

T.R.
GEBZE TECHNICAL UNIVERSITY
GRADUATE SCHOOL

DISPLAY OF ELECTRICAL PROPERTIES AND
APPLICATIONS OF GRAPHENE BASED
ELECTROCHEMICAL BIOSENSOR

ŞEYMA ERKAYA

A THESIS OF MASTER OF SCIENCE
DEPARTMENT OF INTERDISCIPLINARY
NANOSCIENCE AND NANOENGINEERING

ADVISOR: ASST. PROF. DR. NİHAN AYDEMİR

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T.C.
GEBZE TEKNİK ÜNİVERSİTESİ
LİSANSÜSTÜ EĞİTİM ENSTİTÜSÜ

GRAFEN TABANLI ELEKTROKİMYASAL
BİYOSENSÖRÜN ELEKTRİKSEL ÖZELLİKLERİNİN
VE UYGULAMALARININ GÖSTERİMİ

ŞEYMA ERKAYA

YÜKSEK LİSANS TEZİ
DİSİPLİNLERARASI NANOBİLİM VE
NANOMÜHENDİSLİK ANABİLİM DALI

DANIŞMAN: DR. ÖĞR. ÜYESİ NİHAN AYDEMİR

MAYIS 2025



MASTER of SCIENCE JURY APPROVAL FORM

A thesis submitted by Şeyma ERKAYA, defended on 20/05/2025 before the jury formed with the 03/02/2025 date and 2025/08 numbered decision of the GTU Graduate Administration Board, has been accepted as a MASTER of SCIENCE thesis in the Department of Nanoscience and Nanoengineering.

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ABSTRACT

This thesis aims to develop laser-scribed graphene (LSG) based electrochemical biosensors for fast, sensitive, in situ and reliable detection of biochemical analytes. Biosensors offer opportunities for sensitive, fast, low-cost and real-time diagnostics in many fields such as early disease diagnosis, environmental monitoring, food safety and drug delivery. The LSG fabrication technique has recently become a preferred technique for biosensor applications due to its excellent advantages such as chemical-free, direct printing and fast manufacturing process. Graphene has been selected as a suitable material for biosensor sensitivity due to its impressive conductivity, fast electron transfer, large and porous surface area, mechanical strength, thermal and chemical stability.

Within the scope of the study, graphene and graphene fiber electrodes with different parameters were produced by laser scribing method and graphene fiber electrodes produced by applying three different fluence values were compared among themselves according to their surface morphology, chemical and electrochemical properties; one of them, graphene and one graphene fiber, were selected for biosensor applicability. The morphological, chemical and electrochemical properties of these electrodes were characterized by scanning electron microscopy (SEM), Energy dispersive spectroscopy (EDS), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) techniques. Besides these analyses, the biosensor performance was evaluated by cyclic voltammetry (CV) in solvent prepared with ascorbic acid (AA) and phosphate buffered solution (PBS). Moreover, the surface modification of the electrodes was optimized to improve sensitivity and selectivity parameters. The results indicate that graphene electrodes fabricated by laser scribing offer high electrochemical activity and low limit of detection (LOD) values. This study digs that the development of laser-scribed graphene-based biosensors is an important step towards the creation of low-cost, portable and high-performance detection platforms. The broad application potential of these sensors, especially in areas such as healthcare, environment, biomedical applications, food industry and defense industry, is also evaluated.

Keywords: Graphene, Biosensor, Nanomaterials, Nanotechnology, Electrochemical

ÖZET

Bu tez, biyokimyasal analitlerin hızlı, hassas, yerinde ve güvenilir tespiti için lazerle çizilmiş grafen (LSG) tabanlı elektrokimyasal biyosensörler geliştirmeyi amaçlamaktadır. Biyosensörler, erken hastalık teşhisi, çevresel izleme, gıda güvenliği ve ilaç dağıtımı gibi birçok alanda hassas, hızlı, düşük maliyetli ve gerçek zamanlı teşhis fırsatları sunmaktadır. LSG üretim tekniği kimyasal içermeyen, doğrudan baskı ve hızlı üretim süreci gibi mükemmel avantajları nedeniyle son zamanlarda biyosensör uygulamaları için tercih edilen bir teknik haline gelmiştir. Grafen sahip olduğu etkileyici iletkenlik, hızlı elektrokron transferi, geniş ve porlu yüzey alanı, mekanik dayanımı, termal ve kimyasal kararlılık gibi özelliklerinden dolayı biyosensör hassasiyeti açısından uygun bir malzeme olarak seçilmiştir.

Çalışma kapsamında, farklı parametrelere sahip grafen ve grafen fiber elektrotlar lazerle çizdirme yöntemi ile üretilmiş ve üç farklı fluence değeri uygulanarak üretilen grafen fiber elektrotlar yüzey morfolojisi, kimyasal ve elektrokimyasal özelliklerine göre kendi aralarında karşılaştırılmış; bunlardan biri grafen biri de grafen fiber olmak üzere biyosensör uygulanabilirliği için seçilmiştir. Bu elektrotların morfolojik, kimyasal ve elektrokimyasal özellikleri taramalı elektron mikroskobu (SEM), Enerji dağıtıcı spektroskopisi (EDS) Raman spektroskopisi, X-ışını fotoelektron spektroskopisi (XPS) ve X-ışını kırınımı (XRD) teknikleriyle ayrıntılı olarak karakterize edilmiştir. Bu analizlerin yanı sıra, biyosensör performansı askorbik asit (AA) ve fosfat tamponlu çözelti (PBS) ile hazırlanan çözücüde döngüsel voltametri (CV) ile değerlendirildi. Ayrıca duyarlılık ve seçicilik parametrelerini iyileştirmek için elektrotların yüzey modifikasyonu optimize edildi. Sonuçlar, lazerle çizdirilerek üretilen grafen elektrotlarının yüksek elektrokimyasal aktivite ve düşük tespit limitleri (LOD) sunduğunu göstermektedir. Bu çalışma, lazerle çizilmiş grafen bazlı biyosensörlerin geliştirilmesinin düşük maliyetli, taşınabilir ve yüksek performanslı tespit platformlarının oluşturulmasına doğru önemli bir adım olduğunu ortaya koymaktadır. Bu sensörlerin özellikle sağlık, çevre, biyomedikal uygulamalar, gıda endüstrisi ve savunma sanayii gibi alanlardaki geniş uygulama potansiyeli de değerlendirilmiştir.

Anahtar Kelimeler: Grafen, Biyosensör, Nanomalzemeler, Nanoteknoloji, Elektrokimyasal

ACKNOWLEDGEMENTS

I would like to thank my thesis advisor, Asst. Prof. Dr. Nihan Aydemir, who mentored me with her knowledge, support and encouragement throughout my master's degree education. She enlightened my path at every stage with her valuable knowledge and experience. I am grateful to Asst. Prof. Osman Eksik for allowing me to use the laboratory facilities during my research and for his support in technical issues. I would also like to thank Research Assistant Dr. Okan Özdemir for his support and knowledge in the necessary analyzes during my studies. Finally, I would like to thank my dear family and friends who have always believed in me and supported me with their moral support throughout my education.

This thesis was supported by the Gebze Technical University Scientific Research Projects Coordination Office under the project numbers ADEP 2023-A-113-20.

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LIST OF SYMBOLS AND ABBREVIATIONS

AuNPs	: Gold Nanoparticles
AA	: Ascorbic Acid
ALD	: Atomic Layer Deposition
C	: Carbon
CHP	: Cyclohexyl-pyrrolidone
CO ₂	: Carbon dioxide
CV	: Cycle Voltametry
CVD	: Chemical Vapour Deposition
DMF	: Dimethylformamide
EDS	: Energy-Dispersive Spectroscopy
GO	: Graphene Oxide
IPA	: Isopropyl Alcohol
KCl	: Potassium Chloride
LPE	: Liquid Phase Exfoliation
LSG	: Laser Scribed Graphene
LSGF	: Laser Scribed Graphene Fiber
LOD	: Limit of Detection
MBE	: Molecular Beam Epitaxy
mm	: Milimeter
MNC	: Metal Nanoclusters
MOFs	: Metal Organic Frameworks
μm	: Micrometer
μM	: Micromolar
N	: Nitrogen
nm	: Nanometer
NMP	: N-Methyl-2-pyrrolidone
NPs	: Nanoparticles
O	: Oxygen
PBS	: Phosphate Buffer Solution
PEG	: Polyethylene Glycol
PET	: Polyethylene Terephthalate
PI	: Polyimide
PVD	: Physical Vapour Deposition
PVP	: Polyvinylpyrrolidone
SD	: Standart Deviation
SDS	: Sodium dodecyl sulfate
SEM	: Scanning Electron Microscopy
SiC	: Silicon Carbide
TMU	: Tetramethylurea
XPS	: X-ray Photoelectron Spectroscopy
XRD	: X-ray Diffraction

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1. INTRODUCTION

A biosensor is generally defined as an analytical device that can convert a biological or biochemical response into a measurable and actionable signal. Research and development in electrochemical biosensors have made a significant contribution to the field of biochemical analysis with high sensitivity, specificity and fast response times. **(Coroş et al., 2020).**

With its outstanding electrical, mechanical, chemical resistance, great surface area and stability characteristics, graphene has become a top candidate among the several materials under investigation to improve sensor performance. Two-dimensional graphene is made of sp²-hybridized carbon atoms arranged in a hexagonal lattice pattern resembling a honeycomb. **(Coroş et al., 2020).**

Especially for the detection of biochemical analytes, these features make it a suitable material for electrochemical uses in biosensor designs. Graphene-based electrochemical biosensors enhance signal transmission and detection accuracy by means of the electrical characteristics of the component. Combining graphene with biological recognition elements including antibodies, enzymes, nucleic acids, and aptamers allows these sensors to sensitively identify many different biomolecules, including proteins, DNA, glucose, and cholesterol. **(Kuila et al., 2011).**

Furthermore adding graphene to biosensor platforms speeds electron transfer, enables low detection limits, and multiplex analysis is made possible. With uses in medical diagnostics, environmental monitoring, food safety, defence, and biomedical research, these benefits have elevated graphene-based biosensors to the front of diagnostic technologies. **(Wanjari et al., 2023).**

Apart from their great functional adaptability, graphene-based biosensors present a scalable and environmentally friendly approach for analytical problems. A graphene-based biosensor depends critically on the electrode structure that detects the analyte. Among the several materials this electrode structure can incorporate are graphene, gold nanoparticles, carbon nanotubes, and conductive polymers. **(Aydemir et al., 2016).**

This work used graphene as the electrode material for the electrochemical biosensor because of its exceptional characteristics including mechanical stability, thermal

durability, and great electrical conductivity. Portable and wearable biosensor devices, which are rapidly in demand in point-of-care diagnostics and tailored healthcare, depend on these characteristics. Several nanotechnological fabrication methods are applied in graphene development. Among these techniques are liquid phase exfoliation (LPE), Hummer's method, atomic layer deposition (ALD), laser-scribed graphene (LSG), chemical vapour deposition (CVD). This implies that one can change the characteristics of the material to fit different needs. (Wanjari et al., 2023).

Particularly, laser-scribed graphene (LSG) has drawn interest because of its benefits including simple processing, reasonable cost, quick manufacturing, and direct obtaining of graphene structure of the desired design straight on flexible substrates. This work derived graphene and graphene fibre electrodes using the LSG method. After that, physicochemical and electrochemical techniques were used to characterise the materials in order to obtain more exact knowledge and grasp their features. With this fast, low cost and environmentally friendly technique, the fabrication process is realized with predetermined device parameters. Some features of this and all other fabrication techniques such as application details, advantages and disadvantages will be discussed in the following sections.

1.1. Purpose of the Study

This study focuses on the fabrication of graphene and graphene fiber structures by direct laser beam delivery on polyimide polymer. A Universal CO₂ laser system was used for the graphene and fiber electrodes produced by the laser-scribing (LSG), which is known to be fast, cost-effective, chemical-free, and environmentally friendly. To get the best conductivity from these graphene and fiber electrodes, different values for laser power and scanning speed were tried, and the best one was chosen. Then, this thesis focuses on investigating, comparing, and improving the surface chemistry, electrical conductivity, chemical bonding structure, surface defects, porous structure, and electrochemical properties of graphene and fiber electrodes for their integration into electrochemical biosensor applications.

At the same time, this study highlights the advantages of LSG over other fabrication methods by investigating the synthesis, characterization, and performance of graphene-based biosensors in detecting specific biochemical analytes such as ascorbic

acid (AA) and reacting against them in electrochemical tests such as cyclic voltammetry (CV). Moreover, this study aims to contribute to the optimization of future biosensor designs for improved analytical performance and wider applicability by clarifying the interplay between the electrical properties of graphene and biosensor properties.

In the following chapters of this thesis, the theoretical foundations, common fabrication methods, and electrochemical properties of graphene and biosensor structure will be reviewed, followed by an in-depth discussion on graphene-based electrochemical biosensors by presenting the physicochemical and electrochemical characterization methods applied. The results in this thesis will not only show how well graphene works as a biosensor, but they will also stress the importance of solving problems that come up in biochemical analysis. As a result, it aims to pave the way for innovations in fields focused on diagnostics, such as biomedical applications.

2. LITERATURE REVIEW

2.1. 2D Nanomaterials

Two-dimensional (2D) nanomaterials are defined as a class of two-dimensional nanomaterials consisting of one or several atomic layers with atomic-scale thicknesses. Due to their high surface area and good mechanical, electronic and optical properties, they are attracting attention for applications in many fields such as biosensors, energy storage, defense industry, pharmaceutical industry and solar cells. Two-dimensional nanomaterials with great potential include graphene, mxene, hexagonal boron nitride (h-BN), and transition metal dichalcogenides (e.g., MoS₂). Among these nanomaterials, graphene has evolved into a rather popular nanomaterial in sensing technologies because of its exceptional mechanical strength, thermal stability, and great electrical conductivity. Furthermore among 2D nanomaterials, graphene is well-known for its great adaptability and quick manufacturing possibilities. **(K. Li et al., 2023).**

2.2. Graphene

2.2.1. Carbon Element

Carbon, symbolized by the “C” and widely found in nature in various forms, is a non-metallic element with atomic number 6 in the periodic table. Graphene, fullerene, diamond, carbon nanotube (CNT) and graphite are some of the various carbon allotropes. The most important factors for categorizing these carbon allotropes are their basic properties such as their geometric structure and atomic size. **(Kour et al., 2020a).** The ability of carbon atoms to form allotrope structures with these various properties is made possible by their ability to form quadruple bonds. The carbon atom is also a fundamental building block that constitutes the basic components of all living things, especially the human body. **(Y. Zhang et al., 2023).**

2.2.2. Definition of Graphene and Applications

Graphene is an allotropic form of one-atom thick carbon atom with various nanotechnological production methods. Graphene is a 2D nanomaterial formed by the aggregation of C atoms, exhibiting a hexagonal lattice in a honeycomb structure with sp^2 hybridization (Safari et al., 2023). Single-layer graphene was first theoretically discovered in 1947 by a Canadian physicist, P.R. Wallace. Later, in 1962, H.P. Boehm, a German chemist, and his teammates first coined the term “graphene” in 1986 after the experimental discovery of graphene was completed. In 2004, it was first produced and studied by Russian-British physicist K. Novoselov and Dutch-British physicist A. Geim (Kour et al., 2020a).

Research and studies on graphene, which has a recent history of discovery, are still ongoing. Its advantageous properties like excellent electrical and thermal conductivity, large surface-to-volume ratio, thermal stability, mechanical strength, easy surface functionalization and fast electron mobility make graphene a unique nanomaterial. (Safari et al., 2023).

Graphene is also known as an important structural component of carbon allotropes such as 1D carbon nanotubes (CNTs), 0D fullerenes and 3D graphite.

In addition to these properties, it finds a considerable application in biosensor studies due to its large surface area and enhanced electron mobility. Graphene, defined as a 2D nanomaterial, has many applications such as medical diagnostics, health monitoring, drug delivery, energy storage, fuel cells, solar cells, nanoelectronics and biomedical applications as well as biosensor applications. (Zhu et al., 2017). More specifically, graphene, which is hundreds of times stronger than steel, but very lightweight, has exceptional conductivity and transparency, making it a suitable material for use in electronic devices such as solar cells, OLED and touch screens, and sensor technology. Its high surface area and conductivity enables the performance of storage devices such as supercapacitors and batteries to be improved. It is also used in the aerospace, automotive and defense industries by mixing with materials such as metals and polymers to produce lighter, stronger and more flexible composite materials. In addition, thanks to its biocompatibility, it is frequently used in tissue engineering, drug delivery, biomedical device technology, medicine and biotechnology. (Feng & Liu, 2011). In this study, a graphene layer was produced by

laser scribing method to obtain a graphene electrode of electrochemical biosensor for the electrochemical detection of ascorbic acid.

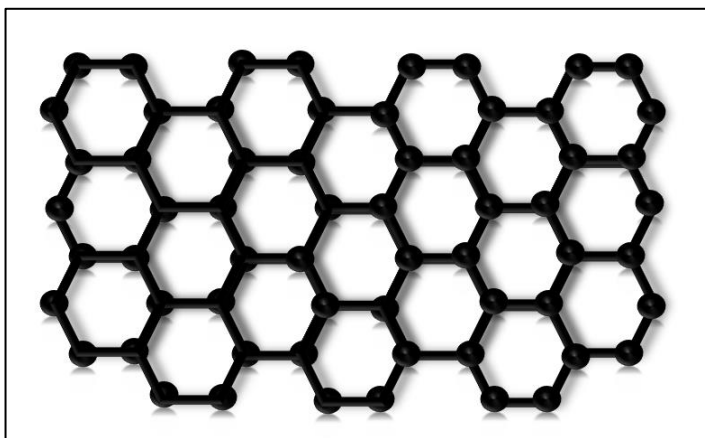


Figure 2.1.: Graphene chemical structure.

2.3. Graphene Fabrication Methods

Graphene, a monolayer of C atoms organized in a hexagonal lattice, has emerged as a fundamental material in nanotechnology owing to its outstanding electrical, mechanical, and thermal characteristics. Nonetheless, harnessing graphene's potential in applications from electronics to biosensors necessitates meticulous production techniques to yield high-quality graphene with adjustable features. Graphene fabrication methods are mainly classified into two categories: top-down and bottom-up. (Arole & Munde, 2014).

Top-down approaches entail the disaggregation of bulk graphite to yield graphene layers, typically via mechanical, chemical, or physical processes. These procedures, including exfoliation, ball-milling, and oxidation, facilitate scale production but may result in structural defects. In contrast, bottom-up approaches fabricate graphene incrementally, usually on a substrate, employing techniques such as chemical vapor deposition (CVD) and epitaxial growth, which produce high-purity, homogeneous graphene sheets but may entail elevated prices and intricate procedures. Each production method presents unique benefits and facilitates customized applications in nanotechnology where particular graphene properties, like conductivity, flexibility, and layer thickness, are essential. (Adetayo et al., 2019).

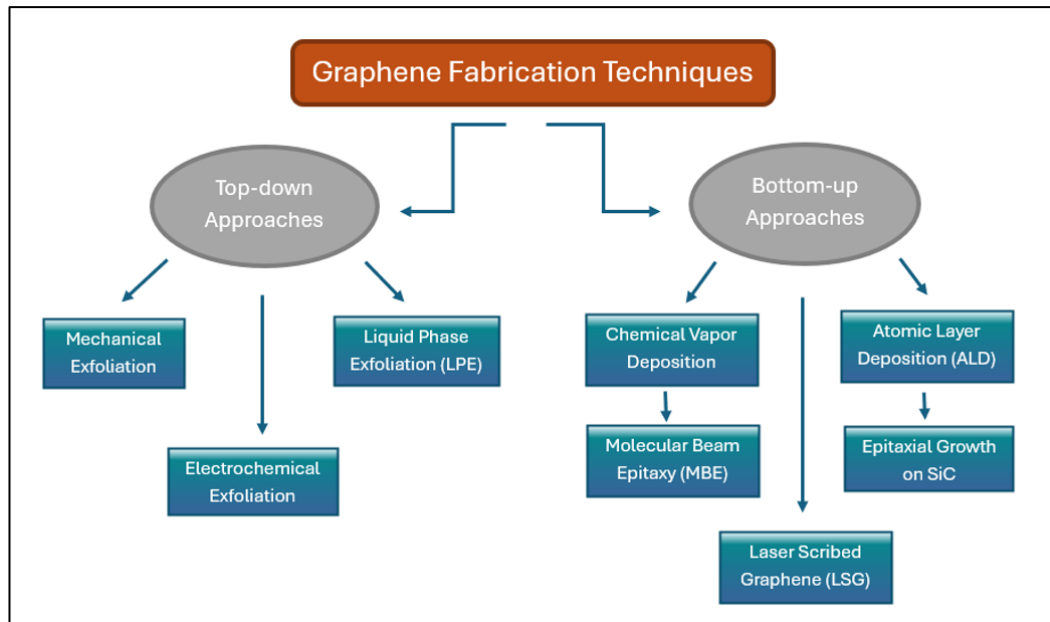


Figure 2.2.: Graphene fabrication methods in nanotechnology.

2.3.1. Top-Down Approach

Top-down approaches are methods of starting with bulk materials, such as graphite, and separating them into individual or multilayer graphene sheets. These methods are applied to separate graphene layers, balancing production efficiency, scalability and material quality. They include mechanical, chemical or electrochemical processes and approaches such as ball-milling. It can be said to be generally more cost-effective and scalable than other methods, but structural defects and impurities can be obtained as disadvantages. **(Nano-Materials: Science of Bottom-up and Top-down: IETE Technical Review: Vol 24, No 1, n.d.).**

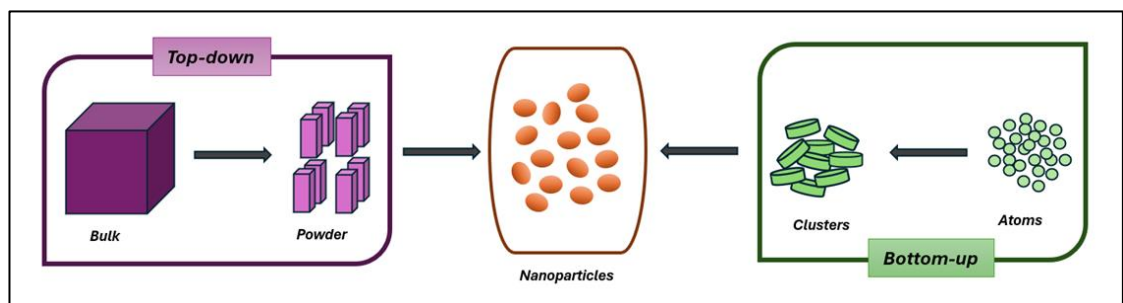


Figure 2.3.: Top-down and Bottom-up approaches in nanotechnology.

2.3.1.1. Mechanical Exfoliation

A process of peeling graphene layers from graphite using adhesive tape. It produces high-quality, single-layer graphene but has limited scalability. Typically used in laboratory environments for basic research. (Olatomiwa et al., 2022).

2.3.1.2. Liquid Phase Exfoliation (LPE)

Graphite is dispersed in solvents such as N-Methyl-2-pyrrolidone (NMP), Dimethylformamide (DMF), Tetramethylurea (TMU), Cyclohexyl-pyrrolidone (CHP), Sodium dodecyl sulfate (SDS), Isopropanol (IPA), ethanol, polyvinylpyrrolidone (PVP) and polyethylene glycol (PEG) and sonicated into separate graphene layers. Each solvent has advantages and disadvantages such as cost, toxicity and environmental considerations. This method offers scalable production of graphene nanosheets but often results in multilayered graphene. It often requires optimization to minimize its defects. (Z. Li et al., 2020).

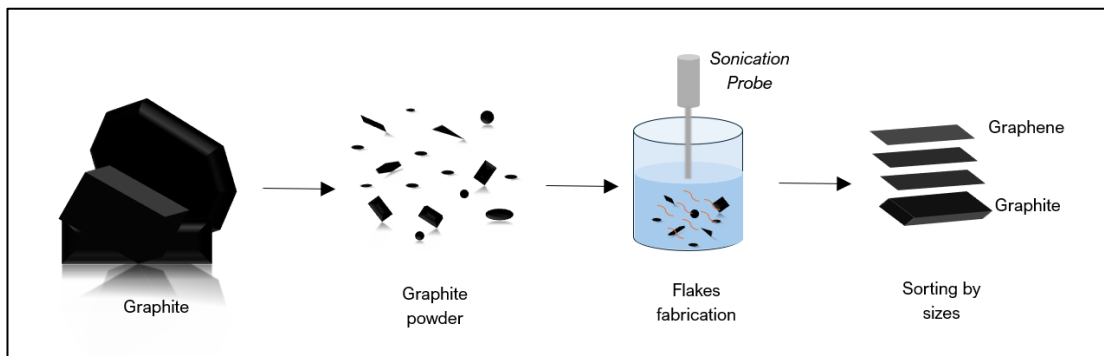


Figure 2.4: Liquid Phase Exfoliation (LPE) method in nanotechnology.

2.3.1.3. Electrochemical Exfoliation

An electrochemical cell is used to separate graphene layers from graphite electrodes. It produces graphene with functional groups that improve solubility and ease of processing. The process can be fine-tuned for special graphene properties. (Adetayo et al., 2019).

2.3.1.4. Ball Milling

Ball milling is one of the scalable, top-down methods of graphene synthesis that involves mechanically stripping stacked graphite using high-energy collisions in a

rotating ball mill (as shown in **Figure 2.5.**). In ball milling, the addition of steel balls of different sizes generates shear and compressive forces that break van der Waals bonds and produce graphene sheets as a result of high-energy collisions. Ball milling can be used for production in both dry and wet conditions. Solvents or surfactants can be added to prevent aggregation during milling. Although it is an easy and low-cost method to produce various nanocomposite materials, some defects may occur in the material, and high quality and yield may not be achieved. However, despite some limitations, it is a versatile and simple method and has widespread use in areas such as sensors, composite materials, and energy storage. (Olatomiwa et al., 2022).

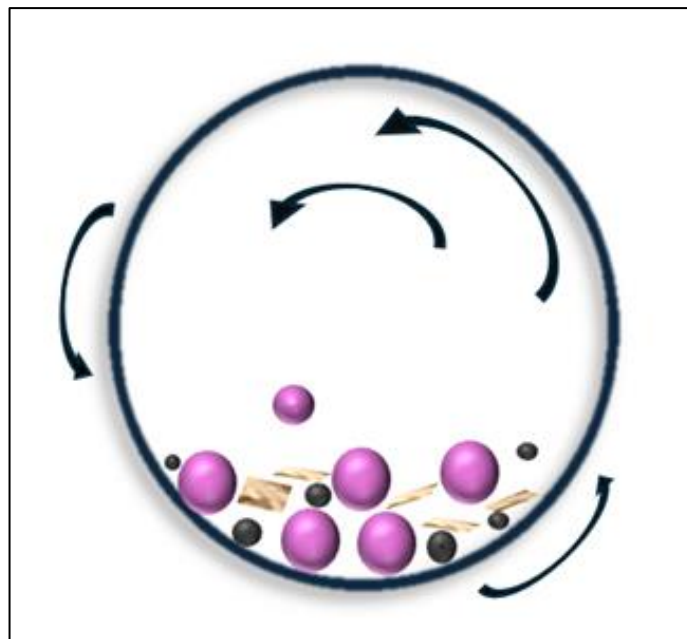


Figure 2.5.: Ball-milling method in nanotechnology.

2.3.2. Bottom-Up Approach

Bottom-up nanofabrication approaches are the process of producing nanostructural materials by self-assembly of atoms or molecules. Bottom-up approaches are based on synthesizing graphene starting from smaller carbon-based molecules or atoms. Thus, this approach is highly advantageous in terms of precise control in the structure, number of layers and some properties of the resulting material. These methods are preferred to produce high-quality graphene with minimal defects and usually require high temperatures, specialized equipment or catalysts.

For controlled deposition of atoms or molecules, some preliminaries are important, such as surface preparation, impurities and uniformity, quality of reactants, etc. This section describes some of the most common bottom-up methods for nanofabrication. (Biswas et al., 2012).

2.3.2.1. Chemical Vapor Deposition (CVD)

Usually under vacuum, CVD is a fabrication method used to generate films or structures, or high-quality and high-performance nanomaterials. It entails the breakdown of carbon-based gases—such as methane or acetylene—at high temperatures ($\sim 1000^{\circ}\text{C}$) on a catalytic metal substrate, say copper or nickel. Adsorbed onto the substrate surface, carbon atoms reorganise and generate graphene sheets. The reaction occurs in the chamber and on the substrate simultaneously. (Adetayo et al., 2019). To ease atom mobility and the deposition reaction, the substrate must also be heated to specific temperature.

This method has the benefit of being able to generate highly crystalline, widely surface area graphene with great quality. Usually, a CVD system comprises of a vapour pressure system, a waste gas delivery system, and a reactor. It fits for uses including optical fibre, semiconductors, flexible electronics, and sensors. Apart from these benefits, it also presents certain difficulties including cost and need of careful control of variables including temperature, pressure, and gas compound.

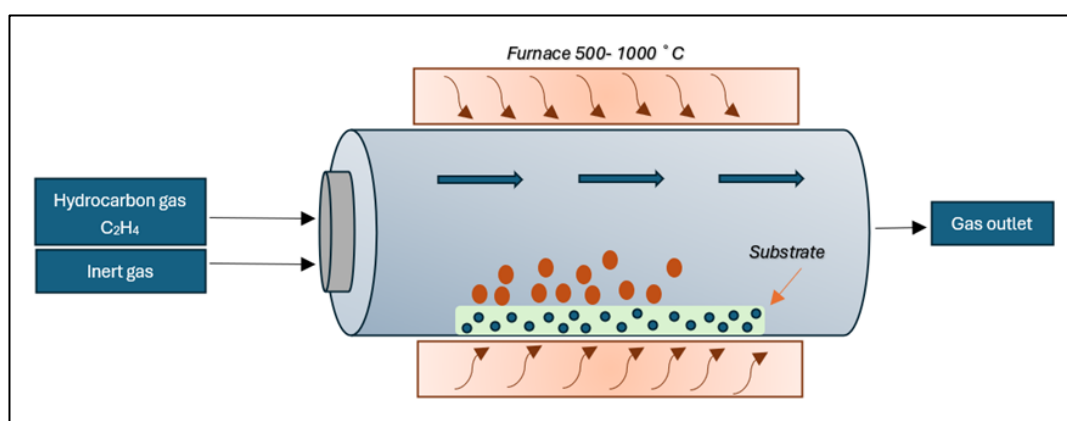


Figure 2.6.: Chemical Vapor Deposition (CVD) technique in nanotechnology.

2.3.2.2. Atomic Layer Deposition (ALD)

Working based on sequential chemical process application under vacuum, ALD is a thin film deposition method. Another controlled layer-by-layer deposition technique is whereby precursor gases react sequentially and slowly on the substrate surface. Important in semiconductor production, the ALD method can produce graphene-like thin films at atomic size.

This approach is appropriate for advanced device architecture since it allows exact control over graphene thickness and uniformity and is fit for complex 3D constructions. Its complexity causes great cost and limited use; it also has slower deposition rates than other techniques. (Biswas et al., 2012).

2.3.2.3. Molecular Beam Epitaxy (MBE)

Applied in a high- or ultra-high vacuum chamber, MBE is an epitaxy technique. The surroundings for this process must be rather dust-free and clean. Under vacuum, carbon atoms vaporise and settle on a substrate, say silicon or metal. On the substrate surface, the atoms lay as graphene layers. Since this production technique does not need carrier gas and has an ultra-high vacuum environment, it can generate high-purity films. It also suffers from very high vacuum, great cost, and limited scalability for industrial manufacture at the same time. (H. Zhang et al., 2011).

2.3.2.4. Epitaxial Growth on Silicon Carbide (SiC)

This approach generates graphene by sublimation of silicon atoms and heating silicon carbide (SiC) in vacuum or in an inert atmosphere to high temperatures (1200-1600°C.). On the surface of the SiC substrate, the remaining carbon atoms reorganise into graphene layers. Graphene is thus obtained straight from the SiC substrate, hence it is a natural part of the material. This technique offers some benefits, including the possibility to reduce some flaws by removing the need for substrate transfer and the capacity to fabricate high-quality graphene straight on an insulating substrate, which is perfect for electronic devices. Furthermore negative are the limited scalability resulting from small graphene growth areas and the great cost of SiC substrates. (Adetayo et al., 2019).

2.3.2.5. Laser-Scribed Graphene (LSG)

A laser beam is directed at carbon precursors (e.g. polyimide films) and converts them into graphene according to a pre-designed pattern via a program (e.g. inkscape, LazerDRW). Once the scanning speed and laser power parameters of the CO₂ laser device connected to a computer are set via the program, the heat from the laser facilitates the carbonization process, breaking the bonds between the C, O and N atoms in the structure of the polyimide, and the C atoms with sp² come together to form graphene layers. The principle of LSG (in **Figure 2.7**) is generally based on the principle that the high energy sent by a laser breaks the functional bonds in the structure of the material, leaving behind a large number of C atoms that are reconnected into a honeycomb-like hexagonal lattice structure. (**Aydemir, 2023**). The LSG technique was first presented by El-Kady and Kaner, who produced LSG by coating graphene oxide (GO) solution on PET substrates using a DVD printer laser with a wavelength of 405 nm. (**El-Kady & Kaner, 2013**). Many materials can be used to obtain graphene by this method, but each material has the capacity to absorb different wavelengths of laser depending on its properties. Therefore, laser wavelength is a very important parameter. In this thesis, polyimide (PI) was used as the material to obtain graphene and graphene fiber with CO₂ laser with a wavelength of 10.6 μm . (**Lin et al., 2014**). The thickness of the obtained graphene films was determined to be approximately 30 μm . LSG is a very fast, scalable and cost-effective graphene production technique. It enables direct patterning of graphene during synthesis and has broad application potential for flexible electronic devices and biosensors. However, the quality of graphene can vary depending on the precursor material and laser parameters. There is limited control over structural uniformity and it is not always possible to achieve a uniform structure. This results in a porous surface in the graphene structure, which is often considered an advantage as it facilitates the integration of graphene with other materials. Moreover, since this method does not require any additional chemical or additive processes, it shows potential as an environmentally friendly production technique. (**Tai et al., 2019**).

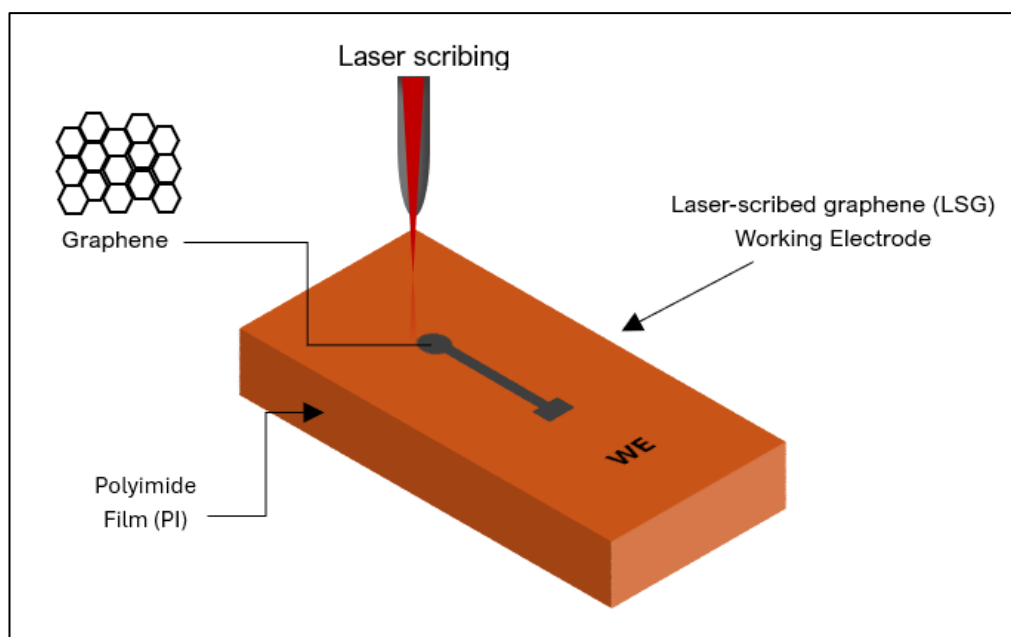


Figure 2.7: Laser-scribed Graphene (LSG) technique in nanotechnology.

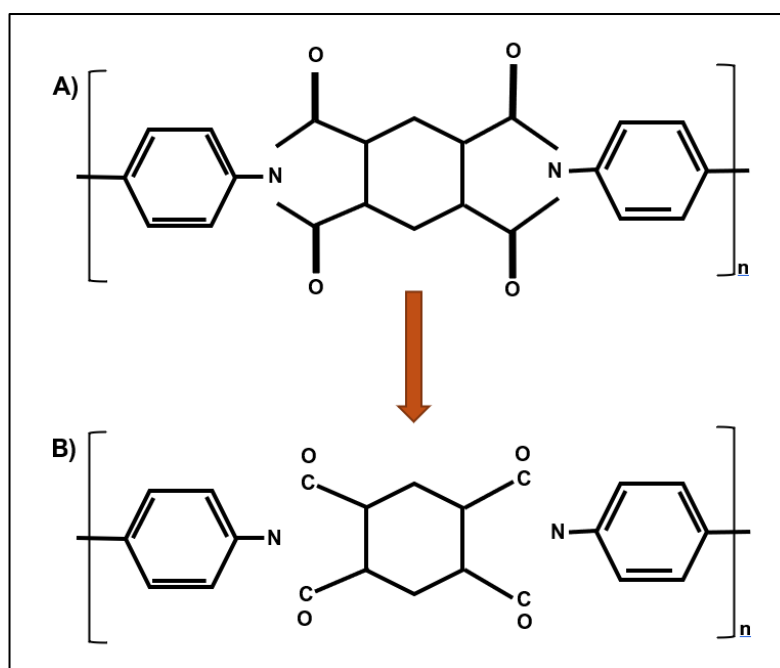


Figure 2.8: The conversion of A) polyimide to B) graphene via laser-scribing method.

2.4. Biosensors

2.4.1. Description and Classification of Biosensors

Biosensors, as analytical devices, comprise several essential components, including the transducer (which may be an optical signal, electrode, or cantilever), signal

amplifier, signal processor, and bioreceptor, also referred to as molecular recognition elements. Biological sensors can employ various biological molecules, such as aptamers, antibodies, and synthetic materials like molecular imprinted polymers (MIPs), as biological receptors. The biological recognition elements of these bioanalytes facilitate the accurate classification of biosensors. A transducer is a device that converts bio-recognition signals into measurable data. Biosensors are classified into optical, electrochemical, and physical sensors depending on their signal transduction.

Biosensors can also be categorized based on the incorporation of nanoparticles (NPs) in their platforms. Nanoparticles (NPs) can be composed of various materials, including gold (AuNPs), C-based nanostructures, quantum dots, magnetic NPs, metal nanoclusters (MNCs), metal-organic frameworks (MOFs), and other forms of NPs and nanocomposites. **(Dadmehr & Korouzhdehi, 2023).**

Sensors are devices that detect and convert chemical, physical, or biological changes into measurable signals. The primary component of sensors is a recognition element, which allows them to respond to specific analytes while reducing interference from other sample components. This primary component is integrated with a transducer, referred to as the detection device, which produces signals. The signal is then collected and amplified by a signal processor. **(Ronkainen et al., 2010).**

2.4.2. Graphene Based Electrochemical Biosensors

Signal transduction techniques help to classify biosensors into optical, electrochemical, and physical sensors. Combining biological recognition systems with the sensitivity of transducers, electrochemical biosensors are a well-known subclass of chemical sensors. Thanks to this link, they allow the identification of even the lowest analyte concentrations, so stressing their relevance in many spheres, including environmental, pharmaceutical, and healthcare sectors. **(Das et al., 2023).**

Target analyte detection in electrochemical biosensors is accomplished using a biological component. This detection starts a binding process that finally generates an electrical signal. The analyte concentration guides a transducer in evaluating this signal. Interacting with the target analyte, the electrochemical sensor generates a direct proportional electrical signal. Usually featuring a working electrode and a reference

electrode split apart by an electrolyte solution, these sensors Furthermore included in the three-electrode system are a working, a counter, and a reference electrode. The three-electrode system is widely used since the three-electrode system has a counter electrode that simplifies the completion of current while the reference electrode is connected to a potentiostat with high input impedance. **(Thévenot et al., 2001)**. Graphene-based electrochemical biosensors are detection systems for measuring electrical signals generated by chemical interactions between the target and the biotransmitter. Biosensor applications make use of impedimetric, potentiometric, amperometric sensors as among electrochemical techniques. Furthermore extensively applied in biosensors for the small molecule detection are electrochemical and fluorescence techniques because of their inherent advantages. Furthermore, the use of nanotechnology has enhanced the detection capacity of enzyme nanobiosensors, so allowing precise measurement of important or toxic small molecules. **(Choi et al., 2023)**.

Thanks to its exceptional physical, chemical, and electrical characteristics, graphene has become rather widely used in the field of electrochemical biosensors. Excellent electrical conductivity, large surface area, and adjustable surface chemistry help to enable efficient interactions with biomolecules, so making it quite appropriate for biosensor uses. These features of graphene-based electrochemical biosensors enable their high sensitivity and selectivity to detect many various biochemical analytes including DNA, neurotransmitters, and enzymes. Because it includes oxygen groups, graphene oxide (GO), another form of graphene, also has useful qualities. **(D. Chen et al., 2012)**. This makes it a good choice for immobilizing biomolecules and drug delivery. Various surface modifications can improve the performance of graphene-based electrochemical biosensors. **(Kuila et al., 2011)**. By means of some modification strategies, defects and edge plane areas can be generated on the graphene surface, so enhancing its electrochemical activity. For biomolecules including dopamine, ascorbic acid, uric acid and NADH, these modified graphene materials have shown exceptional detection sensitivity. **(Keeley et al., 2014)**.

Moreover, graphene exhibits better biocompatibility compared to carbon nanotubes (CNTs) as it is free from toxicity risks such as metallic impurities, making it safer for biosensor applications. **(H. Chen et al., 2008)**, **(Koyama et al., 2009)**. Compared to CNTs, some of the presented studies highlighted that graphene outperforms SWCNTs

for dopamine detection in the presence of serotonin and ascorbic acid shows better potential for biochemical analytes detection such as ascorbic acid, dopamine, serotonin and uric acid. **(Kour et al., 2020b)**. These advances mean that graphene-based electrochemical biosensors should be rather common in next diagnostic uses. In medical, environmental, and industrial contexts, they will enable fast, precise, selective search for particular analytes. **(Kour et al., 2020b)**. This thesis focuses on the detection of ascorbic acid (AA) based on the redox behavior on the electrode surface using cyclic voltammetry (CV) analysis in the presence of phosphate buffered solution (PBS) using graphene and fiber electrodes fabricated by laser-scribed graphene techniques. During CV measurement, oxidation and reduction peaks corresponding to the electron transfer processes of ascorbic acid are observed. These peaks provide valuable information about the redox potential, concentration and interaction of ascorbic acid with graphene-based or fiber electrodes, providing insight into the sensitivity and selectivity of the electrode in such an electrochemical environment. In the light of these studies, the use of laser-drawn graphene electrodes is expected to improve sensitivity and selectivity due to their excellent electrical conductivity, surface functionalization and compatibility with electrochemical techniques.

3. EXPERIMENTAL PROCEDURE

In the current part of this study, LSG and LSGF electrodes produced with different power and speed parameters with the VLS 3.60 CO₂ laser engraver Universal Laser System (see in **Figure 2.**) will be described. These graphene and fiber electrodes will be compared according to their physical and chemical properties. One LSG and three LSGF electrodes were fabricated at three different power values on the Polyimide (PI) film (Kapton HN) with 100 μm thickness. The speed and power parameters applied during the fabrication process will be described in detail in the sub-headings. Scanning Electron Microscopy (SEM), Raman spectroscopy, X-ray Photoelectron Spectroscopy (XPS), X-ray Diffraction (XRD), and finally electrochemical tests were performed to collect precise data about microscope images, chemical bond structures, material properties, conductivity, crystalline bond structures and properties of four different electrodes.

3.1. Materials

The materials required for this thesis study; 100 μm thick polyimide film (PI-Kapton HN) to be used in graphene production was purchased from Yatiz Electrics (Istanbul/Turkey). For electrochemical tests, L-Ascorbic acid (AA), phosphate buffer solution tablets (PBS: 0.1 M, pH:7.4) for the solution to be used in cyclic voltammetry (CV) and potassium chloride (KCl) for storing the pilatin electrode outside the measurement were purchased from Sigma-Aldrich.

3.2. Fabrication of LSG and LSGF Electrodes

The CO₂ laser system used in this part of this thesis for the production of graphene on a 100 μm thick PI film is shown in **Figure 3.1**. The system used in the production phase consists of optical components that focus and transfer the laser beam to the substrate, a 40W CO₂ laser tube, a computer and inkscape software. The Inkscape program was used to easily design the graphene produced by this method and to keep the production process under control. The Universal laser system (wavelength: 10.6 μm) used operates in three different modes: engraving, cutting and vector rasterization, but the mode generally recommended for the production of graphene films on polyimide polymer is the engraving mode. There are two important device parameters

that affect the properties of the graphene film such as surface morphology and conductivity; scanning speed and laser power. These parameters can be adjusted through the program used and should be determined before starting the etching process. In this thesis, two different graphene films, graphene and graphene fiber, were obtained by applying different laser power and scanning speed. In order to obtain the graphene structure with the appropriate electrical conductivity properties, the laser power and scanning speed were varied many times and finally the parameters supported by literature studies were obtained. First, a laser-scribed graphene (LSG) electrode with a diameter of 2 mm was obtained at 12.5% laser power and 10% scan rate. Then, by increasing the laser power to 30%, a laser-drawn graphene fiber (LSGF) structure with further increased carbonization was obtained with a scan rate of 10%. Graphene fiber electrodes with different surface morphology, pore structure and defect rate were produced by increasing the laser power from 30% to 40% and 50%, respectively, without changing the scan rate. All four electrodes were obtained as working electrodes with a diameter of 2 mm. After the fabrication process, physicochemical, electrochemical and electrical conductivity characterizations were carried out in order to make appropriate comparisons and evaluations.

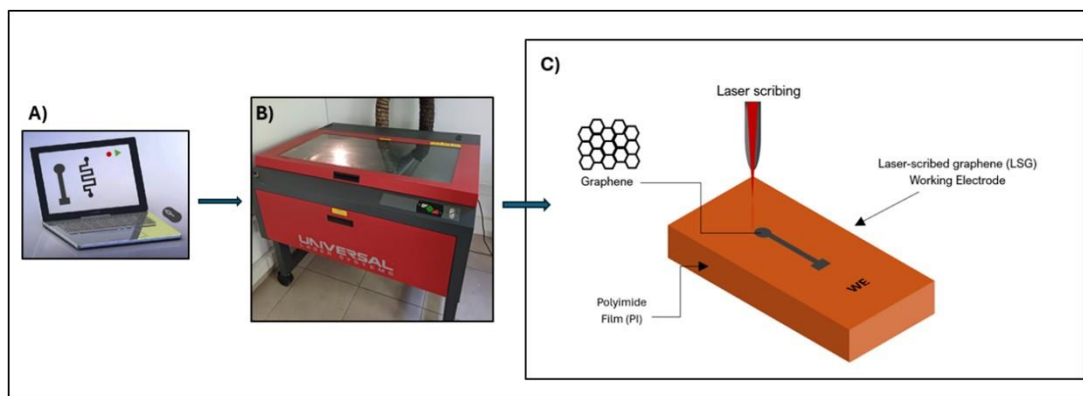


Figure 3.1: Laser-scribed graphene fabrication process; A) computer, B) Universal Laser Engraving and Cutting System, VLS 3.60 (40W, wavelength= 10600 nm), C) laser scribing on polyimide.

3.3. Instrumentations for Characterization

In this thesis, to perform the characterization experiments of (LSG) and LSGF electrodes, some characterization techniques were used such as FEI (Phillips) XL30

SFEG for Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS), Renishaw in Via Raman Microscope and Spectrometer for Raman spectroscopy, (2018 model, laser wavelength; 532 nm, laser power; 100%), Rigaku D-max PCI 2200 for X-ray Diffraction (XRD), SPECS XRC 1000 for X-ray Photoelectron spectroscopy (XPS) and finally, PalmSens4 Potentiostat for Cyclic Voltammetry (CV).

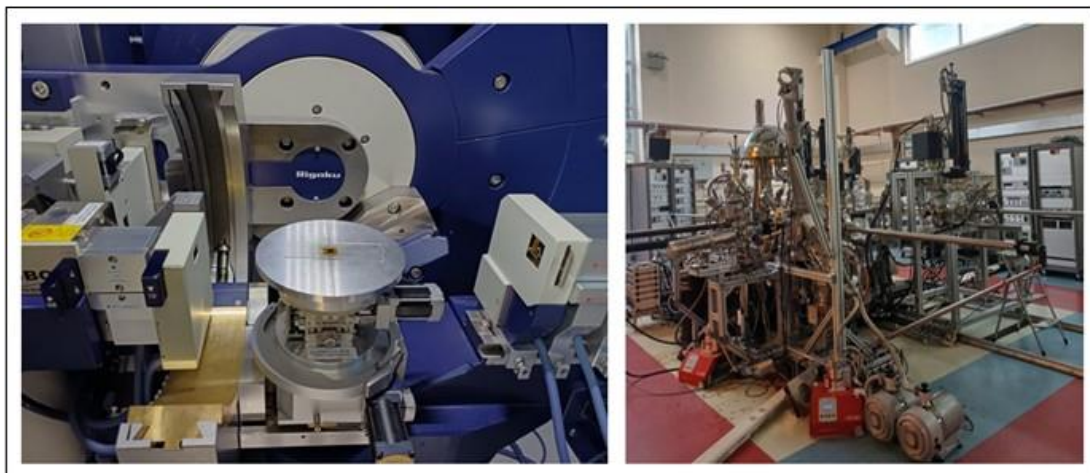


Figure 3.2: X-Ray Diffraction (XRD) in the left and X-Ray Photoelectron Spectroscopy (XPS) in the right.

4. RESULTS AND DISCUSSION

4.1. Physicochemical Characterizations

In the present chapter, some characterizations were performed for graphene and fiber electrodes fabricated by laser scribing at different speed and power parameters. In order to comprehensively evaluate the overall performance, chemical structure and surface chemistry of LSG and LSGF electrodes, SEM, Raman spectroscopy, XPS and XRD characterization techniques were performed under physicochemical characterizations. Scanning electron microscopy was used to evaluate the surface morphology and porosity of the graphene and fiber structures in detail. Raman spectroscopy was then used to evaluate the graphitization state of the material and to observe structural defects by analyzing the D, G and 2D bands. XPS analysis was performed to determine the surface elemental composition and functional groups, which are important for understanding the surface chemistry and the interaction potential of the carbon structure. Consequently, with XRD analysis can be investigated, it was applied to investigate the quality and crystalline structure of the material. All these characterization techniques provided critical information to demonstrate the high potential and applicability of the material for biosensor applications. Each characterization application will be presented in detail with the results obtained under separate headings in the following sections.

4.1.1. Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS)

Scanning electron microscopy is a widely used imaging characterization technique for analyzing the surface morphology of various materials at high resolution. It is particularly useful for imaging the surface texture, edges and layered structure of graphene films at the micro and nanoscale. It provides detailed information about properties such as defects, three-dimensional surface morphology and material thickness that occur during fabrication in the graphene structure produced by techniques such as CVD, LSG and LPE. Energy dispersive spectroscopy is an elemental characterization technique used as a complement to SEM. EDS allows the

detection of impurities or additives in the material structure. SEM and EDS provide detailed information about the material composition in graphene studies.

Following the graphene production process, SEM and EDS analyses were applied to obtain detailed information about surface morphology and elemental analysis. In **Figure 4.1**, we can easily see the obvious morphological difference between the graphene film produced by applying 12.5% laser power and 10% scanning speed and the polyimide (PI) film. The dense pores in the structure of the graphene film are clearly visible at micro-sized magnifications (**Figure 4.1A-D**). While the graphene structure exhibits a foam-like layered structure with a porous appearance, the PI film with 100 μ m thickness shows a very smooth and flat structure (**Figure 4.1E**). This structure of the graphene film consists of flakes only a few nanometers thick. These nanoflakes are densely packed in a foam-like structure with a thickness of about 29.5 μ m (with a standard deviation of ± 2 μ m) (**Figure 4.1F**). The porous structure of the graphene film produced by the laser drawing method, consisting of many interconnected nanopillars, was found to be consistent with previous observations reported in the literature.

EDS analysis of the obtained graphene film showed the presence of carbon, oxygen and nitrogen in the graphene structure, which are shown in detail in **Figure 4.2** and **Table 4.1**. Due to the defective structure of LSG, it is expected to have a high proportion of carbon and oxygen atoms. As a result of EDS analysis, it was also observed that there are very low residual nitrogen atoms in the LSG material due to the photothermal conversion of polyimide, which has nitrogen atoms in its chemical composition during the production of graphene film.

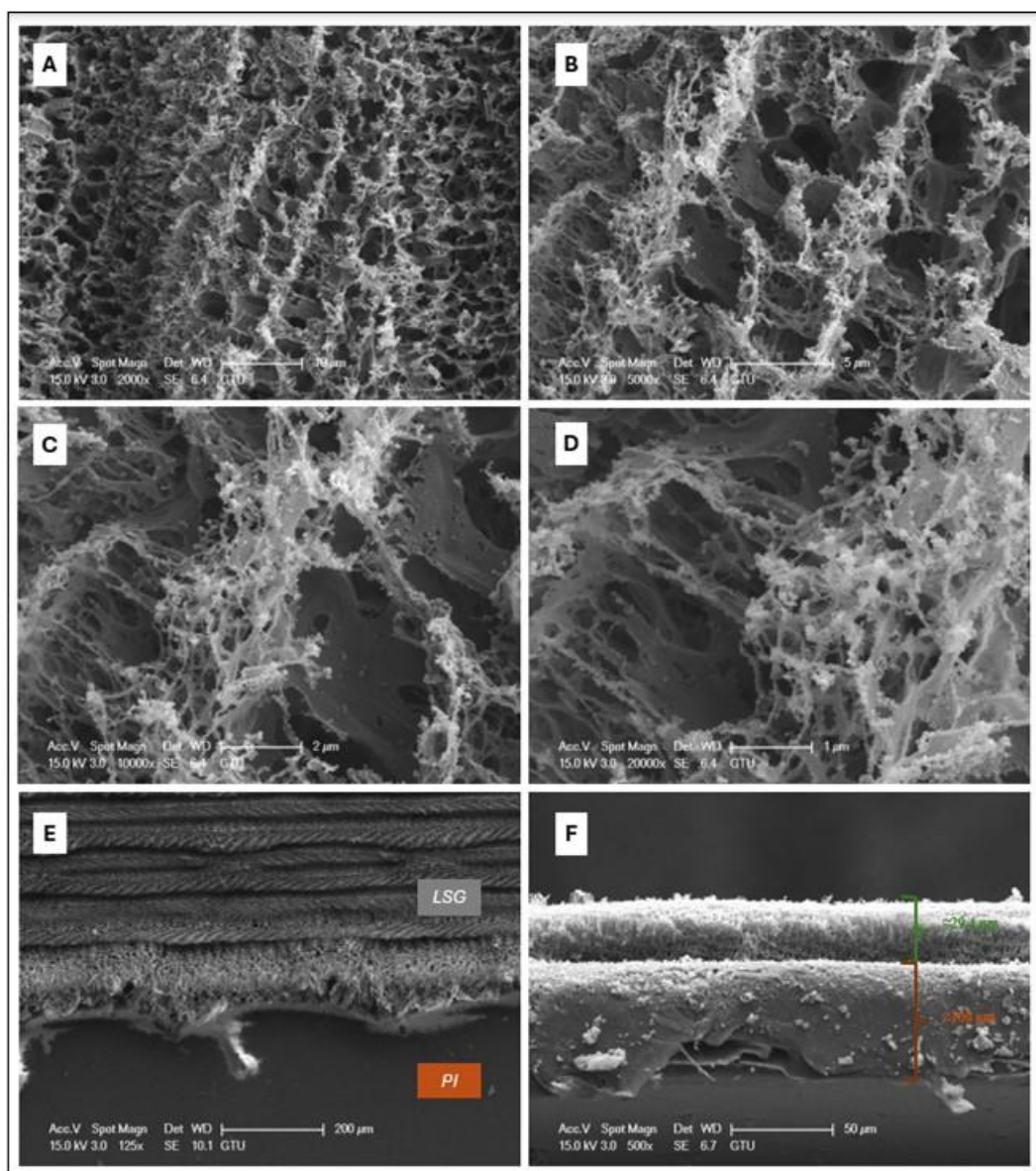


Figure 4.1: SEM surface and cross-sectional results of LSG sample; magnified by A) 2000x, B) 5000x, C) 10000x, D) 20000x, E) image of LSG-PI at 125x and F) thickness of LSG film on PI substrate at 500x.

Table 4.1: EDS result for LSG.

Element	Weight %	Atomic	Net Int.	Net Int. Error
C K	88.58	90.78	7040.42	0
N K	3.92	3.44	25.18	0.07
O K	7.5	5.77	191.67	0.02

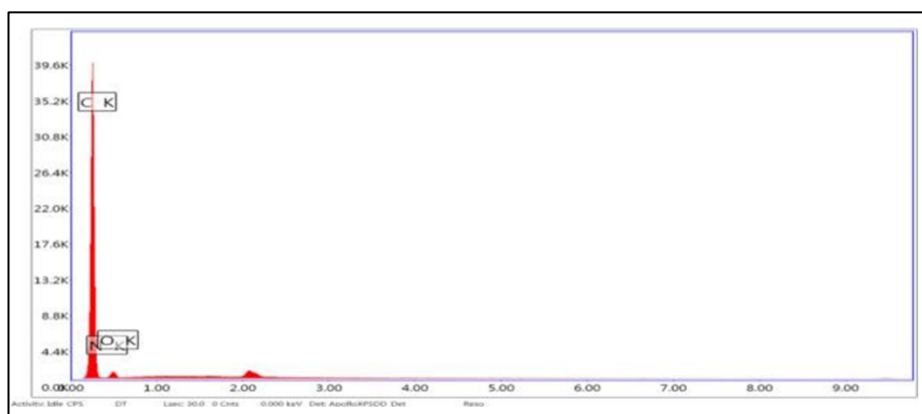


Figure 4.2: EDS analysis of LSG.

After the production process of the graphene film, SEM and EDS analyses were applied to obtain detailed information about the surface morphology and elemental analysis of the graphene fiber structure obtained by applying different laser powers. The SEM images in **Figure 4.3** show the graphene fiber structure produced on PI film by applying 30% laser power and 25% scanning speed. At very low magnifications, the structure's porous and interconnected network structures can be seen. This shows the material's architecture in more detail in this fiber structure (**Figure 4.3 A–D**). This indicates an enhanced surface area suitable for electrochemical applications and exhibits pronounced fiber-like structures that contribute to increased electrical conductivity and mechanical stability. As the power of the laser is increased, the flake graphene with a foam-like structure transforms into fiber-like fringed structures. This indicates that the graphitization of carbon atoms increases at higher energy conditions. A cross-sectional view of the graphene fiber exhibits a fiber structure with a thickness of about 155 μm on a 100- μm -thick PI film (**Figure 4.3E**). The graphene fiber produced by the laser scribed method exhibits a large number of interconnected fibers, which is consistent with previous observations reported in the literature. The obtained graphene fiber, which is shown in more detail in **Figure 4.4** and **Table 4.2**, shows that it contains a lot of C atoms and a low amount of atoms O. This aligns with the observation that functional groups incorporating oxygen are undergoing reduction while networks of sp^2 hybridized carbon are being established. As a result of the EDS analysis, it was observed that during the production of graphene fiber, due to the photothermal conversion of polyimide, which has nitrogen atoms in its chemical

composition, there are also very low residual nitrogen atoms in the graphene fiber structure.

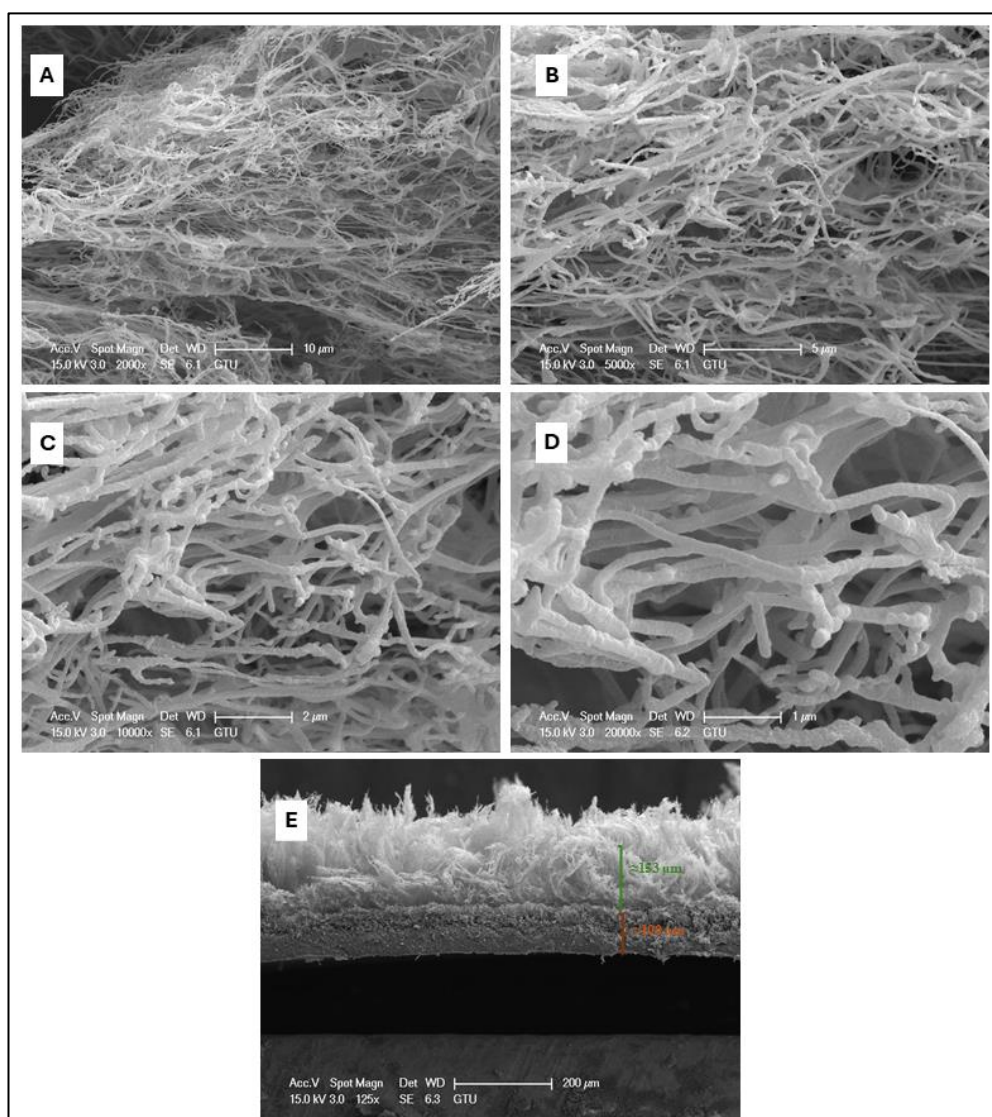


Figure 4.3: SEM surface and cross-sectional results of LSGF(30%) sample; magnified by A) 2000x, B) 5000x, C) 10000x, D) 20000x and E) thickness of LSGF (30%) film on PI substrate at 125x.

Table 4.2: EDS result for LSGF(30%).

Element	Weight %	Atomic	Net Int.	Net Int. Error
C K	90.11	92.08	6326.94	0
N K	3.12	2.73	17.21	0.11
O K	6.77	5.19	150.71	0.02

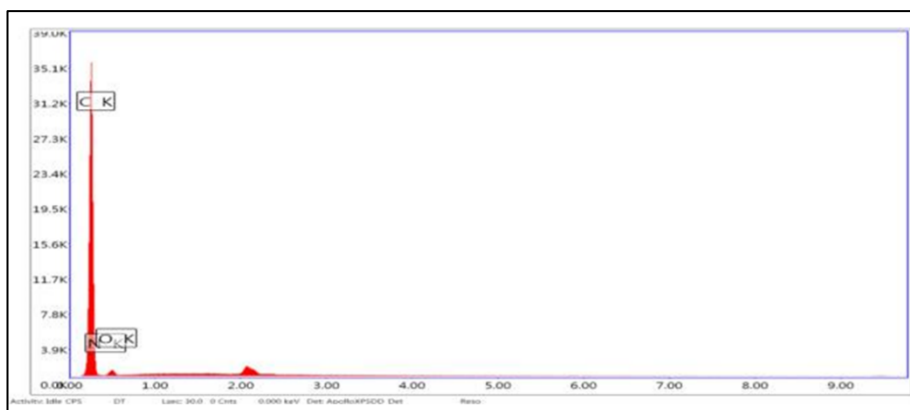


Figure 4.4: EDS analysis of LSGF (30%).

After the graphene fiber obtained by applying 30% laser power, a new graphene fiber was fabricated by increasing the laser power to 40% and the scanning speed to 33%. The SEM images in **Figure 4.5** show the graphene fiber structure produced on PI film by applying 40% laser power and 33% scanning speed. At different magnifications in the SEM analysis, the porous and interconnected network structures of the structure can be seen. This shows the architecture of the material in more detail in the fiber structure (**Figure 4.5 A-D**). This fiber structure also shows an improved surface area suitable for electrochemical applications, exhibits pronounced fiber-like structures that contribute to increased electrical conductivity and mechanical stability, but we have obtained a more hydrophobic structure. It is therefore less applicable compared to graphene and 30% fiber structures. As the power of the laser is increased, fiber-like fringed structures are seen to increase. This indicates that the graphitization of carbon atoms increases again at higher energy conditions. The cross-sectional view of the graphene fiber shows a fiber structure with a thickness of about 220 μm on a 100 μm thick PI film (**Figure 4.5E**). The graphene fiber produced by laser etching exhibits many interconnected fibers, which is consistent with previous literature examples. The resulting graphene fiber, shown in more detail in **Figure 4.6** and **Table 4.3**, shows that it contains many C atoms and a low amount of O atoms. This is consistent with the fact that oxygen-containing functional groups are reduced and sp^2 hybridized carbon networks are formed. EDS analysis showed that very low residual nitrogen atoms are also present in the graphene fiber structure due to the photothermal transformation of polyimide, which has nitrogen atoms in its chemical composition.

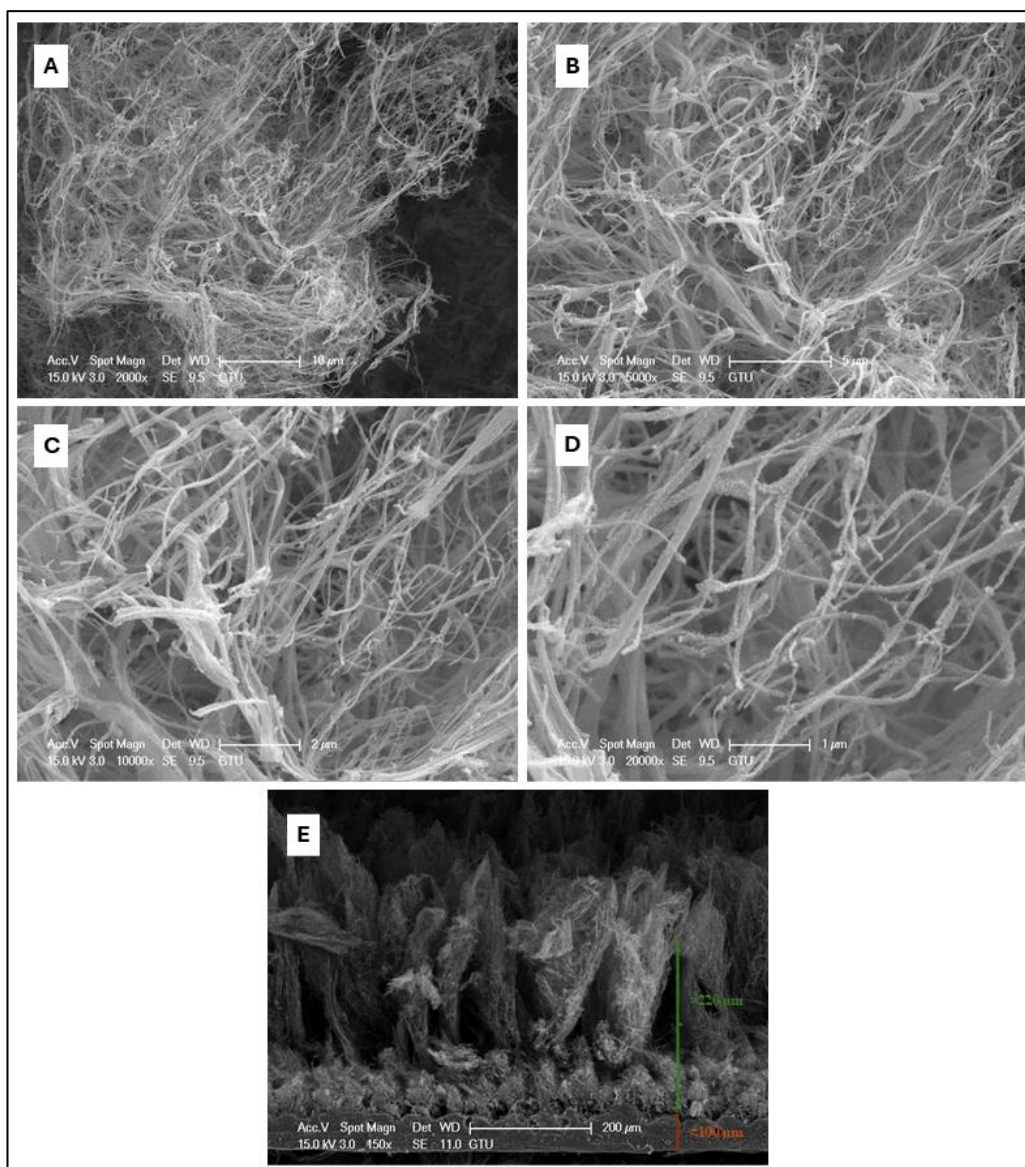


Figure 4.5: SEM surface and cross-sectional results of LSGF (40%) sample; magnified by A) 2000x, B) 5000x, C) 10000x, D) 20000x and E) thickness of LSGF (40%) film on PI substrate at 150x.

Table 4.3: EDS result for LSGF (40%).

Element	Weight %	Atomic	Net Int.	Net Int. Error
C K	88.75	90.91	6517.27	0
N K	4	3.51	23.64	0.09
O K	7.25	5.57	170.2	0.02

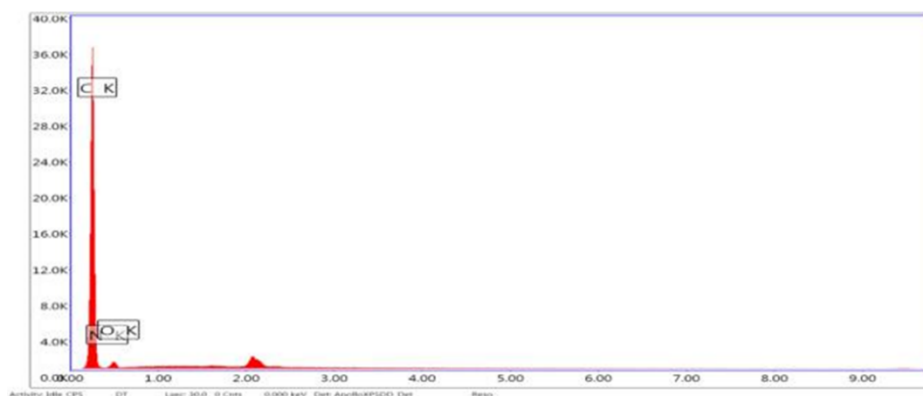


Figure 4.6: EDS analysis of LSGF (40%).

After the graphene fiber obtained by applying 40% laser power, a new graphene fiber was fabricated by increasing the laser power to 50% and the scanning speed to 41%. The SEM images in **Figure 4.7** show the graphene fiber structure produced on PI film by applying 50% laser power and 41% scanning speed. At different magnifications in the SEM analysis, the porous and interconnected network structures of the structure can be seen. This shows the architecture of the material in more detail in the fiber structure (**Figure 4.7 A-D**). This fiber structure also shows an improved surface area suitable for electrochemical applications, exhibits pronounced fiber-like structures that contribute to increased electrical conductivity and mechanical stability, but we have obtained a more hydrophobic structure. Therefore, its applicability is even less compared to graphene and its 30% and 40% fiber structures. As the laser power increases, the fiber-like fringe structures are seen to increase. This indicates that the graphitization of carbon atoms increases again at higher energy conditions. A cross-sectional view of the graphene fiber shows a fiber structure with a thickness of about 280 μm on a 100 μm thick PI film (**Figure 4.7E**). This graphene fiber produced by laser etching also exhibits a large number of interconnected fibers, which consistent with previous literature examples. The resulting graphene fiber, shown in more detail in **Figure 4.8** and **Table 4.4**, shows that it contains a large number of C atoms and a low amount of O atoms. This is consistent with the fact that oxygen-containing functional groups are reduced and sp^2 hybridized carbon networks are formed. EDS analysis showed that very low residual nitrogen atoms were also present in the graphene fiber structure due to the photothermal transformation of polyimide, which has nitrogen atoms in its chemical composition. As a result, when the fiber structures produced at three different powers were compared, the percentages of atoms in the

30% fiber were C=90.11%, O=6.77% and N=3.12%, in the 40% fiber C=88.75%, O=7.25% and N=4% and in the 50% fiber C=87.9%, O=7.62% and N=4.48%. Therefore, when we increased the speed and power parameters of the laser for each fiber in turn, we found that the percentage of C atoms decreased at low rates, while the percentages of O and N atoms increased. Therefore, we decided that the most ideal graphene fiber structure besides graphene film for electrochemical biosensor applications is the structure produced with 30% laser power.

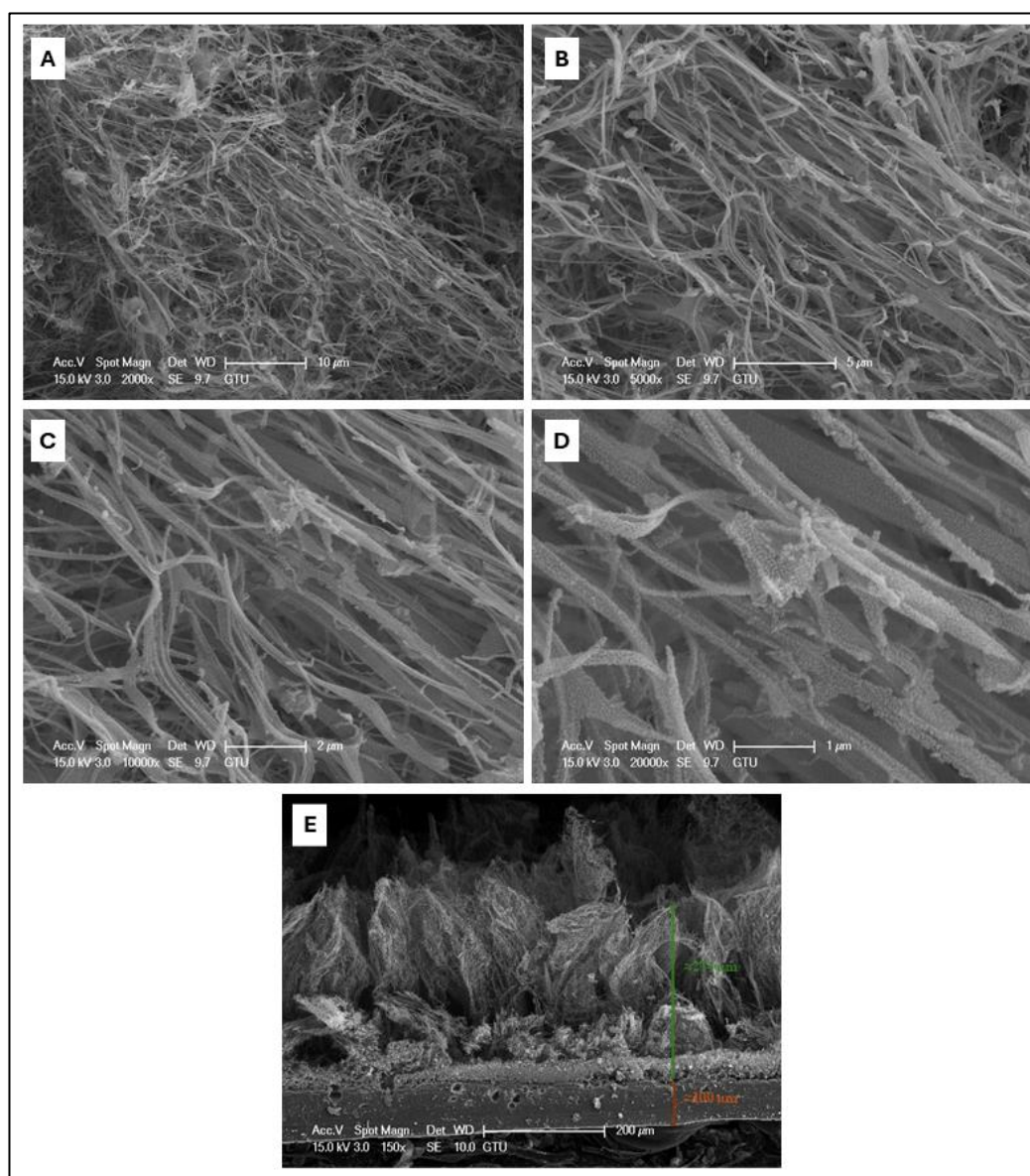


Figure 4.7: SEM surface and cross-sectional results of LSGF (50%) sample; magnified by A) 2000x, B) 5000x, C) 10000x, D) 20000x, E) thickness of LSGF (50%) film on PI substrate at 150x and F) EDS analysis.

Table 4.4: EDS result for LSGF (50%).

Element	Weight %	Atomic	Net Int.	Net Int. Error
C K	87.9	90.19	6328.91	0
N K	4.48	3.95	26.39	0.08
O K	7.62	5.87	176.66	0.02

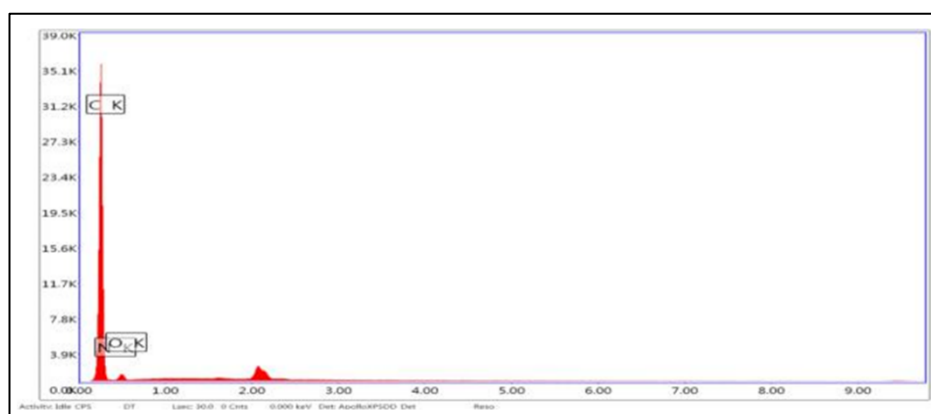


Figure 4.8: EDS analysis of LSGF (50%).

4.1.2. Raman Spectroscopy

Raman spectroscopy is a characterization technique used to study molecular vibrations, crystal structures and material properties without damaging the material. This technique is non-destructive and does not damage the sample, making it ideal for use on samples such as nanomaterials and thin films. Furthermore, each material has a unique Raman spectrum for measurement. In this thesis, Raman spectroscopy analysis was performed with a Renishaw Raman microscope, model 2018 (laser wavelength; 532 nm, laser power; 100%).

Raman spectroscopy analysis of LSG, LSGF30, LSGF40 and LSGF50 samples were performed to determine the structural quality of the graphene and fiber samples and the effects of the laser on the material. The Raman spectra characteristically have three peaks known as D, G and 2D bands (as seen in **Figure 4.9**). From the analysis result, all samples typically showed D band around 1350 cm^{-1} , G band around 1580 cm^{-1} and 2D band around 2700 cm^{-1} (**Figure 4.9**). The D band indicates defects and disorders

in the structure. While the G band represents in-plane vibrations of sp^2 hybridized carbon atoms, the 2D band provides information about the number, arrangement and quality of the graphene layers formed. In the LSG sample, the D band is weak while the G band is prominent. This indicates that the LSG graphene structure is regular and contains some defects. In LSGF30, LSGF40 and LSGF50 samples, it is seen that the D peak is more prominent as the fiberization rate in the structure increases, thus the I_D/I_G ratio (**Table 4.5**) increases. This suggests that the defect ratio increases as the fiber contribution in the structure increases. However, having defects in the structure should not be seen as a disadvantage, a balanced defect ratio can increase the active surface area and electron transfer ability in electrochemical applications. Therefore, a certain level of defect is desirable in electrochemical sensor applications. On the other hand, as the fiberization increases, the I_{2D}/I_G ratio (**Table 4.5**) decreases, indicating that the order in the graphene layers decreases and more amorphous or fiber structures begin to form. Overall, it can be seen that in the fiberization process, the increase in the adjusted fluence values leads to the formation of different carbon phases, moving away from the ordered graphene structure after a certain level. As a result, the LSG sample has a regular and stable graphene structure, while the LSGF30 sample offers the expected structural order and active surface area compared to other fiber electrodes, making it ideal for sensor applications.

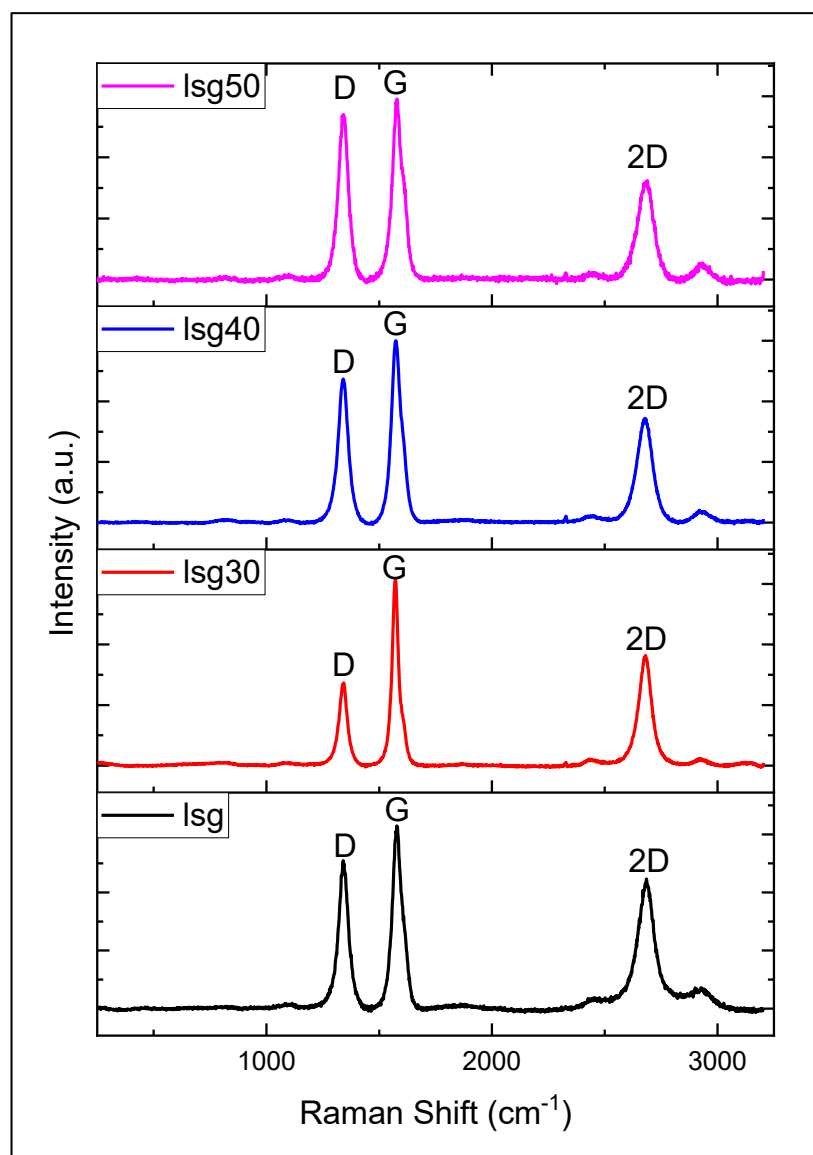


Figure 4.9: LSG, LSGF30, LSGF40 and LSGF50 Raman spectroscopy analysis.

Table 4.5: Raman spectroscopy I_D/I_G and I_{2D}/I_G ratios.

Sample	I_D/I_G (Defect Density)	I_{2D}/I_G (Graphitic Structure)	Interpretation
LSG	0,81	0,71	Moderate defect, good structural order
LSGF30	0,46	0,61	Low defect, good structural order
LSGF40	0,79	0,57	Moderate-high defect, weak order
LSGF50	0,91	0,55	High defect, low structural order

4.1.3. X-Ray Photoelectron Spectroscopy (XPS)

XPS is a characterization technique frequently used in fields such as chemistry, physics, and materials science to analyze the chemical and elemental components of various materials in the field of nanotechnology. The general principle is that X-rays sent to the surface of the material break the core electrons, and the binding energies and kinetic energies of these broken electrons are calculated. The calculated binding energy provides detailed information about the elemental composition, chemical bond structure, and atomic percentages of the elements on the surface of the material. In order to obtain detailed information about the content of the sample produced within the scope of this thesis, XPS analysis of PI, LSG, and LSGF films were performed.

The XPS survey spectrum presented in **Figure 4.10A** reveals that the PI film contains carbon atoms corresponding to sp^2 carbons (C1s) at 284.6 eV energy band, oxygen at 531.5 eV corresponding to O1s and nitrogen atoms corresponding to N1s at 399.99 eV energy band. When we look at the XPS analysis of the untreated polyimide (**Figure 4.10**), in detail, in accordance with the literature, it shows the presence of 62.47% C atoms at the energy level of 284.6 eV corresponding to sp^2 carbon (C1s) atoms (**Figure 4.10B**), 27.22% O atoms corresponding to O1s (**Figure 4.10C**), at the energy level of 531.5 eV, and 10.29% N atoms corresponding to N1s (**Figure 4.10D**), at the energy level of 399.99 eV.

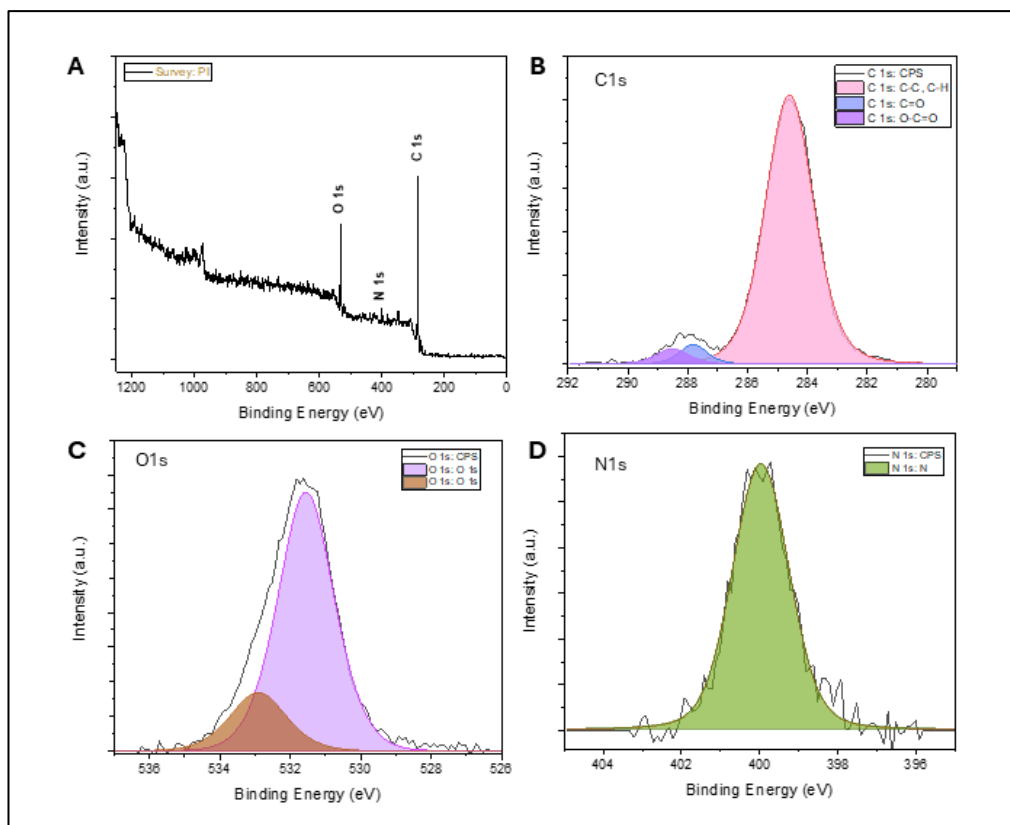


Figure 4.10: PI XPS Survey, C1s, O1s and N1s analysis.

The XPS Survey spectrum presented in **Figure 4.11A** reveals that the LSG film contains carbon atoms corresponding to sp^2 carbons (C1s) at 284.5 eV energy band and oxygen at 532.24 eV corresponding to O1s. In **Figure 4.11B**, we see the Survey spectrum of LSGF (30%), which shows that it contains C1s carbon atoms at the 284.5 eV energy level and O1s oxygen atoms at 532.3 eV.

When we look at the XPS analysis of the CO₂ laser treated polyimide (**Figure 4.11**) in detail, in accordance with the literature, 89.99% C atoms corresponding to sp^2 carbon (C1s) atoms at the 284.5 eV energy level for the LSG film (**Figure 4.11C**) and 10.01% O atoms, while the LSGF (30%) C1s spectrum shows 84.77% C atoms and 15.23% O atoms in the 284.5 eV energy band (**Figure 4.11D**).

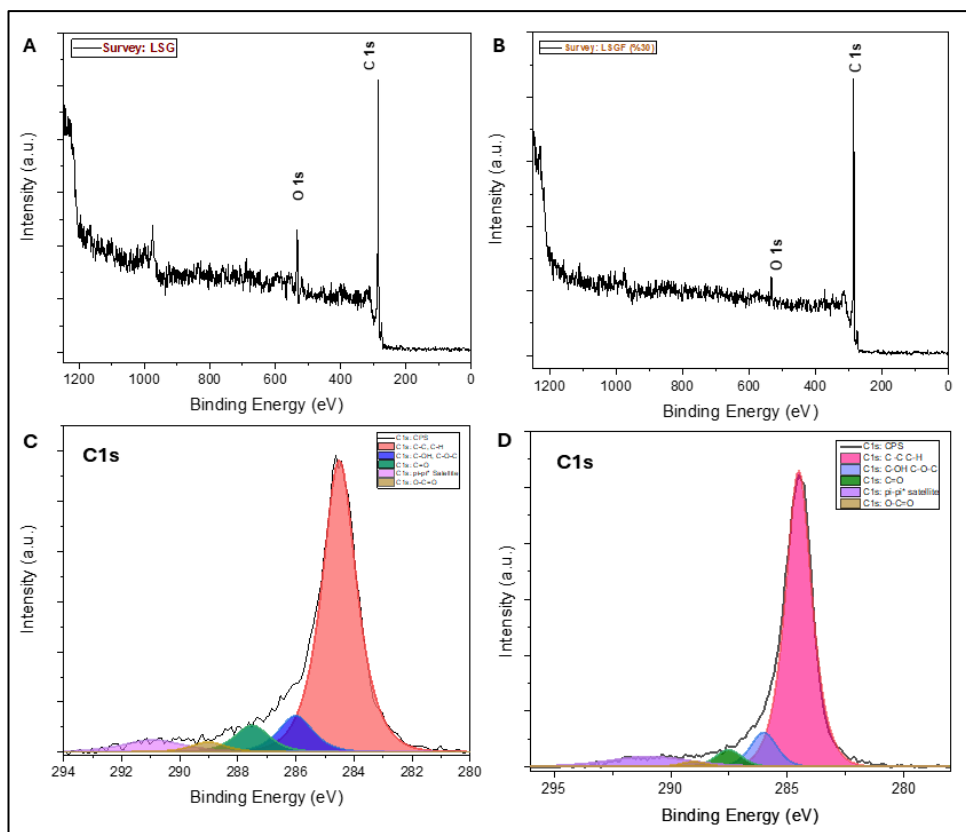


Figure 4.11: LSG and LSGF (30%) XPS Survey and C1s analysis.

The XPS Survey spectrum presented in **Figure 4.12A** reveals that the LSGF (40%) contains carbon atoms corresponding to sp^2 carbons (C1s) at 284.6 eV energy band and oxygen at 536.4 eV corresponding to O1s. In **Figure 4.12B**, we see the Survey spectrum of LSGF (50%), which shows that it contains C1s carbon atoms at the 284.6 eV energy level and O1s oxygen atoms at 533.5 eV.

When we look at the XPS analysis of the CO₂ laser treated polyimide (**Figure 4.12**) in detail, in accordance with the literature, 70.80% C atoms corresponding to sp^2 carbon (C1s) atoms at the 284.6 eV energy level for the LSGF (%40) (**Figure 4.12C**) and 29.2% O atoms, while the LSGF (50%) C1s spectrum shows 70.18% C atoms and 29.82% O atoms in the 284.6 eV energy band (**Figure 4.12D**).

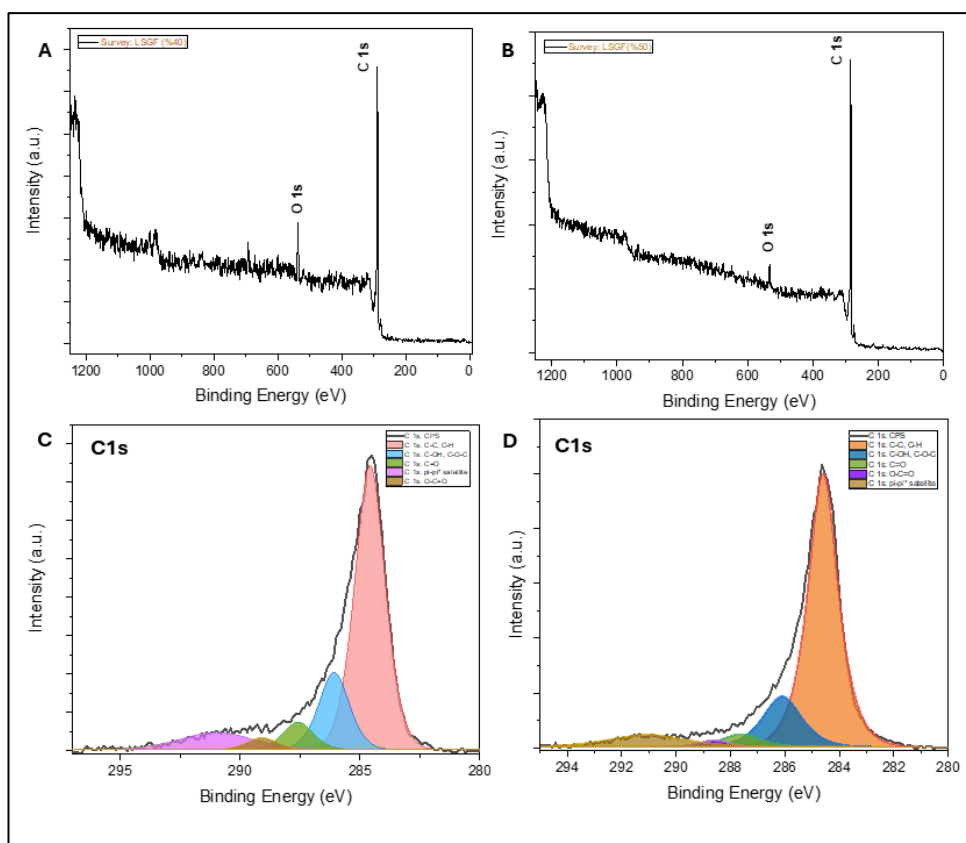


Figure 4.12: LSGF (40%) and LSGF (50%) XPS Survey and C1s analysis.

4.1.4. X-Ray Diffraction Analysis (XRD)

XRD is a characterization technique used to determine the crystal structure of LSG and LSGF samples containing different ratios of fiber. As seen in **Figure 4.13**, a characteristic peak associated with the (002) plane at around 26° was observed in all samples. This peak indicates the presence of a graphite-like structure. While this peak is wider and of low intensity in the LSG sample, this peak narrows and increases in intensity as the fiber ratio increases. This indicates that fiber doping makes the graphitic layers more regular and increases the degree of crystallinity. In addition, the (100) peak observed around 43° represents the planar sp^2 carbon structure of the structure, the atomic order and the in-plane order between the graphene layers. This peak also became more pronounced with the fiber ratio. Especially in LSGF40 and LSGF50 samples, the sharpest (002) peak is obtained, indicating that these samples have the highest crystallinity. Increasing crystallinity can lead to more regular electron conduction pathways; however, too high crystallinity can also lead to a reduction of

active sites on the surface. This can directly affect the electrochemical performance, making the choice of fiber ratio important.

When these findings are evaluated together with other characterization data (Raman, SEM, XPS and CV), it is seen that fiber doping in the LSGF30 sample provides both sufficient structural arrangement and maintains electrochemical performance. As a result, LSG and LSGF30 samples exhibit a crystalline structure suitable for sensor performance while maintaining the active surface area.

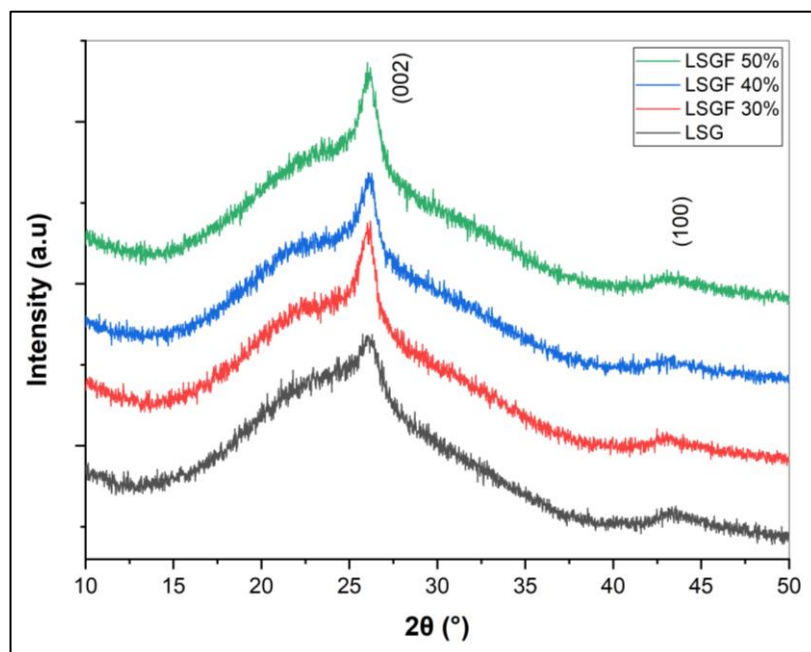


Figure 4.13: LSG, LSGF (30%), LSGF (40%) and LSGF (50%) XRD analysis.

4.2. Electrochemical Characterization

To perform electrochemical measurement, the analyte was dissolved in phosphate buffer solution (PBS, pH=7.4). For the cyclic voltammetry (CV) measurement, a PalmSens4 (in **Figure 4.14**) potentiostat device was used. To start to measurement, electrolyte solution (0.1 M) with PBS was prepared in nine different concentrations as 0.1 μ M, 1 μ M, 5 μ M, 10 μ M, 100 μ M, 1000 μ M, 2000 μ M, 3000 μ M and 4000 μ M. First, one PBS solid tablet added to 200 ml deionized water and mixed about 20 minutes on laboratory conditions. Following this step, 10 ml of the prepared PBS solution was taken, 0.176g of powder ascorbic acid (in **Figure 4.14**) was added and mixed again on a magnetic stirrer approximately 2-3 min.

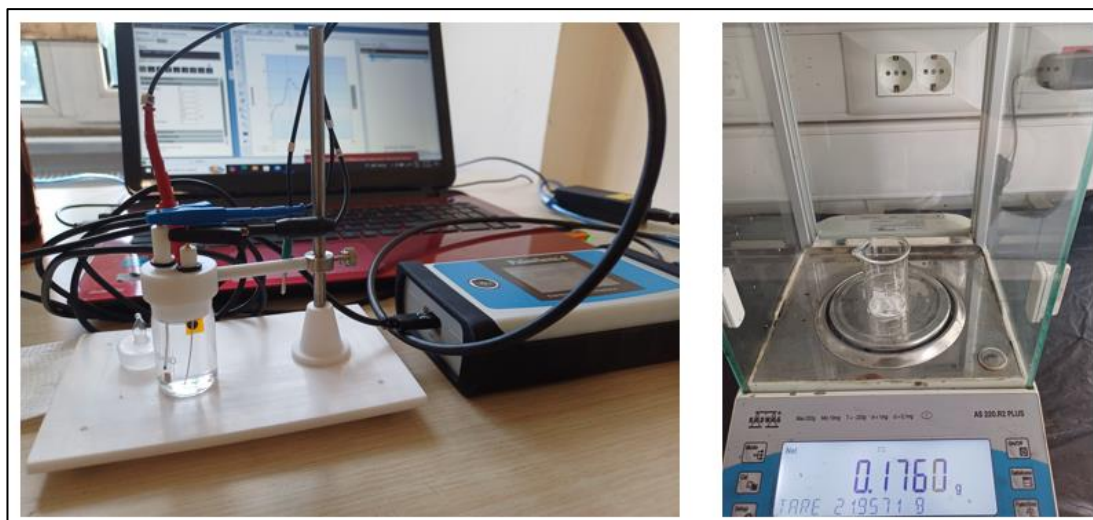


Figure 4.14: CV analysis system.

4.2.1. CV Analysis

CV is one of the most important tools for testing electrochemical properties, and it's also used a lot to look into the redox reactions that happen on the electrode surface. The idea behind this method is to change the potential that is applied to a set of electrodes at a certain rate and then measure the current that comes out of it. CV analysis plays an important role in evaluating the performance of electrode materials by providing both kinetic and thermodynamic information. This study used the CV method to test the electrochemical activity and stability of laser-scribed graphene electrodes. For CV analysis using PalmSens4 portable potentiostat, ascorbic acid (AA) was used as biochemical analyte and phosphate buffered solution (0.1 M PBS, pH 7.4) as reference solution. Ascorbic acid is often used as an analyte in biosensors and is a suitable compound to study the redox mechanisms of graphene-based electrodes. CV measurements were performed at concentrations ranging from 0.1 μM to 4000 μM and dose-response curves were also generated by taking three replicates for each sample. The scan rate applied during the measurements was 100 mV/s and the potential range was fixed between -0.2 V and +0.6 V. In the measurement system, graphene was used as the working electrode, Ag/AgCl as the reference electrode and Pt wire as the counter electrode. The CV raw data obtained reflects the oxidation current and potential obtained at different ascorbic acid concentrations for each electrode (**Figure 4.15A-D**). It was observed that the current response increased significantly with increasing ascorbic acid concentration in all samples.

LSG and LSGF30 samples (**Figure 4.16A-B**) showed a more sensitive response than LSGF40 and LSGF50 samples with high distinguishable peak current. The LSGF40 and LSGF50 (**Figure 4.16C-D**) electrodes showed no oxidation peaks at low concentrations, while at high concentrations the current response was significantly lower compared to the LSG and LSGF30 electrodes. This indicates that the conductivity, active surface area and electrode-electrolyte interaction are at optimum levels in LSG and LSGF30 electrodes. In LSGF40 and LSGF50 electrodes, on the other hand, the peaks were more diffuse and of lower intensity. This indicates that an unbalanced increase in the defect rate and low conductivity due to the increase in the fiber ratio adversely affects the sensor performance.

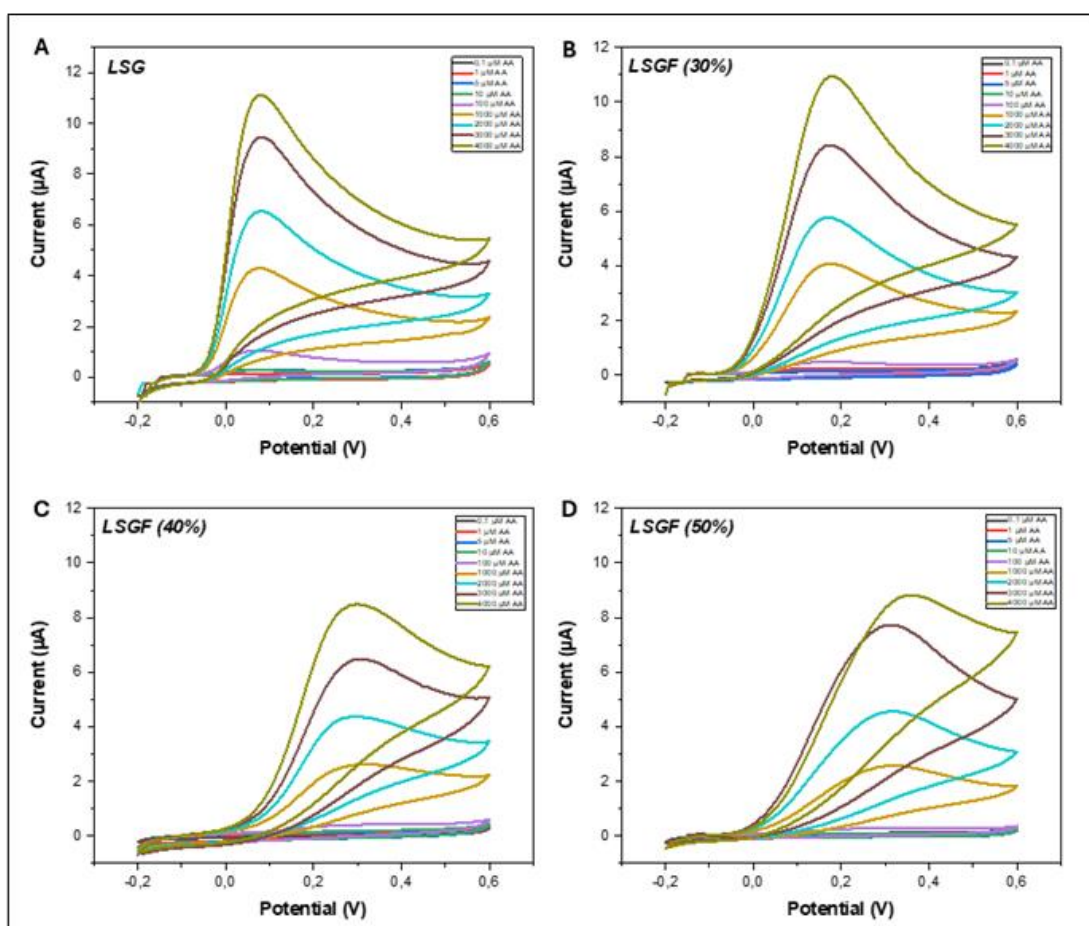


Figure 4.15: CV analysis raw datas of A) LSG, B) LSGF (30%), C) LSGF (40%) and D) LSGF (50%) for detection of ascorbic acid (AA) in different nine concentrations.

Measurements were performed using all electrodes for 9 different ascorbic acid (AA) concentrations in PBS, ranging from 0.1 μM to 4000 μM . The oxidation peak current is observed in all graphs and, increases with increasing concentration. Most repeatable and high-performance signals were observed to be LSG and LSGF (30%). Hence, further investigation to concluded dose-response curve and limit of detection (LOD) were carried out by utilizing LSG and LSGF30 electrodes. The dose-response curve, plotted against the logarithmic concentration (see in **Figure 4.16**), follows a sigmoidal curve. The R^2 value of 0.99757 indicated a strong fit. LOD values were calculated to be approximately 27 μM . These results confirm that our sensor provides a reliable AA detection capability within a specific concentration range. The LOD value represents the lowest analyte concentration that an analytical system can measure and is calculated with the following formula:

$$LOD = \frac{3 \times SD_{\{blank\}}}{\{slope\}} \quad (4.1)$$

$SD_{\{blank\}}$: Standard deviation of the signal obtained from blank samples.

Slope: Slope of the calibration curve (obtained from current vs. concentration graphs).

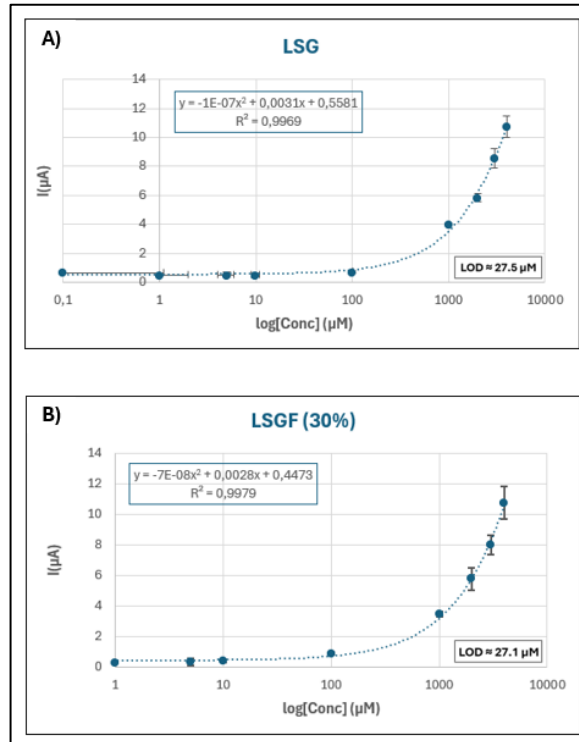


Figure 4.16: CV analysis dose-response curves of A) LSG and B) LSGF (30%).

5. CONCLUSIONS

At the end of this study, various characterization techniques were carried out to evaluate the usability of electrodes containing graphene and fiber structure at different ratios on polyimide by Universal CO₂ laser scribing method in electrochemical biosensor applications. According to the analysis results obtained, the most important factors in determining the performance of the graphene-based electrochemical sensor to be produced are the material properties, atomic bond structures, elemental compositions, atomic ratios such as carbon, oxygen and nitrogen in graphene and graphene fiber electrodes. SEM, Raman spectroscopy, XRD, XPS and CV analyses were performed to investigate and evaluate the morphological, chemical and electrochemical properties of the produced electrodes.

The main objective of this thesis is to examine the effects of changes in the fiberization ratio of graphene structure on polyimide on sensor performance and to demonstrate its suitability for use in electrochemical biosensors.

As a result of SEM analyses, it was observed that the surface morphology and porous structure of graphene and fiber electrodes were affected by changes in laser fluence values applied on the polyimide substrate. Especially in LSG and LSGF30 samples, more homogeneous and porous structures were observed compared to others, and this showed that the sensor structure was suitable for electrochemical interactions. XPS and Raman analyses demonstrated that the obtained graphene and fiber structures exhibited high conductivity by revealing the presence of sp² carbon bonds. XRD results suggested that the crystal structure was maintained in all samples, with minor interlayer changes due to fiberization in the structures. CV measurements were performed at 9 different concentration values in the presence of PBS containing AA to evaluate the electrochemical performances of the four electrodes. As a result of these measurements, LSG and LSGF30 samples were selected as ideal samples for sensor applications due to improved electron transfer and high current response. All analyses support each other. In conclusion, this study has shown that LSG, which exhibits high conductivity, regular graphene structure with some defects, and LSGF30, which shows an increased active surface area with a balanced fiber doping, are suitable for a sensitive electrochemical biosensor. On the other hand, LSGF40 and LSGF50 samples with more fiber incorporation showed poor electrochemical performance due to the

degradation of conductive graphene bonds. When all the findings are evaluated together, the laser parameters were determined according to the C content in the material and the material property for sensor applications.

Thus, it is concluded that optimization of the controlled increase of fiber doping in the electrode content is very important for precise optimization as it directly affects the sensor performance.

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BIOGRAPHY

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