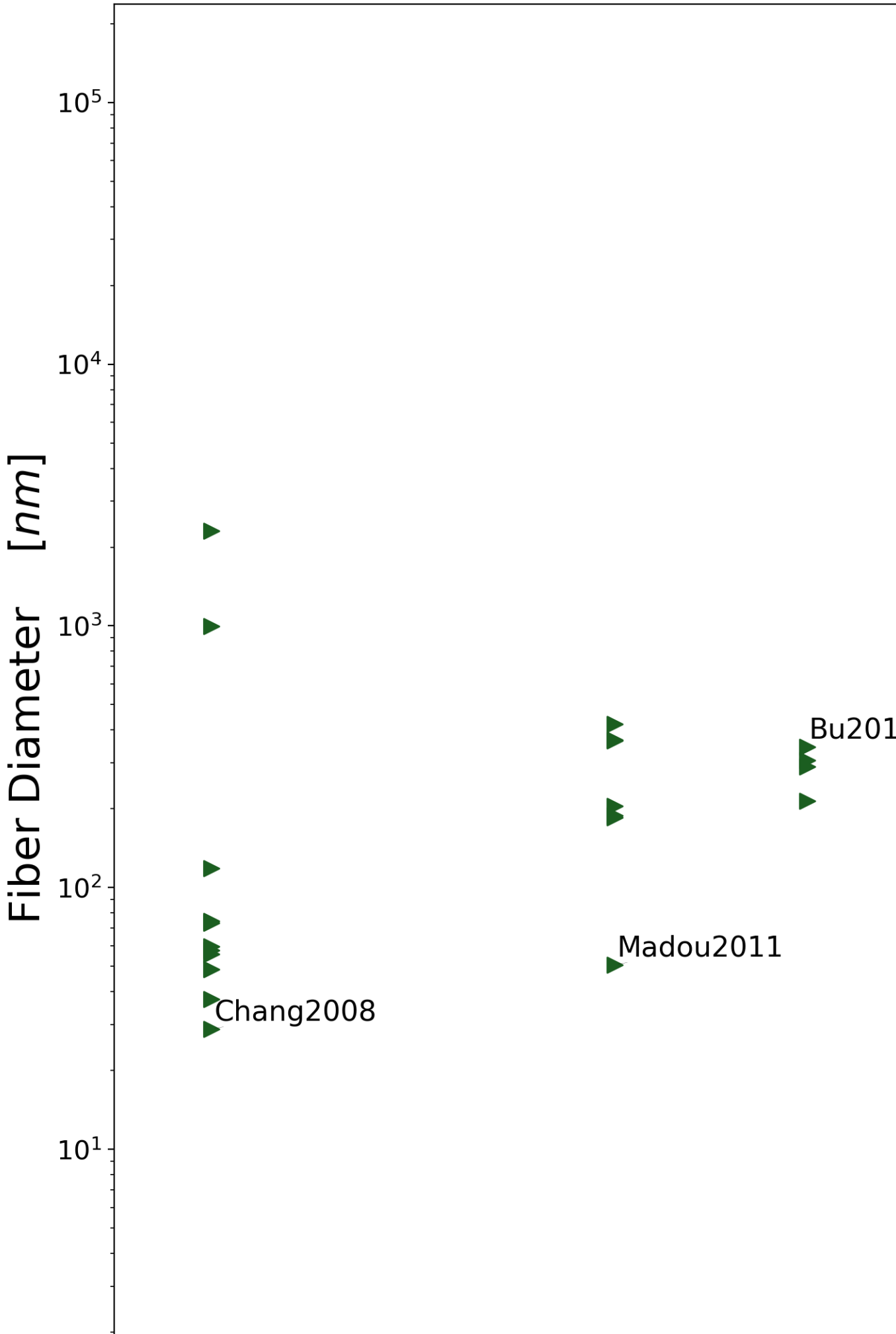
Electrohydrodynamic (EHD) jet printing is a direct-writing technique which ejects ink through a fine nozzle using an electric field, which has the advantages of high-resolution, rapid printing speed and a wide range of ink selectivity. The effect of parameters such as ink concentration, working


Fiber Diameter [nm]
10^5
10^4
10^3
10^2
10^1
Lir
PEO
MEH-PPV/PEO
POSS-PCL-PCU
POSS-PCU
PVK
PS
Gelatin
PMMA
PVDF
PCL
PVP
PDO


Fiber Diameter [nm]
10^5
10^4
10^3
10^2
10^1
Song2015


PEO
MEH-PPV/PEO
POSS-PCL-PCU
POSS-PCU
PVK
PS
Gelatin
PMMA
PVDF
PCL
PVP
PDO
10^5
10^4
10^3
10^2
10^1
Fiber Diameter [nm]
Song2015


Fiber Diameter [nm]
10^5
10^4
10^3
10^2
10^1
Camillo2013
Park2020


Fiber Diameter [nm]
10^5
10^4
10^3
10^2
10^1
Chang2008
Madou2011
Bu201

distance, applied voltage, and stage speed on the diameter of the printed nano fibers was investigated.

Near-field electrospinning (NFES) is widely recognized as a versatile nano fabrication method, one suitable for applications in tissue engineering. Rapid developments in this field have given rise to layered nano fibrous scaffolds. However, this electrostatic fabrication process is limited by the electric field inhibitory effects of polymer deposition. This leads to a major challenge: how to surpass this limitation on planar/layered constructs. While the current focus in this area largely lies with the investigation of new materials, techniques and increasing precision of NFES systems and patterning, exploration of complex collector substrates is often restricted by (i) available technology and (ii) access to complex electrode manufacturing tools.

Although electrospinning (ES) allows the production of unsurpassed nano scale polymer fibers, the major drawbacks are the nozzle-clogging and single-jet spinneret, respectively. This is a real limitation in terms of usable polymers and for patterning active organics. Nowadays the micro-engineering of smart materials could represent a new route for many fields of technology ranging from the production of electronic and photonic devices [1−3] to regenerative medicine and tissue engineering. [4−7] An enormous technological interest is related to the possibility of patterning fibers directly in well-ordered patterns avoiding the deposition of nonwoven sub micrometer mats often occurring in ES. [8,9] In the past decade several attempts have been made using field- induced [10−13] and near-field ES, [14,15] but only very recently, with the introduction of mechano ES, [16] has the production of well- ordered fiber patterns been achieved. Nevertheless, some drawbacks related to the complexity of the setup, the operating temperature, and the selection of usable materials for problems related to nozzle clogging still persist. Moreover, high temperature can cause deterioration of the optical and electronic properties of active organic materials eventually embedded in the functionalize [d fibers. On the other side, interfering effects due to closeness of multiple electrified nozzles ban working with multiple spinnerets.

Chapter 3

Selection of Compatible Polymer-Solvent Combinations for Near-Field Electrospinning and Pyrolysis

3.1 Selection of Candidate Spunable Polymer Solutions

3.1.1 Rheology of candidate polymer solutions

3.2 Effect of aromatic groups in oxygen-free polymers in NFES and Pyrolysis

3.3 *conclude with a collection of potential spunable polymer solutions*

Chapter 4

Fabrication and Characterization of Polymeric Fibers through Near-Field Electrospinning, and Forward-thinking on Photopolymerization and Pyrolysis

4.1

4.2

4.3 Fabrication and Characterization of Legacy SU-8 carbon fibers

4.4 Comparison of the Obtained Polymer Fibres Against SU8-based Carbon Fibres and Potential Applications

4.5 ***conclude with fibre morphology before and after pyrolysis. determine best pyrolysis process***

Chapter 5

Concluding Remarks

5.1

5.2 Future work

Acronyms and Abbreviations

CEM	**C**ampus **E**stado de **M**éxico
CNWs	**C**arbon **N**ano-**w**ire**s**
DC	**D**irect **C**urrent
EMS	**E**lectro**m**echanical **S**pinning
FFES	**F**ar **F**ield de **E**lectro**s**pinning
ITESM	**I**nstituto **T**ecnonólogico y de **E**studios **S**uperiores de **M**onterrey
MA	**Ma**ssachusetts
MEMS	**M**icro**e**lectro**m**echanical **S**ystems
MNT	**M**aestría en **N**ano**t**ecnología *(Master of Science in Nanotechnology)*
MTY	**M**on**t**erre**y** *or* Campus **M**on**t**erre**y**
NFEMS	**N**ear-**F**ield **E**lectro**m**echanical **S**pinning
NFES	**N**ear **F**ield de **E**lectro**s**pinning
USA	**U**nited **S**tates of **A**merica
UV	**U**ltra**v**iolet

Variables and Symbols

Symbol	Name	Unit
ω	angular frequency	rad

Bibliography

[1] R. L. McCreery, "Advanced Carbon Electrode Materials for Molecular Electrochemistry", *Chemical Reviews*, vol. 108, no. 7, pp. 2646–2687, Jul. 2008, ISSN: 0009-2665. DOI: 10.1021/cr068076m. [Online]. Available: https://pubs.acs.org/doi/10.1021/cr068076m.

[2] A. K. Geim, "Random Walk to Graphene (Nobel Lecture)", *Angewandte Chemie International Edition*, vol. 50, no. 31, pp. 6966–6985, Jul. 2011, ISSN: 14337851. DOI: 10.1002/anie.201101174. [Online]. Available: http://doi.wiley.com/10.1002/anie.201101174.

[3] Y. Zhu, S. Murali, W. Cai, X. Li, J. W. Suk, J. R. Potts, and R. S. Ruoff, "Graphene and Graphene Oxide: Synthesis, Properties, and Applications", *Advanced Materials*, vol. 22, no. 35, pp. 3906–3924, Sep. 2010, ISSN: 09359648. DOI: 10.1002/adma.201001068. [Online]. Available: http://doi.wiley.com/10.1002/adma.201001068.

[4] M. Katsnelson and A. Geim, "Electron scattering on microscopic corrugations in graphene", *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences*, vol. 366, no. 1863, pp. 195–204, Jan. 2008, ISSN: 1364-503X. DOI: 10.1098/rsta.2007.2157. [Online]. Available: https://royalsocietypublishing.org/doi/10.1098/rsta.2007.2157.

[5] D. Li and R. B. Kaner, "MATERIALS SCIENCE: Graphene-Based Materials", *Science*, vol. 320, no. 5880, pp. 1170–1171, May 2008, ISSN: 0036-8075. DOI: 10.1126/science.1158180. [Online]. Available: https://www.sciencemag.org/lookup/doi/10.1126/science.1158180.

[6] A. K. Geim and K. S. Novoselov, "The rise of graphene", *Nature Materials*, vol. 6, no. 3, pp. 183–191, Mar. 2007, ISSN: 1476-1122. DOI: 10.1038/nmat1849. [Online]. Available: http://www.nature.com/articles/nmat1849.

[7] A. K. Geim, "Graphene: Status and Prospects", *Science*, vol. 324, no. 5934, pp. 1530–1534, Jun. 2009, ISSN: 0036-8075. DOI: 10.1126/science.1158877. [Online]. Available: https://www.sciencemag.org/lookup/doi/10.1126/science.1158877.

[8] M. Siddiqui, S. Nizamuddin, H. A. Baloch, N. Mubarak, M. Al-Ali, S. A. Mazari, A. Bhutto, R. Abro, M. Srinivasan, and G. Griffin, "Fabrication of advance magnetic carbon nano-materials and their potential applications: A review", *Journal of Environmental Chemical Engineering*, vol. 7, no. 1, p. 102 812, Feb. 2019, ISSN: 2213-3437. DOI: 10.1016/J.JECE.2018.102812. [Online].

Available: https://0-www-sciencedirect-com.millenium.itesm.mx/science/article/pii/S2213343718307358%20https://linkinghub.elsevier.com/retrieve/pii/S2213343718307358.

[9] B. Cárdenas, "Advanced Manufacturing Techniques for the Fabrication and Surface Modification of Carbon Nanowires", p. 160, 2017.

[10] M. J. Madou, D. Dunn-Rankin, L. Kulinsky, A. Mirsepassi, G. S. Bisht, S. Oh, and G. Canton, "Controlled Continuous Patterning of Polymeric Nanofibers on Three-Dimensional Substrates Using Low-Voltage Near-Field Electrospinning", *Nano Letters*, vol. 11, no. 4, pp. 1831–1837, 2011, ISSN: 1530-6984. DOI: 10.1021/nl2006164.

[11] D. R. Flores, "Role of rheological properties in near field electrospun fibers morphology", p. 130, 2017.

[12] G. A. Posthuma-Trumpie, J. H. Wichers, M. Koets, L. B. J. M. Berendsen, and A. van Amerongen, "Amorphous carbon nanoparticles: a versatile label for rapid diagnostic (immuno)assays", *Analytical and Bioanalytical Chemistry*, vol. 402, no. 2, pp. 593–600, Jan. 2012, ISSN: 1618-2642. DOI: 10.1007/s00216-011-5340-5. [Online]. Available: http://link.springer.com/10.1007/s00216-011-5340-5.

[13] L. Zhang, L. Chen, T. Wells, and M. El-Gomati, "Bamboo and Herringbone Shaped Carbon Nanotubes and Carbon Nanofibres Synthesized in Direct Current-Plasma Enhanced Chemical Vapour Deposition", *Journal of Nanoscience and Nanotechnology*, vol. 9, no. 7, pp. 4502–4506, Jul. 2009, ISSN: 15334880. DOI: 10.1166/jnn.2009.M84. [Online]. Available: http://openurl.ingenta.com/content/xref?genre=article%7B%5C&%7Dissn=1533-4880%7B%5C&%7Dvolume=9%7B%5C&%7Dissue=7%7B%5C&%7Dspage=4502.

[14] M. F. L. De Volder, R. Vansweevelt, P. Wagner, D. Reynaerts, C. Van Hoof, and A. J. Hart, "Hierarchical Carbon Nanowire Microarchitectures Made by Plasma-Assisted Pyrolysis of Photoresist", *ACS Nano*, vol. 5, no. 8, pp. 6593–6600, Aug. 2011, ISSN: 1936-0851. DOI: 10.1021/nn201976d. [Online]. Available: https://pubs.acs.org/doi/10.1021/nn201976d.

[15] X. Cao, Q. He, W. Shi, B. Li, Z. Zeng, Y. Shi, Q. Yan, and H. Zhang, "Graphene Oxide as a Carbon Source for Controlled Growth of Carbon Nanowires", *Small*, vol. 7, no. 9, pp. 1199–1202, May 2011, ISSN: 16136810. DOI: 10.1002/smll.201100071. [Online]. Available: http://doi.wiley.com/10.1002/smll.201100071.

[16] H. B. Heersche, P. Jarillo-Herrero, J. B. Oostinga, L. M. K. Vandersypen, and A. F. Morpurgo, "Bipolar supercurrent in graphene", *Nature*, vol. 446, no. 7131, pp. 56–59, Mar. 2007, ISSN: 0028-0836. DOI: 10.1038/nature05555. [Online]. Available: http://www.nature.com/articles/nature05555.

[17] R. Heimann, S. Evsvukov, and Y. Koga, "Carbon allotropes: a suggested classification scheme based on valence orbital hybridization", *Carbon*, vol. 35, no. 10-11, pp. 1654–1658, 1997, ISSN: 00086223. DOI: 10.1016/S0008-

6223(97)82794-7. [Online]. Available: https://linkinghub.elsevier.com/retrieve/pii/S0008622397827947.

[18] E. A. Belenkov, "Classification of carbon structures", in *Carbon Nanotubes and Graphene*, Chelyabinsk, Russia: Chelyabinsk State University, 2003, p. 5.

[19] M. Fedel, "Blood compatibility of diamond-like carbon (DLC) coatings", in *Diamond-Based Materials for Biomedical Applications*, Dlc, Elsevier, 2013, pp. 71–102, ISBN: 9780857093400. DOI: 10.1533/9780857093516.1.71. [Online]. Available: http://dx.doi.org/10.1533/9780857093516.1.71%20https://linkinghub.elsevier.com/retrieve/pii/B9780857093400500047.

[20] M. Razeghi, *Fundamentals of Solid State Engineering*. Cham: Springer International Publishing, 2019, pp. 1–689, ISBN: 978-3-319-75707-0. DOI: 10.1007/978-3-319-75708-7. [Online]. Available: http://link.springer.com/10.1007/978-3-319-75708-7.

[21] K. Alstrup Jensen, J. Bogelund, P. Jackson, N. Raun Jacobsen, R. Birkedal, P. Axel Clausen, A. Thoustrup Saber, H. Wallin, and U. Birgitte Vogel, *Carbon nanotubes - Types, products, market, and provisional assessment of the associated risks to man and the environment*, 1805. The Danish Environmental Protection Agency, 2015, pp. 49–82, ISBN: 978-87-93352-98-8.

[22] Y. A. Kim, T. Hayashi, M. Endo, and M. S. Dresselhaus, "Carbon Nanofibers", in *Springer Handbook of Nanomaterials*, R. Vajtai, Ed., Berlin, Heidelberg: Springer Berlin Heidelberg, 2013, pp. 233–262, ISBN: 978-3-642-20594-1. DOI: 10.1007/978-3-642-20595-8_7. [Online]. Available: http://link.springer.com/10.1007/978-3-642-20595-8%20http://link.springer.com/10.1007/978-3-642-20595-8%7B%5C_%7D7.

[23] H. Marsh, *Introduction to Carbon Science*, 1. Elsevier, Apr. 1989, vol. 46, p. 43, ISBN: 9780408038379. DOI: 10.1016/C2013-0-04111-4. [Online]. Available: https://linkinghub.elsevier.com/retrieve/pii/C20130041114.

[24] P. Hugh, *Handbook of Carbon, Graphite, Diamonds and Fullerenes*. Elsevier, 1994, p. 419, ISBN: 9780815513391.

[25] K. S. Novoselov, "Electric Field Effect in Atomically Thin Carbon Films", *Science*, vol. 306, no. 5696, pp. 666–669, Oct. 2004, ISSN: 0036-8075. DOI: 10.1126/science.1102896. [Online]. Available: https://www.sciencemag.org/lookup/doi/10.1126/science.1102896.

[26] F. Schedin, A. K. Geim, S. V. Morozov, E. W. Hill, P. Blake, M. I. Katsnelson, and K. S. Novoselov, "Detection of individual gas molecules adsorbed on graphene", *Nature Materials*, vol. 6, no. 9, pp. 652–655, Sep. 2007, ISSN: 1476-1122. DOI: 10.1038/nmat1967. [Online]. Available: http://www.nature.com/articles/nmat1967.

[27] Y. Ohno, K. Maehashi, Y. Yamashiro, and K. Matsumoto, "Electrolyte-Gated Graphene Field-Effect Transistors for Detecting pH and Protein Adsorption", *Nano Letters*, vol. 9, no. 9, pp. 3318–3322, Sep. 2009, ISSN: 1530-6984. DOI: 10.

1021/nl901596m. [Online]. Available: https://pubs.acs.org/doi/10.1021/nl901596m.

[28] V. K. Khanna, *Nanosensors*, 4. CRC Press, Apr. 2016, vol. 53, pp. 391–392, ISBN: 9780429093951. DOI: 10.1201/b11289. [Online]. Available: http://www.tandfonline.com/doi/abs/10.1080/00107514.2012.689351%20https://www.taylorfrancis.com/books/9781439827130.

[29] J. Guo, T. Ning, Y. Han, Y. Sheng, C. Li, X. Zhao, Z. Lu, B. Man, Y. Jiao, and S. Jiang, "Preparation, characterization, and nonlinear optical properties of hybridized graphene @ gold nanorods nanocomposites", *Applied Surface Science*, vol. 433, pp. 45–50, Mar. 2018, ISSN: 01694332. DOI: 10.1016/j.apsusc.2017.10.042. [Online]. Available: http://dx.doi.org/10.1016/j.apsusc.2017.10.042%20https://linkinghub.elsevier.com/retrieve/pii/S0169433217329653.

[30] S. Kundu, U. Mogera, S. J. George, and G. U. Kulkarni, "A planar supercapacitor made of supramolecular nanofibre based solid electrolyte exhibiting 8 V window", *Nano Energy*, vol. 61, no. April, pp. 259–266, Jul. 2019, ISSN: 22112855. DOI: 10.1016/j.nanoen.2019.04.054. [Online]. Available: https://doi.org/10.1016/j.nanoen.2019.04.054%20https://linkinghub.elsevier.com/retrieve/pii/S2211285519303556.

[31] Y. Bencheikh, M. Harnois, R. Jijie, A. Addad, P. Roussel, S. Szunerits, T. Hadjersi, S. El Hak Abaidia, and R. Boukherroub, "High performance silicon nanowires/ruthenium nanoparticles micro-supercapacitors", *Electrochimica Acta*, vol. 311, pp. 150–159, Jul. 2019, ISSN: 00134686. DOI: 10.1016/j.electacta.2019.04.083. [Online]. Available: https://linkinghub.elsevier.com/retrieve/pii/S0013468619307698.

[32] M. Dresselhaus, Y.-M. Lin, O. Rabin, M. Black, J. Kong, and G. Dresselhaus, "Nanowires", in *Springer Handbook of Nanotechnology*, Berlin, Heidelberg: Springer Berlin Heidelberg, 2007, pp. 113–160. DOI: 10.1007/978-3-540-29857-1_4. [Online]. Available: http://link.springer.com/10.1007/978-3-540-29857-1%7B%5C_%7D4.

[33] E. D. Weil, "Carbon fibers, 2nd edition by J. B. Donnet and R. C. Bansal, Marcel Dekker, New York (1990), ISBN 470 pp., price $150.00", *Polymers for Advanced Technologies*, vol. 3, no. 1, pp. 47–47, Feb. 1992, ISSN: 10427147. DOI: 10.1002/pat.1992.220030109. [Online]. Available: http://doi.wiley.com/10.1002/pat.1992.220030109.

[34] X. Huang, "Fabrication and Properties of Carbon Fibers", *Materials*, vol. 2, no. 4, pp. 2369–2403, Dec. 2009, ISSN: 1996-1944. DOI: 10.3390/ma2042369. [Online]. Available: http://www.mdpi.com/1996-1944/2/4/2369.

[35] D. Chung and D. Chung, *Carbon Fiber Composites*. Elsevier Science, 2012, ISBN: 9780080500737. [Online]. Available: https://books.google.com.mx/books?id=UYQXAAAAQBAJ.

[36] S. Subramoney, "Science of fullerenes and carbon nanotubes. ByM. S. Dresselhaus,G. Dresselhaus, andP. C. Eklund, XVIII, 965 pp., Academic press, San Diego, CA 1996, hardcover, ISBN 012-221820-5", *Advanced Materials*, vol. 9, no. 15, pp. 1193–1193, 1997, ISSN: 0935-9648. DOI: 10.1002/adma.19970091518. [Online]. Available: http://doi.wiley.com/10.1002/adma.19970091518.

[37] M. S. Dresselhaus, G. Dresselhaus, P. C. Eklund, and A. M. Rao, "Carbon Nanotubes", in *Electronics*, 1, 2000, pp. 331–379. DOI: 10.1007/978-94-011-4038-6_9. [Online]. Available: http://link.springer.com/10.1007/978-94-011-4038-6%7B%5C_%7D9.

[38] N. Rodriguez, "A review of catalytically grown carbon nanofibers", *Journal of Materials Research*, vol. 8, no. 12, pp. 3233–3250, Dec. 1993, ISSN: 0884-2914. DOI: 10.1557/JMR.1993.3233. [Online]. Available: https://www.cambridge.org/core/product/identifier/S0884291400072551/type/journal%7B%5C_%7Darticle.

[39] S.-H. Yoon, S. Lim, Y. Song, Y. Ota, W. Qiao, A. Tanaka, and I. Mochida, "KOH activation of carbon nanofibers", *Carbon*, vol. 42, no. 8-9, pp. 1723–1729, 2004, ISSN: 00086223. DOI: 10.1016/j.carbon.2004.03.006. [Online]. Available: https://linkinghub.elsevier.com/retrieve/pii/S0008622304001630.

[40] Q. Liu, W. Ren, Z.-G. Chen, L. Yin, F. Li, H. Cong, and H.-M. Cheng, "Semiconducting properties of cup-stacked carbon nanotubes", *Carbon*, vol. 47, no. 3, pp. 731–736, Mar. 2009, ISSN: 00086223. DOI: 10.1016/j.carbon.2008.11.005. [Online]. Available: http://dx.doi.org/10.1016/j.carbon.2008.11.005%20https://linkinghub.elsevier.com/retrieve/pii/S0008622308006003.

[41] M. Endo, Y. A. Kim, M. Ezaka, K. Osada, T. Yanagisawa, T. Hayashi, M. Terrones, and M. S. Dresselhaus, "Selective and Efficient Impregnation of Metal Nanoparticles on Cup-Stacked-Type Carbon Nanofibers", *Nano Letters*, vol. 3, no. 6, pp. 723–726, Jun. 2003, ISSN: 1530-6984. DOI: 10.1021/nl034136h. [Online]. Available: https://pubs.acs.org/doi/10.1021/nl034136h.

[42] T. Yokozeki, Y. Iwahori, M. Ishibashi, T. Yanagisawa, K. Imai, M. Arai, T. Takahashi, and K. Enomoto, "Fracture toughness improvement of CFRP laminates by dispersion of cup-stacked carbon nanotubes", *Composites Science and Technology*, vol. 69, no. 14, pp. 2268–2273, Nov. 2009, ISSN: 02663538. DOI: 10.1016/j.compscitech.2008.12.017. [Online]. Available: http://dx.doi.org/10.1016/j.compscitech.2008.12.017%20https://linkinghub.elsevier.com/retrieve/pii/S0266353808005265.

[43] E. Frackowiak and F. Béguin, "Electrochemical storage of energy in carbon nanotubes and nanostructured carbons", *Carbon*, vol. 40, no. 10, pp. 1775–1787, Aug. 2002, ISSN: 00086223. DOI: 10.1016/S0008-6223(02)00045-3. [Online]. Available: https://linkinghub.elsevier.com/retrieve/pii/S0008622302000453.

[44] M. Endo, C. Kim, K. Nishimura, T. Fujino, and K. Miyashita, "Recent development of carbon materials for Li ion batteries", *Carbon*, vol. 38, no. 2, pp. 183–197, 2000, ISSN: 00086223. DOI: 10.1016/S0008-6223(99)00141-4. [Online]. Available: https://linkinghub.elsevier.com/retrieve/pii/S0008622399001414.

[45] M. Winter, J. O. Besenhard, M. E. Spahr, and P. Novák, "Insertion Electrode Materials for Rechargeable Lithium Batteries", *Advanced Materials*, vol. 10, no. 10, pp. 725–763, Jul. 1998, ISSN: 0935-9648. DOI: 10.1002/(SICI)1521-4095(199807)10:10<725::AID-ADMA725>3.0.CO;2-Z. [Online]. Available: https://onlinelibrary.wiley.com/doi/10.1002/(SICI)1521-4095(199807)10:10%7B%5C%%7D3C725::AID-ADMA725%7B%5C%%7D3E3.0.CO;2-Z.

[46] M. Endo, T. Maeda, T. Takeda, Y. J. Kim, K. Koshiba, H. Hara, and M. S. Dresselhaus, "Capacitance and Pore-Size Distribution in Aqueous and Nonaqueous Electrolytes Using Various Activated Carbon Electrodes", *Journal of The Electrochemical Society*, vol. 148, no. 8, A910, 2001, ISSN: 00134651. DOI: 10.1149/1.1382589. [Online]. Available: https://iopscience.iop.org/article/10.1149/1.1382589.

[47] E. Frackowiak and F. Béguin, "Carbon materials for the electrochemical storage of energy in capacitors", *Carbon*, vol. 39, no. 6, pp. 937–950, May 2001, ISSN: 00086223. DOI: 10.1016/S0008-6223(00)00183-4. [Online]. Available: https://linkinghub.elsevier.com/retrieve/pii/S0008622300001834.

[48] A. Pandolfo and A. Hollenkamp, "Carbon properties and their role in supercapacitors", *Journal of Power Sources*, vol. 157, no. 1, pp. 11–27, Jun. 2006, ISSN: 03787753. DOI: 10.1016/j.jpowsour.2006.02.065. [Online]. Available: https://linkinghub.elsevier.com/retrieve/pii/S0378775306003442.

[49] B. E. Conway, *Electrochemical Supercapacitors*, 3. Boston, MA: Springer US, 1999, vol. 25, pp. 907–915, ISBN: 978-1-4757-3060-9. DOI: 10.1007/978-1-4757-3058-6. [Online]. Available: http://link.springer.com/10.1007/978-1-4757-3058-6.

[50] H. C. Choi, M. Shim, S. Bangsaruntip, and H. Dai, "Spontaneous Reduction of Metal Ions on the Sidewalls of Carbon Nanotubes", *Journal of the American Chemical Society*, vol. 124, no. 31, pp. 9058–9059, Aug. 2002, ISSN: 0002-7863. DOI: 10.1021/ja026824t. [Online]. Available: https://pubs.acs.org/doi/10.1021/ja026824t.

[51] W. Li, C. Liang, J. Qiu, W. Zhou, H. Han, Z. Wei, G. Sun, and Q. Xin, "Carbon nanotubes as support for cathode catalyst of a direct methanol fuel cell", *Carbon*, vol. 40, no. 5, pp. 791–794, Apr. 2002, ISSN: 00086223. DOI: 10.1016/S0008-6223(02)00039-8. [Online]. Available: https://linkinghub.elsevier.com/retrieve/pii/S0008622302000398.

[52] J. M. Planeix, N. Coustel, B. Coq, V. Brotons, P. S. Kumbhar, R. Dutartre, P. Geneste, P. Bernier, and P. M. Ajayan, "Application of Carbon Nanotubes

as Supports in Heterogeneous Catalysis", *Journal of the American Chemical Society*, vol. 116, no. 17, pp. 7935–7936, Aug. 1994, ISSN: 0002-7863. DOI: 10.1021/ja00096a076. [Online]. Available: https://pubs.acs.org/doi/abs/10.1021/ja00096a076.

[53] M. Román-Martínez, D. Cazorla-Amorós, A. Linares-Solano, C.-M. De Lecea, H. Yamashita, and M. Anpo, "Metal-support interaction in Pt/C catalysts. Influence of the support surface chemistry and the metal precursor", *Carbon*, vol. 33, no. 1, pp. 3–13, 1995, ISSN: 00086223. DOI: 10.1016/0008-6223(94)00096-I. [Online]. Available: https://linkinghub.elsevier.com/retrieve/pii/000862239400096I.

[54] P. Serp and J. L. Figueiredo, Eds., *Carbon Materials for Catalysis*. Hoboken, NJ, USA: John Wiley & Sons, Inc., Dec. 2008, ISBN: 9780470403709. DOI: 10.1002/9780470403709. [Online]. Available: http://doi.wiley.com/10.1002/9780470403709.

[55] F. Bach, J. Fishman, N. Daniels, J. Proimos, B. Anderson, C. Carpenter, L. Forrow, S. Robson, and H. Fineberg, "Uncertainty in xenotransplantation: Individual benefit versus collective risk", *Nature Medicine*, vol. 4, no. 2, pp. 141–144, Feb. 1998, ISSN: 1078-8956. DOI: 10.1038/nm0298-141. [Online]. Available: http://www.nature.com/articles/nm0298-141.

[56] D. Butler, M. Wadman, S. Lehrman, and Q. Schiermeier, "Last chance to stop and think on risks of xenotransplants", *Nature*, vol. 391, no. 6665, pp. 321–322, Jan. 1998, ISSN: 0028-0836. DOI: 10.1038/34749. [Online]. Available: http://www.nature.com/articles/34749.

[57] F. Delustro, J. Dasch, J. Keefe, and L. Ellingsworth, "Immune Responses to Allogeneic and Xenogeneic Implants of Collagen and Collagen Derivatives", *Clinical Orthopaedics and Related Research*, vol. 260, pp. 263–279, Nov. 1990, ISSN: 0009-921X. DOI: 10.1097/00003086-199011000-00043. [Online]. Available: http://journals.lww.com/00003086-199011000-00043.

[58] J. C. Chachques, J. C. Trainini, N. Lago, M. Cortes-Morichetti, O. Schussler, and A. Carpentier, "Myocardial Assistance by Grafting a New Bioartificial Upgraded Myocardium (MAGNUM Trial): Clinical Feasibility Study", *The Annals of Thoracic Surgery*, vol. 85, no. 3, pp. 901–908, Mar. 2008, ISSN: 00034975. DOI: 10.1016/j.athoracsur.2007.10.052. [Online]. Available: https://linkinghub.elsevier.com/retrieve/pii/S0003497507021819.

[59] A. Atala, S. B. Bauer, S. Soker, J. J. Yoo, and A. B. Retik, "Tissue-engineered autologous bladders for patients needing cystoplasty", *The Lancet*, vol. 367, no. 9518, pp. 1241–1246, Apr. 2006, ISSN: 01406736. DOI: 10.1016/S0140-6736(06)68438-9. [Online]. Available: https://linkinghub.elsevier.com/retrieve/pii/S0140673606684389.

[60] J. Glowacki and S. Mizuno, "Collagen scaffolds for tissue engineering", *Biopolymers*, vol. 89, no. 5, pp. 338–344, May 2008, ISSN: 00063525. DOI: 10.

1002/bip.20871. [Online]. Available: http://doi.wiley.com/10.1002/bip.20871.

[61] M. T. Valarmathi, M. J. Yost, R. L. Goodwin, and J. D. Potts, "The influence of proepicardial cells on the osteogenic potential of marrow stromal cells in a three-dimensional tubular scaffold", *Biomaterials*, vol. 29, no. 14, pp. 2203–2216, May 2008, ISSN: 01429612. DOI: 10.1016/j.biomaterials.2008.01.025. [Online]. Available: https://linkinghub.elsevier.com/retrieve/pii/S0142961208000550.

[62] K. A. Faraj, T. H. van Kuppevelt, and W. F. Daamen, "Construction of Collagen Scaffolds That Mimic the Three-Dimensional Architecture of Specific Tissues", *Tissue Engineering*, vol. 13, no. 10, pp. 2387–2394, Oct. 2007, ISSN: 1076-3279. DOI: 10.1089/ten.2006.0320. [Online]. Available: https://www.liebertpub.com/doi/10.1089/ten.2006.0320.

[63] T. Visuri, O. Kiviluoto, and M. Eskelin, "Carbon fiber for repair of the rotator cuff: A 4-year follow-up of 14 cases", *Acta Orthopaedica Scandinavica*, vol. 62, no. 4, pp. 356–359, Jan. 1991, ISSN: 0001-6470. DOI: 10.3109/17453679108994469. [Online]. Available: http://www.tandfonline.com/doi/full/10.3109/17453679108994469.

[64] J. R. Parsons, A. B. Weiss, R. S. Schenk, H. Alexander, and F. Pavlisko, "Long-Term Follow-up of Achilles Tendon Repair with an Absorbable Polymer Carbon Fiber Composite", *Foot & Ankle*, vol. 9, no. 4, pp. 179–184, Feb. 1989, ISSN: 0198-0211. DOI: 10.1177/107110078900900406. [Online]. Available: http://journals.sagepub.com/doi/10.1177/107110078900900406.

[65] S. Ramakrishna, K. Fujihara, W.-E. Teo, T.-C. Lim, and Z. Ma, *An Introduction to Electrospinning and Nanofibers*. WORLD SCIENTIFIC, Jun. 2005, pp. 1–382, ISBN: 978-981-256-415-3. DOI: 10.1142/5894. [Online]. Available: https://www.worldscientific.com/worldscibooks/10.1142/5894.

[66] D. H. Reneker, A. L. Yarin, H. Fong, and S. Koombhongse, "Bending instability of electrically charged liquid jets of polymer solutions in electrospinning", *Journal of Applied Physics*, vol. 87, no. 9, pp. 4531–4547, May 2000, ISSN: 0021-8979. DOI: 10.1063/1.373532. [Online]. Available: http://aip.scitation.org/doi/10.1063/1.373532.

[67] I. D. Norris, M. M. Shaker, F. K. Ko, and A. G. MacDiarmid, "Electrostatic fabrication of ultrafine conducting fibers: polyaniline/polyethylene oxide blends", *Synthetic Metals*, vol. 114, no. 2, pp. 109–114, Aug. 2000, ISSN: 03796779. DOI: 10.1016/S0379-6779(00)00217-4. [Online]. Available: https://linkinghub.elsevier.com/retrieve/pii/S0379677900002174.

[68] G. Vozzi, C. J. Flaim, F. Bianchi, A. Ahluwalia, and S. Bhatia, "Microfabricated PLGA scaffolds: a comparative study for application to tissue engineering", *Materials Science and Engineering: C*, vol. 20, no. 1-2, pp. 43–47, May 2002,

ISSN: 09284931. DOI: 10.1016/S0928-4931(02)00011-5. [Online]. Available: https://linkinghub.elsevier.com/retrieve/pii/S0928493102000115.

[69] C. Kim and K. S. Yang, "Electrochemical properties of carbon nanofiber web as an electrode for supercapacitor prepared by electrospinning", *Applied Physics Letters*, vol. 83, no. 6, pp. 1216–1218, Aug. 2003, ISSN: 0003-6951. DOI: 10.1063/1.1599963. [Online]. Available: http://aip.scitation.org/doi/10.1063/1.1599963.

[70] R. Dersch, M. Steinhart, U. Boudriot, A. Greiner, and J. H. Wendorff, "Nanoprocessing of polymers: applications in medicine, sensors, catalysis, photonics", *Polymers for Advanced Technologies*, vol. 16, no. 2-3, pp. 276–282, 2005, ISSN: 1042-7147. DOI: 10.1002/pat.568. [Online]. Available: http://doi.wiley.com/10.1002/pat.568.

[71] B. Cardenas-Benitez, C. Eschenbaum, D. Mager, J. G. Korvink, M. J. Madou, U. Lemmer, I. D. Leon, and S. O. Martinez-Chapa, "Pyrolysis-induced shrinking of three-dimensional structures fabricated by two-photon polymerization: experiment and theoretical model", *Microsystems & Nanoengineering*, vol. 5, no. 1, 2019, ISSN: 2055-7434. DOI: 10.1038/s41378-019-0079-9. [Online]. Available: http://dx.doi.org/10.1038/s41378-019-0079-9.

[72] V. Baudrit J, "Recycling and Elimination of Wastes obtained from Agriculture by using Nanotechnology: Nanosensors", *International Journal of Biosensors & Bioelectronics*, vol. 3, no. 5, pp. 368–375, Dec. 2017, ISSN: 25732838. DOI: 10.15406/ijbsbe.2017.03.00084. [Online]. Available: https://medcraveonline.com/IJBSBE/recycling-and-elimination-of-wastes-obtained-from-agriculture-by-using-nanotechnology-nanosensors.html.

[73] J. Boer and C. Blitterswijk, *Tissue Engineering*, 2nd, A. P. o. E. AP, Ed. Safary O Reilly, 2014. [Online]. Available: https://learning.oreilly.com/library/view/tissue-engineering-2nd/9780124201453/XHTML/B9780124201453000109/B9780124201453000109.xhtml.

[74] K. C. Hribar, P. Soman, J. Warner, P. Chung, and S. Chen, "Light-assisted direct-write of 3D functional biomaterials", *Lab Chip*, vol. 14, no. 2, pp. 268–275, Jan. 2014, ISSN: 1473-0197. DOI: 10.1039/C3LC50634G. [Online]. Available: http://www.ncbi.nlm.nih.gov/pubmed/24257507%20http://xlink.rsc.org/?DOI=C3LC50634G.

[75] S. Landis, *Nano-Lithography*, S. Landis, Ed. Hoboken, NJ USA: John Wiley & Sons, Inc., Feb. 2013, p. 325, ISBN: 9781118622582. DOI: 10.1002/9781118622582. [Online]. Available: https://learning.oreilly.com/library/view/nano-lithography/9781118621707/%20http://doi.wiley.com/10.1002/9781118622582.

[76] F. Anton, *Process and apparatus for preparing artificial threads*, 1930. DOI: https://patents.google.com/?q=D01D5\%2f0076.

[77] Z.-M. Huang, Y. .-.-Z. Zhang, M. Kotaki, and S. Ramakrishna, "A review on polymer nanofibers by electrospinning and their applications in nanocomposites", *Composites Science and Technology*, vol. 63, no. 15, pp. 2223–2253, Nov. 2003. DOI: 10.1016/S0266-3538(03)00178-7.

[78] D. H. Reneker and A. L. Yarin, "Electrospinning jets and polymer nanofibers", *Polymer*, vol. 49, no. 10, pp. 2387–2425, May 2008. DOI: 10.1016/J.POLYMER.2008.02.002.

[79] J. D. Schiffman and C. L. Schauer, "A Review: Electrospinning of Biopolymer Nanofibers and their Applications", *Polymer Reviews*, vol. 48, no. 2, pp. 317–352, May 2008. DOI: 10.1080/15583720802022182.

[80] Q. Li, *Chapter 7: Liquid Crystal-Functionalized Nano- and Microfibers Produced by Electrospinning - Liquid Crystals Beyond Displays: Chemistry, Physics, and Applications*. John Wiley & Sons, 2012. DOI: 9781118078617.

[81] L. Zhang, T. Si, A. J. Fischer, A. Letson, S. Yuan, C. J. Roberts, and R. X. Xu, "Coaxial electrospray of ranibizumab-loaded microparticles for sustained release of anti-VEGF therapies", *PLoS ONE*, vol. 10, no. 8, pp. 1–16, 2015. DOI: 10.1371/journal.pone.0135608.

[82] G. I. Taylor, "Disintegration of water drops in an electric field", *Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences*, vol. 280, no. 1382, pp. 383–397, Jul. 1964. DOI: 10.1098/rspa.1964.0151.

[83] J. Doshi and D. H. Reneker, "Electrospinning process and applications of electrospun fibers", *Journal of Electrostatics*, vol. 35, no. 2-3, pp. 151–160, Aug. 1995. DOI: 10.1016/0304-3886(95)00041-8.

[84] A. Cisquella-Serra, M. Magnani, Á. Gual-Mosegui, S. Holmberg, M. Madou, and M. Gamero-Castaño, "Study of the electrostatic jet initiation in near-field electrospinning", *Journal of Colloid and Interface Science*, vol. 543, pp. 106–113, May 2019. DOI: 10.1016/J.JCIS.2019.02.041.

[85] Y. M. Shin, M. M. Hohman, M. P. Brenner, and G. C. Rutledge, "Electrospinning: A whipping fluid jet generates submicron polymer fibers", *Applied Physics Letters*, vol. 78, no. 8, pp. 1149–1151, Feb. 2001. DOI: 10.1063/1.1345798.

[86] R. Kessick, J. Fenn, and G. Tepper, "The use of AC potentials in electrospraying and electrospinning processes", *Polymer*, vol. 45, no. 9, pp. 2981–2984, Apr. 2004. DOI: 10.1016/j.polymer.2004.02.056.

[87] G. R. Williams, B. T. Raimi-Abraham, and C. J. Luo, "Alternative nanofibre fabrication approaches", *Nanofibres in Drug Delivery*, pp. 160–186, 2018. DOI: 10.2307/j.ctv550dd1.10.

[88] S. Sarkar, S. Deevi, and G. Tepper, "Biased AC electrospinning of aligned polymer nanofibers", *Macromolecular Rapid Communications*, vol. 28, no. 9, pp. 1034–1039, 2007. DOI: 10.1002/marc.200700053.

[89] C. Attila, R. Demuth, null Balazs, G. Verreck, J. Mensch, G. Marosi, Z. Nagy, and null Kristof, "Alternating current electrospinning for preparation of

fibrous drug delivery systems", *International Journal of Pharmaceutics*, vol. 495, no. 1, pp. 75–80, 2015, Alternating current electrospinning,Dissolution enhancement,Electrospinning,Poorly water-soluble drugs. Solid dispersion. DOI: 10.1016/j.ijpharm.2015.08.069. [Online]. Available: http://dx.doi.org/10.1016/j.ijpharm.2015.08.069.

[90] K. Sarkar, C. Gomez, S. Zambrano, M. Ramirez, E. D. Hoyos, H. Vasquez, and K. Lozano, "Electrospinning to Forcespinning™", *Materials Today*, vol. 13, no. 11, pp. 12–14, 2010. DOI: 10.1016/S1369-7021(10)70199-1.

[91] S. Mahalingam and M. Edirisinghe, "Forming of polymer nanofibers by a pressurised gyration process", *Macromolecular Rapid Communications*, vol. 34, no. 14, pp. 1134–1139, 2013. DOI: 10.1002/marc.201300339.

[92] M. R. Badrossamay, H. A. McIlwee, J. A. Goss, and K. K. Parker, "Nanofiber Assembly by Rotary Jet-Spinning", *Nano Letters*, vol. 10, no. 6, pp. 2257–2261, Jun. 2010. DOI: 10.1021/nl101355x.

[93] N. E. Zander, "Formation of melt and solution spun polycaprolactone fibers by centrifugal spinning", *Journal of Applied Polymer Science*, vol. 132, no. 2, pp. 1–9, 2015. DOI: 10.1002/app.41269.

[94] L. A. Mary, T. Senthilram, S. Suganya, L. Nagarajan, J. Venugopal, S. Ramakrishna, and V. R. G. Dev, "Centrifugal spun ultrafine fibrous web as a potential drug delivery vehicle", *Express Polymer Letters*, vol. 7, no. 3, pp. 238–248, 2012. DOI: 10.3144/expresspolymlett.2013.22.

[95] X. Zhang and Y. Lu, "Centrifugal spinning: An alternative approach to fabricate nanofibers at high speed and low cost", *Polymer Reviews*, vol. 54, no. 4, pp. 677–701, 2014. DOI: 10.1080/15583724.2014.935858.

[96] O. O. Dosunmu, G. G. Chase, W. Kataphinan, and D. H. Reneker, "Electrospinning of polymer nanofibres from multiple jets on a porous tubular surface", *Nanotechnology*, vol. 17, no. 4, pp. 1123–1127, Feb. 2006. DOI: 10.1088/0957-4484/17/4/046.

[97] M. Kancheva, A. Toncheva, N. Manolova, and I. Rashkov, "Advanced centrifugal electrospinning setup", *Materials Letters*, vol. 136, pp. 150–152, 2014. DOI: 10.1016/j.matlet.2014.08.045.

[98] A. E. Erickson, D. Edmondson, F. C. Chang, D. Wood, A. Gong, S. L. Levengood, and M. Zhang, "High-throughput and high-yield fabrication of uniaxially-aligned chitosan-based nanofibers by centrifugal electrospinning", *Carbohydrate Polymers*, vol. 134, pp. 467–474, 2015. DOI: 10.1016/j.carbpol.2015.07.097.

[99] C. C. Liao, C. C. Wang, K. C. Shih, and C. Y. Chen, "Electrospinning fabrication of partially crystalline bisphenol A polycarbonate nanofibers: Effects on conformation, crystallinity, and mechanical properties", *European Polymer Journal*, vol. 47, no. 5, pp. 911–924, 2011. DOI: 10.1016/j.eurpolymj.2011.01.006.

[100] D. Edmondson, A. Cooper, S. Jana, D. Wood, and M. Zhang, "Centrifugal electrospinning of highly aligned polymer nanofibers over a large area", *Journal of Materials Chemistry*, vol. 22, no. 35, p. 18 646, Aug. 2012. DOI: 10.1039/c2jm33877g.

[101] M. A. Souza, K. Y. Sakamoto, and L. H. C. Mattoso, "Release of the diclofenac sodium by nanofibers of poly(3-hydroxybutyrate- co -3-hydroxyvalerate) obtained from electrospinning and solution blow spinning", *Journal of Nanomaterials*, vol. 2014, 2014. DOI: 10.1155/2014/129035.

[102] J. E. Oliveira, E. S. Medeiros, L. Cardozo, F. Voll, E. H. Madureira, L. H. C. Mattoso, and O. B. G. Assis, "Development of poly(lactic acid) nanostructured membranes for the controlled delivery of progesterone to livestock animals", *Materials Science and Engineering C*, vol. 33, no. 2, pp. 844–849, 2013. DOI: 10.1016/j.msec.2012.10.032.

[103] T. Ondarçuhu and C. Joachim, "Drawing a single nanofibre over hundreds of microns", *Europhysics Letters (EPL)*, vol. 42, no. 2, pp. 215–220, Apr. 1998. DOI: 10.1209/epl/i1998-00233-9.

[104] A. S. Nain, J. C. Wong, C. Amon, and M. Sitti, "Drawing suspended polymer micro-/nanofibers using glass micropipettes", *Applied Physics Letters*, vol. 89, no. 18, 2006. DOI: 10.1063/1.2372694.

[105] A. Tokarev, D. Asheghali, I. M. Griffiths, O. Trotsenko, A. Gruzd, X. Lin, H. A. Stone, and S. Minko, "Touch- and Brush-Spinning of Nanofibers", *Advanced Materials*, vol. 27, no. 41, pp. 6526–6532, 2015. DOI: 10.1002/adma.201502768.

[106] J. Cheng, Y. Jun, J. Qin, and S. H. Lee, "Electrospinning versus microfluidic spinning of functional fibers for biomedical applications", *Biomaterials*, vol. 114, pp. 121–143, 2017. DOI: 10.1016/j.biomaterials.2016.10.040.

[107] E. Kang, G. S. Jeong, Y. Y. Choi, K. H. Lee, A. Khademhosseini, and S. H. Lee, "Digitally tunable physicochemical coding of material composition and topography in continuous microfibres", *Nature Materials*, vol. 10, no. 11, pp. 877–883, 2011. DOI: 10.1038/nmat3108.

[108] J. E. Dıaz, A. Barrero, M. Márquez, and I. G. Loscertales, "Controlled encapsulation of hydrophobic liquids in hydrophilic polymer nanofibers by co-electrospinning", *Advanced Functional Materials*, vol. 16, no. 16, pp. 2110–2116, 2006. DOI: 10.1002/adfm.200600204.

[109] I. G. Loscertales, A. Barrero, I. Guerrero, R. Cortijo, M. Marquez, and A. M. Gañán-Calvo, "Micro/nano encapsulation via electrified coaxial liquid jets", *Science*, vol. 295, no. 5560, pp. 1695–1698, 2002. DOI: 10.1126/science.1067595.

[110] Z. Sun, E. Zussman, A. L. Yarin, J. H. Wendorff, and A. Greiner, "Compound Core-Shell Polymer Nanofibers by Co-Electrospinning", *Advanced Materials*, vol. 15, no. 22, pp. 1929–1932, 2003. DOI: 10.1002/adma.200305136.

[111] P. Sofokleous, W. K. Lau, M. Edirisinghe, and E. Stride, "The effect of needle tip displacement in co-axial electrohydrodynamic processing", *RSC Advances*, vol. 6, no. 79, pp. 75 258–75 268, 2016. DOI: 10.1039/c6ra08877e.

[112] Z. Ahmad, H. B. Zhang, U. Farook, M. Edirisinghe, E. Stride, and P. Colombo, "Generation of multilayered structures for biomedical applications using a novel tri-needle coaxial device and electrohydrodynamic flow", *Journal of the Royal Society Interface*, vol. 5, no. 27, pp. 1255–1261, 2008. DOI: 10.1098/rsif.2008.0247.

[113] ——, "Generation of multilayered structures for biomedical applications using a novel tri-needle coaxial device and electrohydrodynamic flow", *Journal of the Royal Society Interface*, vol. 5, no. 27, pp. 1255–1261, 2008. DOI: 10.1098/rsif.2008.0247.

[114] T. D. Brown, P. D. Dalton, and D. W. Hutmacher, "Melt electrospinning today: An opportune time for an emerging polymer process", *Progress in Polymer Science*, vol. 56, pp. 116–166, 2016. DOI: 10.1016/j.progpolymsci.2016.01.001.

[115] Z. K. Nagy, A. Balogh, G. Drávavölgyi, J. Ferguson, H. Pataki, B. Vajna, and G. Marosi, "Solvent-Free Melt Electrospinning for Preparation of Fast Dissolving Drug Delivery System and Comparison with Solvent-Based Electrospun and Melt Extruded Systems", *Journal of Pharmaceutical Sciences*, vol. 102, no. 2, pp. 508–517, Feb. 2013. DOI: 10.1002/jps.23374.

[116] A. Balogh, G. Drávavölgyi, K. Faragó, A. Farkas, T. Vigh, P. L. Sóti, I. Wagner, J. Madarász, H. Pataki, G. Marosi, and Z. K. Nagy, "Plasticized drug-loaded melt electrospun polymer mats: Characterization, thermal degradation, and release kinetics", *Journal of Pharmaceutical Sciences*, vol. 103, no. 4, pp. 1278–1287, 2014. DOI: 10.1002/jps.23904.

[117] H. Lian and Z. Meng, "Melt electrospinning vs. solution electrospinning: A comparative study of drug-loaded poly (ε-caprolactone) fibres", *Materials Science and Engineering C*, vol. 74, pp. 117–123, 2017. DOI: 10.1016/j.msec.2017.02.024.

[118] G. Hochleitner, M. Kessler, M. Schmitz, A. R. Boccaccini, J. T. Teβmar, and J. Groll, "Melt electrospinning writing of defined scaffolds using polylactide-poly(ethylene glycol) blends with 45S5 bioactive glass particles", *Materials Letters*, vol. 205, pp. 257–260, 2017. DOI: 10.1016/j.matlet.2017.06.096.

[119] J. T. McCann, ‡, M. Marquez, and Y. Xia*, "Melt Coaxial Electrospinning: A Versatile Method for the Encapsulation of Solid Materials and Fabrication of Phase Change Nanofibers", 2006. DOI: 10.1021/NL0620839.

[120] C. Chang, K. Limkrailassiri, and L. Lin, "Continuous near-field electrospinning for large area deposition of orderly nanofiber patterns", *Appl Phys Lett*, p. 3, 2008. DOI: 10.1063/1.2975834.

[121] J. Zheng, Y. Z. Long, B. Sun, Z. H. Zhang, F. Shao, H. D. Zhang, Z. M. Zhang, and J. Y. Huang, "Polymer nanofibers prepared by low-voltage near-field electrospinning", *Chinese Physics B*, vol. 21, no. 4, pp. 1–6, 2012. DOI: 10.1088/1674-1056/21/4/048102.

[122] S. Chakraborty, I.-C. Liao, A. Adler, and K. W. Leong, "Electrohydrodynamics: A facile technique to fabricate drug delivery systems", *Advanced Drug Delivery Reviews*, vol. 61, no. 12, pp. 1043–1054, Oct. 2009. DOI: 10.1016/j.addr.2009.07.013.

[123] J. Xue, T. Wu, Y. Dai, and Y. Xia, "Electrospinning and Electrospun Nanofibers: Methods, Materials, and Applications", *Chemical Reviews*, vol. 119, no. 8, pp. 5298–5415, Apr. 2019. DOI: 10.1021/acs.chemrev.8b00593.

[124] G. R. Williams, B. T. Raimi-Abraham, and C. J. Luo, "Monoaxial electrospinning", *Nanofibres in Drug Delivery*, pp. 60–105, 2018. DOI: 10.2307/j.ctv550dd1.7.

[125] K. A. G. Katsogiannis, G. T. Vladisavljević, and S. Georgiadou, "Porous electrospun polycaprolactone (PCL) fibres by phase separation", *European Polymer Journal*, vol. 69, pp. 284–295, 2015. DOI: 10.1016/j.eurpolymj.2015.01.028.

[126] G. S. Bisht, G. Canton, A. Mirsepassi, L. Kulinsky, S. Oh, D. Dunn-Rankin, and M. J. Madou, "Controlled Continuous Patterning of Polymeric Nanofibers on Three-Dimensional Substrates Using Low-Voltage Near-Field Electrospinning", *Nano Letters*, vol. 11, no. 4, pp. 1831–1837, Apr. 2011. DOI: 10.1021/nl2006164.

[127] J. Kim, B. Maeng, and J. Park, "Characterization of 3D electrospinning on inkjet printed conductive pattern on paper", *Micro and Nano Systems Letters*, vol. 6, no. 1, p. 12, Dec. 2018. DOI: 10.1186/s40486-018-0074-1.

[128] A. Gupta, A. M. Seifalian, Z. Ahmad, M. J. Edirisinghe, and M. C. Winslet, "Novel Electrohydrodynamic Printing of Nanocomposite Biopolymer Scaffolds", *Journal of BIOACTIVE AND COMPATIBLE POLYMERS*, vol. 22, 2007. DOI: 10.1177/0883911507078268.

[129] H. Wang, S. Huang, F. Liang, P. Wu, M. Li, S. Lin, and X. Chen, "Research on Multinozzle Near-Field Electrospinning Patterned Deposition", *Journal of Nanomaterials*, vol. 2015, pp. 1–8, Jul. 2015. DOI: 10.1155/2015/529138.

[130] Z. Wang, X. Chen, J. Zeng, F. Liang, P. Wu, and H. Wang, "Controllable deposition distance of aligned pattern via dual-nozzle near-field electrospinning", *AIP Advances*, vol. 7, no. 3, p. 035 310, Mar. 2017. DOI: 10.1063/1.4974936.

[131] Z. Wang, X. Chen, J. Zhang, Y.-J. Lin, K. Li, J. Zeng, P. Wu, Y. He, Y. Li, and H. Wang, "Fabrication and evaluation of controllable deposition distance for aligned pattern by multi-nozzle near-field electrospinning", *AIP Advances*, vol. 8, no. 7, p. 075 111, Jul. 2018. DOI: 10.1063/1.5032082.

[132] Y. Huang, Y. Duan, Y. Ding, N. Bu, Y. Pan, N. Lu, and Z. Yin, "Versatile, kinetically controlled, high precision electrohydrodynamic writing of micro/nanofibers", *Scientific Reports*, vol. 4, no. 1, p. 5949, May 2015. DOI: 10.1038/srep05949.

[133] N. Bu, Y. Huang, X. Wang, and Z. Yin, "Materials and Manufacturing Processes Continuously Tunable and Oriented Nanofiber Direct-Written by Mechano-Electrospinning Continuously Tunable and Oriented Nanofiber Direct-Written by Mechano-Electrospinning", 2012. DOI: 10.1080/10426914.2012.700145.

[134] A. R. Nagle, C. D. Fay, Z. Xie, G. G. Wallace, X. Wang, and M. J. Higgins, "A direct 3D suspension near-field electrospinning technique for the fabrication of polymer nanoarrays", *Nanotechnology*, vol. 30, no. 19, p. 195 301, May 2019. DOI: 10.1088/1361-6528/ab011b.

[135] J. Kameoka and H. G. Craighead, "Fabrication of oriented polymeric nanofibers on planar surfaces by electrospinning", *Applied Physics Letters*, vol. 83, no. 2, pp. 371–373, Jul. 2003. DOI: 10.1063/1.1592638.

[136] D. Sun, C. Chang, S. Li, and L. Lin, "Near-Field Electrospinning", 2006. DOI: 10.1021/nl0602701.

[137] N. Xue, X. Li, C. Bertulli, Z. Li, A. Patharagulpong, A. Sadok, and Y. Y. S. Huang, "Rapid Patterning of 1-D Collagenous Topography as an ECM Protein Fibril Platform for Image Cytometry", *PLoS ONE*, vol. 9, no. 4, W.-C. Chin, Ed., e93590, Apr. 2014. DOI: 10.1371/journal.pone.0093590.

[138] S. Coppola, V. Vespini, G. Nasti, O. Gennari, S. Grilli, M. Ventre, M. Iannone, P. A. Netti, and P. Ferraro, "Tethered Pyro-Electrohydrodynamic Spinning for Patterning Well-Ordered Structures at Micro-and Nanoscale", *Chem. Mater*, vol. 26, p. 3360, 2014. DOI: 10.1021/cm501265j.

[139] D. D. Camillo, V. Fasano, F. Ruggieri, S. Santucci, L. Lozzi, A. Camposeo, and D. Pisignano, "Near-field electrospinning of conjugated polymer light-emitting nanofibers", *Nanoscale*, vol. 5, pp. 11 637–11 642, 2013. DOI: 10.1039/C3NR03094F.

[140] Q. Xiang, Y.-M. Ma, D.-G. Yu, M. Jin, and G. R. Williams, "Electrospinning using a Teflon-coated spinneret", *Applied Surface Science*, vol. 284, pp. 889–893, Nov. 2013. DOI: 10.1016/j.apsusc.2013.08.030.

[141] Q. Wang, D. G. Yu, S. Y. Zhou, C. Li, and M. Zhao, "Electrospun amorphous medicated nanocomposites fabricated using a Teflon-based concentric spinneret", *E-Polymers*, vol. 18, no. 1, pp. 3–11, 2018. DOI: 10.1515/epoly-2017-0110.

[142] C. Song, J. A. Rogers, J.-M. Kim, and H. Ahn, "Patterned polydiacetylene-embedded polystyrene nanofibers based on electrohydrodynamic jet printing", *Macromolecular Research*, vol. 23, no. 1, pp. 118–123, Jan. 2015. DOI: 10.1007/s13233-015-3024-2.

[143] G. Taylor, "Electrically Driven Jets", *Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences*, vol. 313, no. 1515, pp. 453–475, Dec. 1969. DOI: 10.1098/rspa.1969.0205.

[144] J. J. Feng, "The stretching of an electrified non-Newtonian jet: A model for electrospinning", *Physics of Fluids*, vol. 14, no. 11, pp. 3912–3926, Nov. 2002. DOI: 10.1063/1.1510664.

[145] G. Zheng, W. Li, X. Wang, D. Wu, D. Sun, and L. Lin, "Precision deposition of a nanofibre by near-field electrospinning", *Journal of Physics D: Applied Physics*, vol. 43, no. 41, p. 415 501, Oct. 2010. DOI: 10.1088/0022-3727/43/41/415501.

[146] Z. H. Liu, C. T. Pan, L. W. Lin, J. C. Huang, and Z. Y. Ou, "Direct-write PVDF nonwoven fiber fabric energy harvesters via the hollow cylindrical near-field electrospinning process", pp. 25 003–25 014, 2014. DOI: 10.1088/0964-1726/23/2/025003.

[147] W. S. Choi, G. H. Kim, J. H. Shin, G. Lim, and T. An, "Electrospinning onto Insulating Substrates by Controlling Surface Wettability and Humidity", *Nanoscale Research Letters*, vol. 12, 2017. DOI: 10.1186/s11671-017-2380-6.

[148] Y. Duan, Y. Ding, Z. Xu, Y. Huang, and Z. Yin, "Helix Electrohydrodynamic Printing of Highly Aligned Serpentine Micro/Nanofibers.", *Polymers*, vol. 9, no. 9, Sep. 2017. DOI: 10.3390/polym9090434.

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EDUCATION

TECNOLÓGICO DE MONTERREY
MSc in Nanotechnology
Jan 2019 - Dec 2020 | Estado de México, MX

TECNOLÓGICO DE MONTERREY
BS in Digital Systems and Robotics
Aug2012 - May 2016 | Querétaro, MX
Cum. GPA: 3.6 / 4.0

LINKS

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COURSEWORK

GRADUATE
Thermodynamics of Materials
Nano-structured Materials
Plastics and Composites Engineering
Rheology & Electrospinning

UNDERGRADUATE
Sensors
Control Engineering
Digital Systems
Computer Architecture
Embedded Systems
Web Application Design
Microcontrollers
Electric Circuits

SKILLS

PROGRAMMING
Over 5000 lines:
Python • Javascript • LaTeX
Over 2000 lines:
C • C++ • ADA • Verilog • VHDL
Over 1000 lines:
Java • CSS • PHP • Assembly
Familiar:
Android • MySQL

EXPERIENCE

GE AVIATION | Embedded Software Eng.
Jun 2018 - Dec 2019 | Querétaro, MX

- At General Electric's Business & General Aviation Power Software team, I develop and test critical software for Aviation Power products. I have high responsibility in the development and in the documentation of the features and interactions with other systems.

GE AVIATION | SW Edison Engineering Development Program
June 2016 – May 2018 | Querétaro, MX

- EEDP is an intensive program for people who have a passion for technology, a drive for technical excellence, and share in GE's core values. It is designed to accelerate participants' professional development through intense technical training.

GE POWER | Software EID Intern
May 2015 – May 2016 | Querétaro, MX

- Support and improve engineering projects and activities.
- Worked on the analysis and optimization of +20 wind turbines for every GE wind farm worldwide.

RESEARCH

MACROPHOTOSCIENCE RESEACH GROUP | MSc Student
Jan 2019 – Dec 2020 | Nuevo León, MX
Worked with **Phd. Alan Aguirre** and **Phd. Dora Medina** to determine the electro-spunability of various polymer solutions for the fabrication of carbon nano-wires.

AWARDS

May 2018	top 4%	Software EEDP graduate at GE Aviation
Aug 2015	1st/1000	GE 9th Lean Challenge
Nov 2014	1st/50	GEIQ's Robotics Project

PUBLICATIONS

[1] Saeed Beigi-boroujeni, Osamu Katagiri-tanaka, Braulio Cardenas-benitez, O Sergio, and Alan Aguirre-soto. Pyrolytic Carbon from Novolac Epoxy Resin Compressed before Photocrosslinking and Pyrolysis. *Materials Today: Proceedings*, 2020.