INSTITUTO TECNONÓLOGICO Y DE ESTUDIOS SUPERIORES DE MONTERREY

MASTERS THESIS PROPOSAL

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

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The committee members, hereby, recommend that the proposal by Antonio Osamu KATAGIRI Tanaka to be accepted to develop the thesis project as a partial requirement for the degree of Master of Science in Nanotechnology (MNT).

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List of Abbreviations

ITESM	**I**nstituto **T**ecnonólogico y de **E**studios **S**uperiores de **M**onterrey
CEM	**C**ampus **E**stado de **M**éxico
MNT	**M**aestría en **N**ano**t**ecnología *(Master of Science in Nanotechnology)*
CNWs	**C**arbon **N**ano-**w**ire**s**
EMS	**E**lectro**m**echanical **S**pinning
FFES	**F**ar **F**ield de **E**lectro**s**pinning
NFES	**N**ear **F**ield de **E**lectro**s**pinning
SU-8	a photoresist

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 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 frabication 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 a 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. [12] Carbon nano-materials are suitable for the catalysis, adsorption, carbon capture, energy and hydrogen storage, drug delivery, bio-sensing and cancer detection. [12] 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. [12]

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, 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 [7] for electrochemical sensing and energy storage purposes.

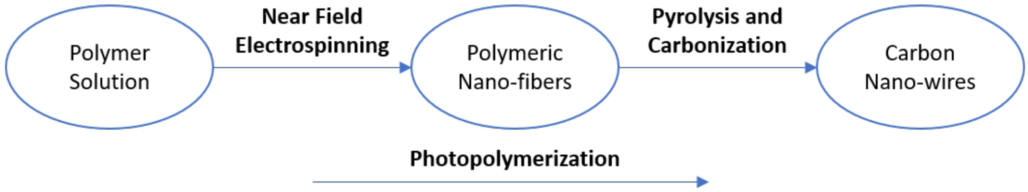


FIGURE 1.1: Fabrication process of carbon nano-wires to achieve through the proposed dissertation.

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 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.

Traditional near-field electrospinning or NFES allows large scale manufacturability combined with controlled guidance. [7] 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. [7] 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 lack of research relays on the fact that in the past years, it was assumed that most polymers are non-graphitic through pyrolysis [4]. In the past years photon polymerization processes have been applied to the fabrication of nano-structures with the use of a epoxy based photoresist. [1] Photon polymerization techniques deliver patterning resolutions with nano-scale tolerances for the production of highly detailed structures [5].

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. Cárdenas [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. 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. [12] Carbon nano-materials are suitable for the catalysis, adsorption, carbon capture, energy and hydrogen storage, drug delivery, bio-sensing and cancer detection. [12] 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 cinstituent points of the pattern can only be addressed at the same time, and the process requires the pattern to be encoded into a mask. [6]

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 through rheological analyses 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

- Is there any evidence of carbon nano-wire fabrication though electrospunable 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 a electrospunable 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?

- Are the optimal fabrication parameters defined [2] for the synthesis of carbon nano-wires through near-field electromechanical spinning?

4 Objectives

[Chapter ready for review]

4.1 General objective

Study 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; by the integration of mechano-electrospinning technique.

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 Photoresists

The electronic industry requires sustainable raw material supply for its development [15]. Photoresists are a type of raw material used in microelectronics, which is composed by four main elements: a polymer (resin), a photoactive compound, a solvent, and an additive [10]. The additive requires to be with a low molecular weight as it is intended to act as a photosensitive material. Photoresists are used within the manufacturing process of printed circuit boards [14]. Photoresists are classified into two categories. The resist is defined as positive if the radiation exposed material is soluble in photoresist developer; otherwise, for negative photoresist the exposed material remains to stay in the photoresist surface as it crosslinks upon exposure [6, 11]. In the manufacturing process of a semiconductor, the radiation sources which are often used in a lithography process are ultraviolet (UV) and X-ray [8].

The polymeric material is available on the broad market either in liguid or solid state; *MicroChem Corp.* (Westborough, MA, USA) is the principal provider of SU-8 photoresist. SU-8 and similar photoresists are inexpensive with good adhesion on the semiconductor surface and high sensitivity [14]. Epoxy resins are copolymer-thermosetting plastics which are normally produced by a chemical reaction process that involves epichlorohydrin and bisphenol-A compound [13]. A epoxy-based polymer is typically used to produce patterns by lithography with the application of UV radiation. Lithography is a technique to transfer patterns from a mask and then transferred onto the substrate [6, 16]. SU-8 is a epoxy-based negative photoresist with the advantages of being inexpensive with good mechanical properties, good chemical resistance, and good electrical isolation [16]. SU-8 photoresists are used in the production processes of MEMS [17]. Photoresist-wise, the contrast and quality level of UV radiation lithography is affected by the wavelengths of radiation sources. The higher the sensitivity of the material, the better is the lithography process as it absorbs radiation energy with ease to perform photochemical reactions in forming patterns [17].

In summary, a photoresist is a "epoxy-based resin (polymeric) material which changes its dissolution rate in a liquid solvent, called a developer, under high energy radiation.“ [6]

5.2 Electro-Mechanical Spinning

A number of techniques have being develop for the fabrication of nanofibers, such as arc discharge [22], chemical vapor deposition, laser ablation [23], and vapor growth [21]. Nonetheless, those processes are expensive due to either the low product yield or the expensive equipment required. The electrospinning method can produce fibers with a range of diameters between 10 nm and 10 μm

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. [9] 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. [9]

5.3 Carbon nano-fibers

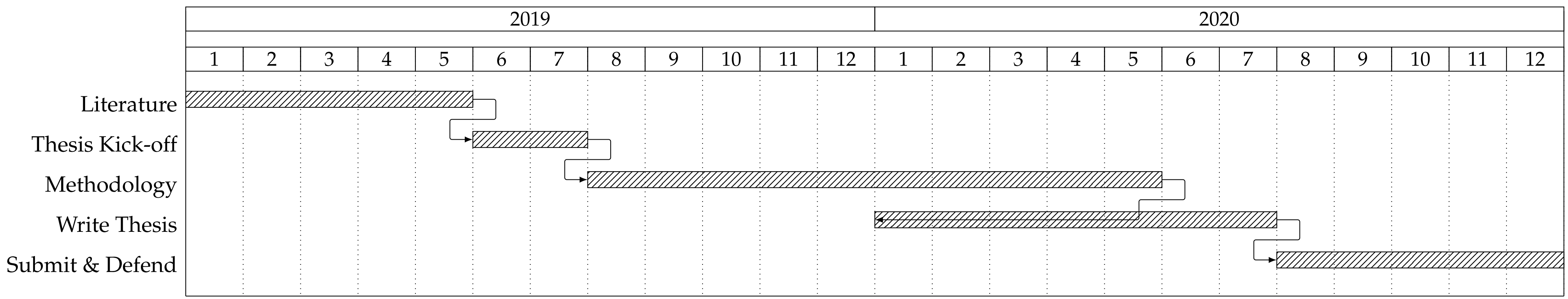
Carbon nano-wires (CMWs) are known as long, thin strings with diameters between 10 and 1 thousand nm; composed mostly by carbon atoms aligned parallel to the long axis of the fiber. [9] Carbon nano-wires are different from carbon nano-tubes, as CMWs are not composed by graphene sheets in cylindrical form. [9]

6 Methodology

[Chapter under work]

7 Work Plan

[Chapter under work]



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