INSTITUTO TECNONÓLOGICO Y DE ESTUDIOS
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MASTERS THESIS PROPOSAL

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

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# Declaration of Authorship

I, Antonio Osamu KATAGIRI Tanaka, declare that this thesis titled, "Fabrication of graphitic-carbon suspended nanowires through mechanoelectrospinning of photocrosslinkable polymers" 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.
- Where any part of this thesis has previously been submitted for a degree or any other qualification at this University or any other institution, this has been clearly stated.
- Where I have consulted the published work of others, this is always clearly attributed.
- Where I have quoted from the work of others, the source is always given. With the exception of such quotations, this thesis is entirely my own work.
- I have acknowledged all main sources of help.
- Where the thesis is based on work done by myself jointly with others, I have made clear exactly what was done by others and what I have contributed myself.

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INSTITUTO TECNONÓLOGICO 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 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, electrospinning, NFES

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# List of 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**errey *or* Campus **M**on**t**erre**y** |
| **NFES** | **N**ear **F**ield de **E**lectro**s**pinning |
| **USA** | **U**nited **S**tates of **A**merica |
| **UV** | **U**ltra**v**iolet |

# List of Symbols

| Symbol | Name | Unit |
|---|---|---|
| $\omega$ | angular frequency | rad |

# 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. [7] Carbon nano-materials are suitable for catalysis, adsorption, carbon capture, energy and hydrogen storage, drug delivery, bio-sensing, and cancer detection. [7] 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. [7]

This document bestows 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, pyrolization, 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 led to the study of 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 are

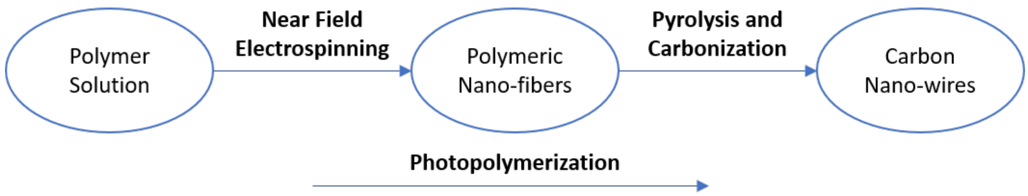


FIGURE 1.1: Fabrication process of conductive carbon nano-wires to achieve through the proposed dissertation.

then 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 patterning polymeric nano-fibers. [2]

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. [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 by Cardenas [2] 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. [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. Madou et al. [6] 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 Problem definition and motivation

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. [1] Photopolymerization techniques deliver patterning resolutions with nano-scale tolerances through two-photon lithography for the production of highly detailed structures [4].

On the other hand, electrospinning has been acknowledged 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. Cardenas [2] 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 [2], 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 potential applications in diverse areas that take advantage of the nano-scale properties. [7] Carbon nano-materials are suitable for the catalysis, adsorption, carbon capture, energy and hydrogen storage, drug delivery, bio-sensing and cancer detection. [7] 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. [5]

## 1.2 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 [3] and Cardenas [2] 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.

## 1.3 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?

## 1.4 Objectives

### 1.4.1 General objective

Study the practice and feasibility of a new fabrication process to achieve mass scale manufacturing of carbon nano-wires in an inexpensive, continuous, simple and reproducible manner; by the integration of mechano-electrospinning technique.

### 1.4.2 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.

## 1.5 Dissertation Outline

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