

INSTITUTO TECNOLÓGICO Y DE ESTUDIOS
SUPERIORES DE MONTERREY



MASTERS THESIS PROPOSAL

**Fabrication of graphitic-carbon suspended
nanowires through
mechanoelectrospinning of
photocrosslinkable polymers**

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List of Abbreviations

ITESM	Instituto Tecnológico y de Estudios Superiores de Monterrey
CEM	Campus Estado de México
MNT	Maestría en Nanotecnología (<i>Master of Science in Nanotechnology</i>)
CNWs	Carbon Nano-wires
EMS	Electromechanical Spinning
FFES	Far Field de Electrospinning
NFES	Near Field de Electrospinning
SU-8	a photoresist

INSTITUTO TECNOLÓGICO Y DE ESTUDIOS SUPERIORES DE
MONTERREY

Abstract

Faculty: Nanotechnology

School of Engineering and Sciences

Master of Science in Nanotechnology (MNT)

Fabrication of graphitic-carbon suspended nanowires through mechanoelectrospinning of photocrosslinkable polymers

by Antonio Osamu KATAGIRI Tanaka

Carbon nano-wires are versatile materials composed of carbon chains with a wide range of applications due to their unrivalled properties in electrical matters. 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. 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 processes, 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 properties 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 carbon nano-wires in an inexpensive, continuous, simple and reproducible manner.

keywords: nanotechnology, carbon, nano-wires, electrospinning, NFES

1 Introduction

[Chapter ready for review]

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. [9] Carbon nano-materials are suitable for the catalysis, adsorption, carbon capture, energy and hydrogen storage, drug delivery, bio-sensing and cancer detection. [9] Due to some of matchless properties that allow carbon nano-materials to be utilized within multiple functionalities including high porosity, distinguished structures, uniform morphologies, high stability, high magnetic properties and high conductivity. [9]

This document bestow a thesis proposal to perform a research to engineer and design 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, photopolymerization, pyrolyzation and carbonization, as they have shown to be promising methods for the fabrication of carbon nano-materials. [2] See Figure 1.1. A number of processes have been developed for specific purposes of polymeric nano-fibers, some include surface deposition, composites, and chemical adjustments. Polymeric nano-fibers must be also pyrolyzed to generate carbon nano-wires with conductive capabilities [6] for electrochemical sensing and energy storage purposes.

Nanotechnology has explored different polymer patterning techniques to integrate carbon nano-wires structures. One technique is known as far-field electrospinning, a process in which electrified jets of polymer solution are dispensed to synthesize nano-fibers which then are pyrolyzed at high temperatures. One sub-technique derived from electrospinning is near field electromechanical spinning or EMS. EMS has proved to deliver high control in

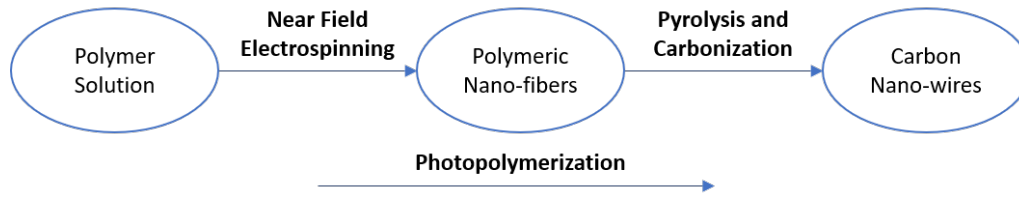


FIGURE 1.1: Fabrication process of carbon nano-wires to achieve through the proposed dissertation.

patterning polymeric nano-fibers. [2]

The proposal is to continue the previous work done in regards of 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. [2] This research proposal is intended to focus on electro-mechanical spinning processes only, to bring off polymer solutions that can be electrospun by near field electrospinning (NFES), photopolymerized and pyrolyzed into conducting carbon nano-wires. The polymer solutions described in [2] are to be amended to achieve the goal mentioned in the previous statement.

Near-field electrospinning or NFES allows large scale manufacturability combined with controlled guidance. [6] 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. [6] the current state-of-the-art synthesis processes for polymer nano-fibers lack to yield precise, inexpensive, fast, and continuous manufacturing properties.

2 Problem Definition and Motivation

[Chapter ready for review]

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. The problem relays on the fact that it had been known that most polymers are non-graphitic [4]. In the past years photon polymerization processes have been applied to the fabrication of nano-structures with the use of a photoresist. [1] Photon polymerization techniques deliver patterning resolutions with nano-scale tolerances for the production of highly detailed structures, [5] However, it is typical of photon polymerization processes to yield small objects with waste resins that are often toxic. [8]

On the other hand, electrospinning has been acknowledged for as a process with promising results at nano-structure fabrication [1], 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. [2] shows 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 [2], mechano-electrospinning is an early technology invention, and brings new challenges, such as the reproducibility of carbon nano-wire production.

Since electrospinning seems to be a better alternative for carbon nano-wire synthesis 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 potential applications in diverse areas that take advantage of the nano-scale properties. [9] Carbon nano-materials are suitable for the catalysis, adsorption, carbon capture, energy and hydrogen storage, drug delivery, bio-sensing and cancer detection. [9] However most application are not currently feasible due to the lack of a continuous, simple and reproducible fabrication method. 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.

3 Hypothesis and Research Questions

[Chapter ready for review]

3.1 Research Hypothesis

The rheological properties of polymer solutions along with synthesis parameters (stage velocity, voltage, dispense rate) can be amended to obtain a low voltage electrospun-able, photopolymerizable and graphitizable fibers for the synthesis of carbon nano-wires with specified dimensions (diameter and length).

3.2 Research Questions

- Are there any evidence of carbon nano-wire fabrication through electrospun-able and pyroizable 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 a electrospun-able and pyroizable polymer solution?
- Are there any efforts employed to the design of polymer solutions that can be electrospun, photopolymerized, and pyrolyzed into conducting carbon nanowires?
- Are the fabrication parameters defined in [2] optimal for the synthesis of carbon nano-wires through near-field electromechanical spinning?

4 Objectives

[Chapter ready for review]

4.1 General objective

Exercise the practice and feasibility of a new synthesis process to achieve mass scale manufacturing of carbon nano-wires in an inexpensive, continuous, simple and reproducible manner.

4.2 Particular 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.

5 Theoretical Framework

[Chapter under work]

5.1 Electro-Mechanical Spinning

Diverse polymer patterning techniques have been developed to integrate and synthesize carbon nano-wires. A typical technique is electrospinning. Electrospinning requires the application of an electrostatic force to a polymer solution to spin fibers. The applied electric field, the solution conductivity, jet length, solution viscosity surrounding gas, flow rate and the collector geometry are important parameters that influence the fiber formation during the spinning. [7] Two sub-techniques can be derived from electrospinning depending on the distance between the dispensing electrode and the collector. The process in which the electrospun jet can be controlled near the tip is called NFES or near-field electrospinning. [3] Moreover, if the distance between the collector and the dispensing needle is farther, the configuration is known as FFES or far-field electrospinning. [7]

5.2 Carbon nano-fibers

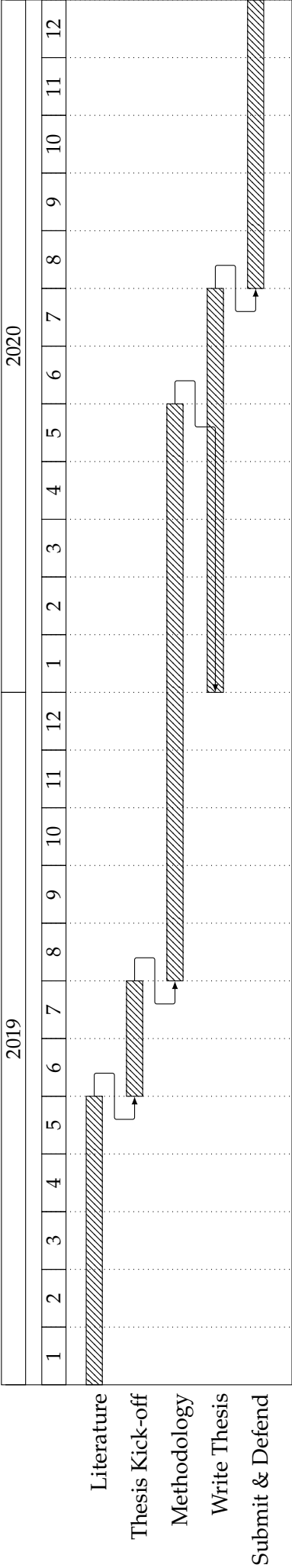
Carbon nano-wires (CMWs) are known as long, thin strings with diameters between 10 and 1 thousand nm; composed mostly by carbon atoms aligned parallel to the long axis of the fiber. [7] Carbon nano-wires are different from carbon tubes, as CMWs are not composed by graphene sheets in cylindrical form. [7]

6 Methodology

[Chapter under work]

7 Work Plan

[Chapter under work]



References

- [1] Jan Boer and Clemens Blitterswijk. *Tissue Engineering*. Ed. by Academic Press of Elsevier AP. 2nd. Safary O Reilly, 2014. URL: <https://learning.oreilly.com/library/view/tissue-engineering-2nd/9780124201453/XHTML/B9780124201453000109/B9780124201453000109.xhtml>.
- [2] Braulio Cárdenas. "Advanced Manufacturing Techniques for the Fabrication and Surface Modification of Carbon Nanowires". In: (2017), p. 160.
- [3] Albert Cisquella-Serra et al. "Study of the electrostatic jet initiation in near-field electrospinning". In: *Journal of Colloid and Interface Science* 543 (May 2019), pp. 106–113. ISSN: 0021-9797. DOI: [10.1016/J.JCIS.2019.02.041](https://doi.org/10.1016/J.JCIS.2019.02.041). URL: <https://0-www-sciencedirect-com.millennium.itesm.mx/science/article/pii/S0021979719302152>.
- [4] Rosalind Elsie Franklin. "Crystallite growth in graphitizing and non-graphitizing carbons". In: *Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences* 209.1097 (Oct. 1951), pp. 196–218. ISSN: 2053-9169. DOI: [10.1098/rspa.1951.0197](https://doi.org/10.1098/rspa.1951.0197). URL: <http://www.royalsocietypublishing.org/doi/10.1098/rspa.1951.0197>.
- [5] Kolin C Hribar et al. "Light-assisted direct-write of 3D functional biomaterials." In: *Lab on a chip* 14.2 (Jan. 2014), pp. 268–75. ISSN: 1473-0189. DOI: [10.1039/c3lc50634g](https://doi.org/10.1039/c3lc50634g). URL: <http://www.ncbi.nlm.nih.gov/pubmed/24257507>.
- [6] Marc J. Madou et al. "Controlled Continuous Patterning of Polymeric Nanofibers on Three-Dimensional Substrates Using Low-Voltage Near-Field Electrospinning". In: *Nano Letters* 11.4 (2011), pp. 1831–1837. ISSN: 1530-6984. DOI: [10.1021/nl2006164](https://doi.org/10.1021/nl2006164).
- [7] S.K. Nataraj, K.S. Yang, and T.M. Aminabhavi. "Polyacrylonitrile-based nanofibers—A state-of-the-art review". In: *Progress in Polymer Science* 37.3 (Mar. 2012), pp. 487–513. ISSN: 0079-6700. DOI: [10.1016/J.PROGPOLYMSCI.2011.07.001](https://doi.org/10.1016/J.PROGPOLYMSCI.2011.07.001). URL: <https://0-www-sciencedirect-com.millennium.itesm.mx/science/article/pii/S0079670011000931>.
- [8] Aleksandr Ovsianikov et al. "Engineering 3D cell-culture matrices: Multiphoton processing technologies for biological and tissue engineering applications". In: *Expert review of medical devices* 9 (Sept. 2012). DOI: [10.1586/erd.12.48](https://doi.org/10.1586/erd.12.48).
- [9] M.T.H Siddiqui et al. "Fabrication of advance magnetic carbon nano-materials and their potential applications: A review". In: *Journal of Environmental Chemical*

Engineering 7.1 (Feb. 2019), p. 102812. ISSN: 2213-3437. DOI: [10.1016/J.JECE.2018.102812](https://doi.org/10.1016/j.jece.2018.102812). URL: <https://0-www-sciencedirect-com.millennium.itesm.mx/science/article/pii/S2213343718307358>.