Instituto Tecnonólogico y de Estudios Superiores de Monterrey

Masters Thesis Proposal

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

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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.
- 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.

Signed:

Date:

"No great discovery was ever made without a bold guess."

Newton, Sir Isaac
In W.I.B. Beveridge
The Art of Scientific Investigation
Scientist (p. 145)

INSTITUTO TECNONÓLOGICO Y DE ESTUDIOS SUPERIORES DE MONTERREY

Abstract

Faculty: Nanotechnology

School of Engineering and Sciences

Master of Science in Nanotechnology (MNT)

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

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**errey
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
ω	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. 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

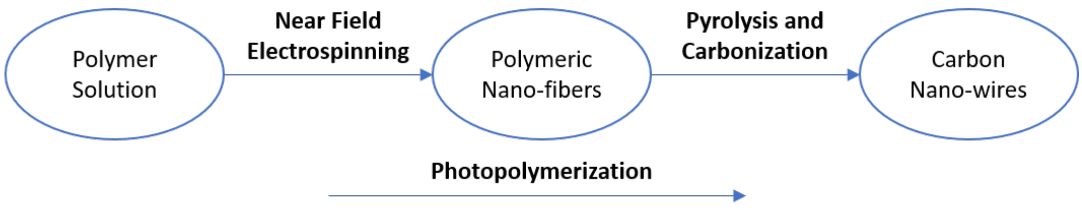

FIGURE 1.1: Fabrication process and characterization techniques of conductive carbon nano-wires to achieve through the dissertation.

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

Carbon is a versatile element capable to form a number of bonds with other elements or with itself. Furthermore, carbon orbitals have the ability to hybridize in sp1, sp2 and sp3 configurations, hence the existence of different types of allotropes, see Figure **??**. Currently, the three carbon allotropes (diamond, amorphous carbon and graphite), have been joined by additional ones deriving from synthetic processes (such as graphene, carbon nano-tubes, fullerenes, carbon nanohorns, nanodiamonds) [[12]; Fig. 1].

The interest in CBNs has increased exponentially in the last decades, first with the discovery offullerenes (1985), then with that of carbon nanotubes (CNTs; 1991) and finally with the synthesis of graphene (GR) (2004).

The properties of these CBNs make them widely used in many fields ranging from material science [13], energy production and storage [14], environmental sciences [15,16], biology [17-19] and medicine [20,21]. Table 1 summarizes the main properties of the most common CBNs [22-25]:

Among the many carbon nanomaterials, CNTs and GR are currently the most popular representatives and have been extensively studied for their excellent mechanical strength, electrical and thermal conductivity and optical properties. The Young's modulus and tensile strength of CNTs and GR can reach 1 TPa and 130 GPa respectively [20,21]. Carrier mobility of graphene is around 860 $cm^2V^{-1}s^{-1}$ (hole mobility of 844 $cm^2V^{-1}s^{-1}$ and carrier mobility of 866 $cm^2V^{-1}s^{-1}$), and the current density of metallic CNTs is orders of magnitude higher than those of metals such as copper [26,27]. Thermal conductivities of CNTs and GR are about 3000e3500W/mK and 5000 W/mK respectively [28]. The light absorption ratio of single-layer graphene is limited to 2.5% [29]. A large amount of the research efforts were focused on exploiting these properties for various applications including electronics, biological engineering, filtration, lightweight/strong composite materials, photovoltaic and energy storage [30-32]. CNTs and GR are naturally good electrical conductors and their biocompatibility can be modulated [33], making them good candidates for improving electrodes for neural interfaces. Electrical recording or stimulation of nerve cells is widely employed in neural prostheses (for hearing, vision, and limb-movement recovery), in clinical therapies (treating Parkinson's disease, dystonia, and chronic pain), as well as in basic neuroscience studies. In all these applications, electrodes of various shapes and dimensions stimulate and/or record neuronal activity to directly modulate behavior or to interface machine. The performance of the electrodes can be significantly improved by implementing the device with nanomaterial-based coatings (such as CBNs), since their high surface area can drastically increase charge injection capacity and decrease the interfacial impedance with neurons [34].

It is well known that the morphology of the electroactive material play an important role in electrochemical systems, once the intimate contact at the electrode/electrolyte interface is crucial to guarantee the charge transfer process [11,12]. In this sense, nanostructured electroactive materials such as nanorods [13], nanofiber [14], nanoflowers [15,16], nanowires [17,18], among others [19,20], are being widely used to obtain improved electrochemical properties such as higher charge/discharge rate and improved task to accommodate stress due to volume changes occasioned by intercalation process.

1.1.2 Carbon nanowires

Carbon nanofibers (CNFs) have been classified as linear, sp2-based discontinuous filaments, where the aspect ratio is greater than 100 [207]. Depending on the angle of the graphene layers that compose the filament, CNFs have even been classified as stacked (graphene layers stacked perpendicularly to the fiber axis) or herringbone/cupstacked (graphene layers stacked at an angle between parallel and perpendicular to the fiber axis) [208].

Nanowires are one-dimensional, anisotropic structures, small in diameter, and large in surface-to-volume ratio. These characteristics confer to the nanowires special physical properties than those of traditional scale and dimensionality materials, such as electrical, optical thermal and mechanical properties. However, this make this kind of materials to have properties deeply dependent on their surface condition and geometrical configuration [21]. The transport properties in the 1D nanostructures like the nanowires are affected by wire diameter, surface conditions, crystal quality, crystallographic orientation and material composition, thus the synthesis conditions are a crucial factor to obtain reproducible and high-quality nanowires for different application [21].

The typical lengths and diameters of carbon nanofibers are in the ranges of 5e100mm and 5e500 nm, respectively [209]. CNTs and GR are the most studied carbon nanomaterials for neural interfaces, however CNFs are also attractive in bio-interfacing developments due to their chemical and physical properties [1]: CNFs are chemically stable and inert in physiological environment [2], they are biocompatible for long-term implantation due to CNFs solid carbon skeleton [3], they are electrically robust and conductive for signal detection [4], they can be manufactured into 3D structures allowing intra-tissue and intracellular penetration [210], CNFs possess high surface-to-volume ratio, which greatly reduces electrical impedance, and [5] ultra-micro scale sizes that provide high spatial resolution. CNFs have been applied as promising materials in many fields, such as energy conversion and storage, reinforcement of composites and self-sensing devices.

In addition, CNF based materials have been developed as electroconductive scaffolds for neural tissues to facilitate communication through neural interfaces. Electrical fields are able to enhance and direct nerve growth [211], therefore electroconductive scaffolds have been applied to enhance the nerve regeneration process, not only providing physical support for cell growth but also delivering the functional stimulus. CNFs may represent novel, versatile neural interfaces, being capable of dual-mode operation by detecting electrophysiological and neurochemical signals, not only at the extracellular level with high spatial resolution, but also at the intracellular level by penetrating into single neurons [9].

Despite the longstanding experience on these nanomaterials and the deep knowledge of the CNFs-neuron interface in vitro, in vivo experiments on their possible application for the treatment of brain and spinal cord injuries or diseases are still limited to few examples [53,212,213]. In the first report CNFs impregnated with subventricular stem cells were employed to promote neuroregeneration after experimental stroke [53]. The animals receiving the CNF-based treatment show reduction of the infarcted volume as well as recovery ofmotor and somatosensory activity. These data indicate that CNFs are optimal support material for neuronal tissue regeneration [53].

Recently, Guo and collaborators [104] developed a polymer-based neural probe with CNFs composites as recording electrodes via the thermal drawing process [213]. They demonstrated that in situ CNFs alignment was achieved during the thermal drawing, which contributes to a drastic improvement of electrical conductivity by 2 orders of magnitude compared to a conventional polymer electrode. The resulting neural probe has a miniature footprint, with a recording site reduced in size to match single neuron, yet maintaining impedance value able to capture neural signals. In chronic settings, long-term reliable electrophysiological recordings with single-spike resolution and minimal tissue response over extended period of implantation in wild-type mice were shown [213].

Nanostructured materials are particularly good for supercapacitor applications, providing high surface area, which leads to a high specific capacitance [22]. Compared to 3D and 2D materials, 1D nanostructures have smaller dimension and higher aspect ratio, improving the transport of electrical carriers in one controllable direction and also can be exploited as elements in different kinds of nanodevices [23]. In this way, nanowires have been satisfactorily used in supercapacitor electrodes due to their reduced ion diffusion path in comparison with 2D and 3D nanostructures, leading in higher charge/discharge rates [22,24].

Amongst the innumerous materials used to obtain 1D nanostructures, such as, carbon, silicon, transition metal oxides, the 1D nanostructured conductive polymers are a important group to fabricate energy storage devices, due their attractive characteristic, such as, mechanical properties, electrical conductivity, low cost, easy processing, high surface area and unique electroactive behavior, including high voltage window and high-doping rate during charge-discharge process [25]. During the charge/discharge process in the conducting polymer occur the insertion/desertion ions from the electrolyte in the polymer backbone that could result in swelling and shrinkage of the polymer chain, leading to mechanical degradation of the electrodes and fading the electrochemical performance [26]. An alternative to diminishment this drawback of the conductive polymers is fabricate composites that could improve the stability and conductivity of the electrodes [27].

In this way, composites based on conducting polymers and carbon or metal oxides materials in a nanowire architecture are a good strategy to develop high-performance devices due to the combination of the electrochemical properties of the polymer and/or composites with the morphological advantages of the nanowires. These combination results in large interface between electrode/electrolyte, effective electronic transport pathway, short ion diffusion distance and easy relaxation strain, which could improve both capacity/capacitance and rate performance of battery and supercapacitors devices, respectively [28]. Furthermore, the mechanical properties of nanowires allow the development of flexible devices, that require materials with versatile functionalities including high flexibility and foldability without losing its high power and energy density and long lifetime [29].

1.1.3 Nanowires synthesis

Numerous methods to prepare nanowires, which include template-assisted synthesis [30], vapor–liquid-solid (VLS) [31], electrodeposition [32], electrospinning [33], hydrothermal [34], also hierarchical arrangement techniques [35–37] to organize the nanowires have been studies in the last ten years. Nanowires based on organic, inorganic or hybrid materials have been applied in order to get single or composites nanomaterials for innumerous purposes, such as chemical and biochemical sensing devices, thermoelectric, optical, magnetic and electrical application. In this section, we are focusing on the synthesis of conducting polymer and composites to develop materials in nanowires architectures.

Synthesis of conducting polymer nanowires

1.1.4 *conclude that NFES is the way to go*

1.2 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. [16] Photopolymerization techniques deliver patterning resolutions with nano-scale tolerances through two-photon lithography for the production of highly detailed structures [17].

On the other hand, electrospinning has been acknowledged as a process with promising results at nano-structure fabrication [16], 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 potential applications in diverse areas that take advantage of the nano-scale properties. [1] Carbon nano-materials are suitable for the catalysis, adsorption, carbon capture, energy and hydrogen storage, drug delivery, bio-sensing and cancer detection. [1] 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. [18]

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 carbon nano-wires in an inexpensive, continuous, simple and reproducible manner; by the integration of mechano-electrospinning technique.

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

2.2 *conclude with a NFES fabrication parameter baseline to yield the desired fibres*

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

References

[1] 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.

[2] 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.

[3] 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.

[4] 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.

[5] 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.

[6] 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.

[7] 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.

[8] 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.

[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] 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.

[17] 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.

[18] 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.