

Aim and Objective

The Objectives of this Dissertation are twofold and encompass the study of a broad range of physical phenomenon and differing skillsets. They can be divided into 2 distinct parts

1. Laser Induced Graphene

The study of a laser ablation technique, it involves:

- ❖ The preparation of Laser Induced graphene using a low-cost diode laser
- ❖ Study of the variations in LIG W.R.T. Laser fluence.
- ❖ To understand the basic mechanism of laser ablation of Polyimide
- ❖ Optimization of the CNC code to create patterned LIG
- ❖ Qualitative study of LIG using Characterization techniques such as Raman spectroscopy, UV-Vis Spectroscopy and X-Ray Diffraction

2. TiO₂ Nano-structure Synthesis by Anodic Dissolution

The Study of an Electrochemical technique, it involves:

- ❖ The synthesis of TiO₂ Nanomaterials by Anodic Dissolution.
- ❖ To understand the basic mechanism of TiO₂ Nanostructures formed in electrolyte containing chlorate ions.
- ❖ To Study the variation of TiO₂ with Annealing.
- ❖ Qualitative study of annealed TiO₂ Nanostructures using Characterization techniques such as Raman spectroscopy, UV-Vis Spectroscopy and X-Ray Diffraction.

Chapter I

Laser Induced Graphene

1.1 Introduction

In 2004 Andre Geim and Kostya Novoselov conducted what is now considered a ground breaking experiment in materials science by isolating high quality few-layer graphene, exfoliated through “Scotch Tape” method. Their report of high electron mobility and stability of few-layer graphene won them the 2010 Nobel Prize in Physics. Since then, the possibility of developing applications for graphene in broad fields has caused many researchers to be devoted to exploring its fundamental properties. Graphene has received much attention due to its exceptional electrical, physical, mechanical and chemical properties while having a simple honeycomb lattice structure composed of 2-dimensional sp_2 -hybridized carbon making it simple to study. Graphene, through synthesis and engineering design, can possess 3-dimensional (3D) structures and porosity, allowing it to have wide range of applications like: energy storage devices, flexible electronic, composite filter and disposable electronics. It also has broad applications in supercapacitors, batteries, sensors, solar cells and flexible screens, owing to its outstanding optical, thermal, and electrical properties. The shortage of Graphene growth and patterning techniques has become a serious issue affecting its deployment in several specialised applications and industries.

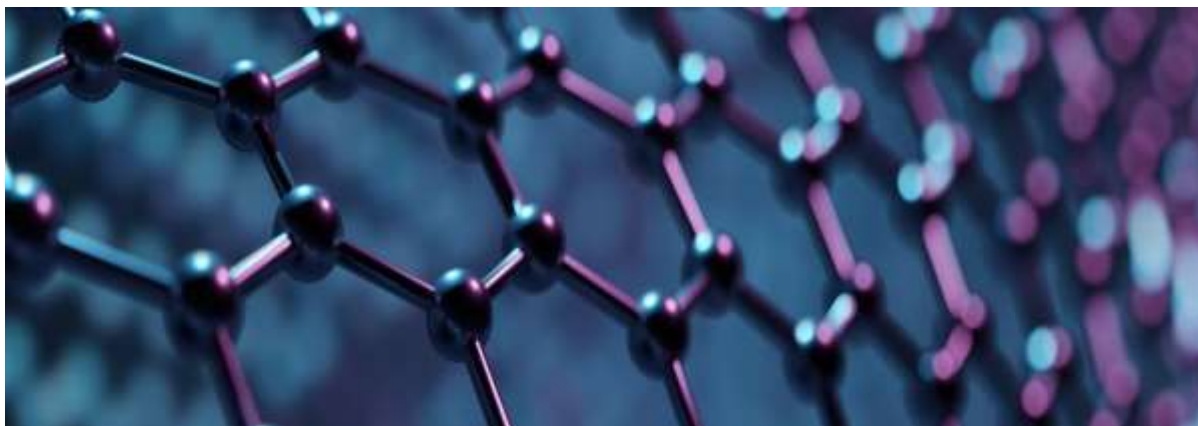


Fig 1.1 Graphic representation of Graphene structure

A large variety synthesis protocols for the commercialization of graphene have been developed, such as liquid-phase exfoliation, graphite oxide reduction, chemical vapor deposition (CVD), epitaxial growth and electrochemical exfoliation. These methods are advantageous in the manufacturing of varying grades of graphene, however scaling-up their productions is hampered by drawbacks such as high energy consumption, massive wastes generation and low productivity.

Graphene owes its remarkable properties to its band structure and low dimensionality because of which its carrier dynamics is strictly confined in a 2D layer. The below figure illustrates the honeycomb lattice(a) which has two lattice sites A and B that are equivalent and allow special electron hopping. The electronic band structure for the monolayer graphene, according to the results of the tight-binding model is shown on the right(b). Take note of the conical valleys that touch at the Dirac points K and K' in the Brillouin zone these are the valence and conduction bands of graphene. This unique band structure allows graphene to behave as a zero band-gap semiconductor with extremely high carrier mobility. The velocity of electrons in graphene is calculated through the dispersion relation to be approximately ~ 106 m/s, about 1/300 of the velocity of light

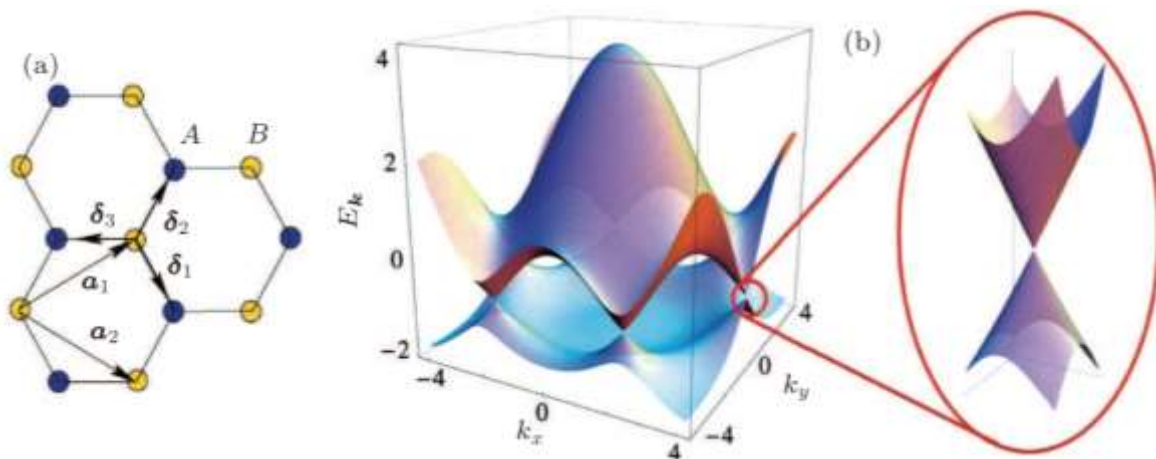


Fig 1.2 (a) Graphene lattice structure and(b) Graphene electronic band structure [15]

The “Formation of a Porous, Patternable, Electrically Conducting Carbon Network by the Ultraviolet Laser Irradiation of the Polyimide (PMDA-ODA)” was reported as early as 1994 by R. Srinivasan et.al. however, at the time the scope of the discovery was unknown. The growing interest of renewable energy sources and energy storage materials coupled with new understanding of the potential of graphene in 21st century has resulted in a renewed interest in this phenomenon.

In 2014, Lin et al. used a CO₂ laser to prepare three-dimensional porous graphene electrodes on a non-transparent Polyimide (PI) by Direct laser Writing method (DLW). The graphene derivative produced by the DLW method has varying properties from pure 2d single layer graphene and is Termed as Laser Induced Graphene (LIG). Compared with the conventional lithographic techniques, such as screen-printing, inkjet printing and layer-by-layer assembly, direct laser writing is advantageous due to the maskless and non-contact fabrication. This top-down approach combines large-area graphene preparation and patterning with a single fabrication step without the need for wet chemical steps, expensive cleanroom equipment, solvents, reducing agents, subsequent treatments, or other supporting processes. Due to these perks laser-induced graphene (LIG) has stimulated research in many areas, ranging from fundamental to applied sciences, investigating the laser graphitization process, effects of various lasers, environments, and lasing parameters, to the development of a large variety of flexible physical and chemical sensors.

1.2 Properties of Laser Induced Graphene

1.2.1 Nomenclature

Laser-induced graphene (LIG) is a foamy multifunctional graphene that is commonly direct-written into a carbon-based precursor material using a suitable laser. Laser irradiation of various carbon precursors including polyether-sulfone, polyimide, wood, clothing paper and food to name a few can form LIG. Since this technology is in its initial development phase, occasional dissimilarities in the nomenclature are also encountered. For example, essentially the same material is designated as glassy carbon, laser-scribed graphene and laser-induced graphene in various studies. We will use the terminology Laser Induced Graphene or LIG in this work.

1.2.2 Surface Morphology and porosity

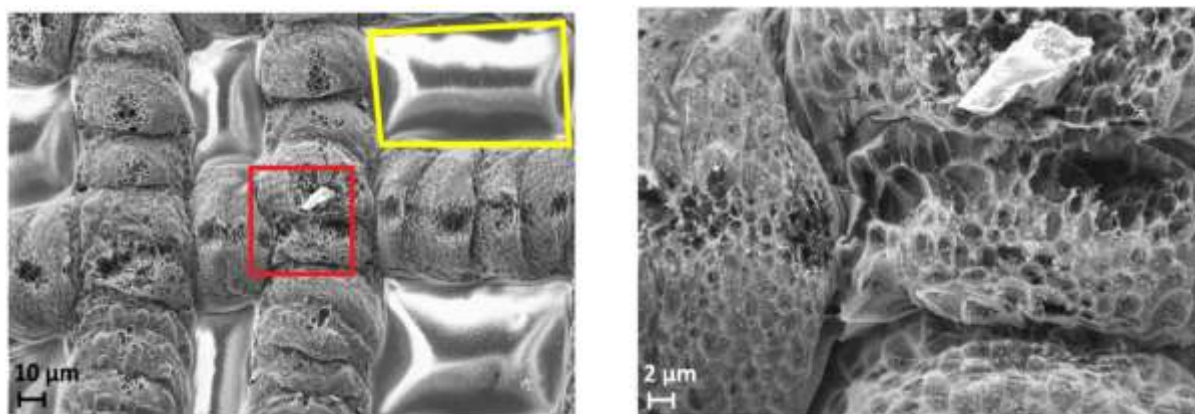


Fig 1.3 SEM image of laser ablated Kapton, non-irradiated surfaces shown in yellow rectangle (left) and porous structure in red rectangle, magnified on the right [13]

LIG surface morphology is known to have a complex and inhomogeneous porous pattern, differentiating LIG from single layer graphene or graphene nanotubes. The transformation of PI to LIG Under laser irradiation, occurs due to a photothermal process caused in part due to the localized high temperature and pressure produced by the laser, which leads to the pyrolysis of materials. The rapid release of gas associated with pyrolysis gives the carbonized material a compact sheet-like stacked and porous structure. Thus, compared with traditional graphene preparation methods LIG combines the benefits of graphene's fantastic electrochemical properties, with a higher specific surface area, resulting in many opportunities and advantages for the field of energy storage materials.

1.2.3 Chemical nature

It should be noted that LIG is distinct from simple laser carbonization of carbon precursors and it consists of a network of porous multi-layer graphene. LIG possesses the previously mentioned high conductivity of graphene, resistance to strain and corrosion as well as large surface area. However, for more than three-layer graphene, the energy band structure

becomes more complicated, and the valence and conduction bands begin to overlap and therefore LIG does not share the unique quantum mechanical behaviour of monolayer graphene. LIG can also be functionalized to catalyse reactions or sense pressure, temperature, intensity of magnetic field, and concentration of chemicals.

1.2.4 Crystallinity and Defects

Unlike the perfect hexagonal honey comb crystal structure observed in single layer or few layer graphene, LIG contains defects in the form of 5- and 7- member rings which can be seen in the figure below. The occurrence of which is due to the short time scale of graphene formation during the ablation process that prevents the rearranging of the carbon rings into a uniform 2D lattice.

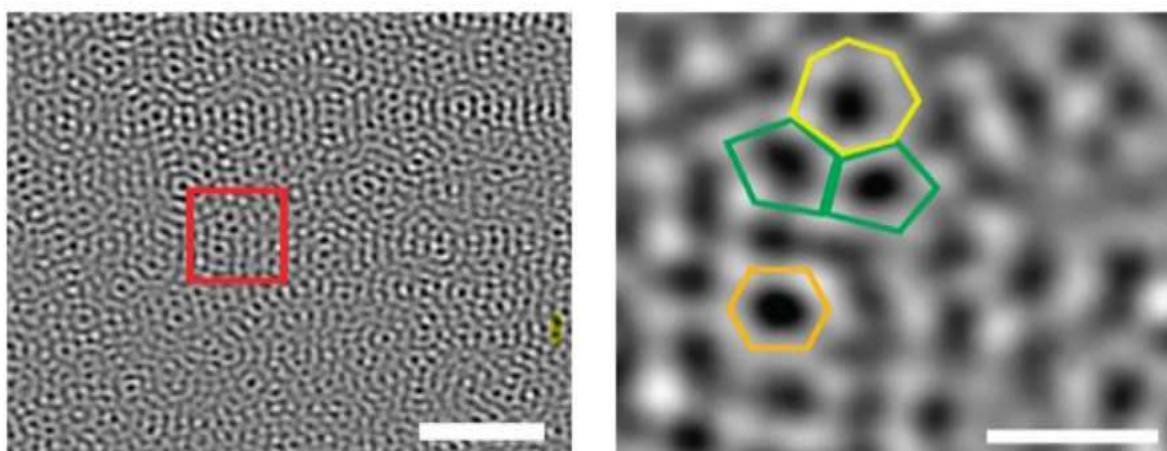


Fig 1.4 TEM images of LIG showing right, graphene structure and left, 5 and 7 membered ring defects Vivaldi et.al.[2]

The abundance of these pentagon-heptagon results in an increase in curvature among the carbon atoms in the graphene layer. Nanoscale ripples also appear at the edge of graphene because of thermal expansion caused by laser irradiation. These factors lead to the possibility of millions of defects in LIG materials, which can be used advantageously for further material doping and modification aspects.

1.2.5 Mechanical properties

The presence of defects however reduces the mechanical strength in LIG much lower than that of single-layer and few-layer graphene. LIG forms as a thin layer of material tightly attached to the surface of the polymer film. This allows it to be a suitable candidate for the manufacture of micro-electronic devices such as flexible electronics. The thermal power of the LASER plays an important role in determining the mass of LIG on the film, and the increase of laser power leads to the increase of graphitization degree. When the thermal power exceeds a certain level, the oxidation process begins to cause an increasing bad impact on the quality of the film. Further increase of LASER energy may cause the LIG on the surface of PI sheet to fracture or even fall off, and the porous structure of the 3D graphene surface will also be affected.

1.3 Factors Affecting LIG

LIG morphology, crystallinity, and composition can be fine-tuned by appropriate choice of substrate, type of laser, in particular the actual laser fluence, as well as the lasing environment. Core components and possible variations of the LIG process are depicted in the below figure. The major factors are the substrate, the environment and the radiation source i.e., the LASER itself.

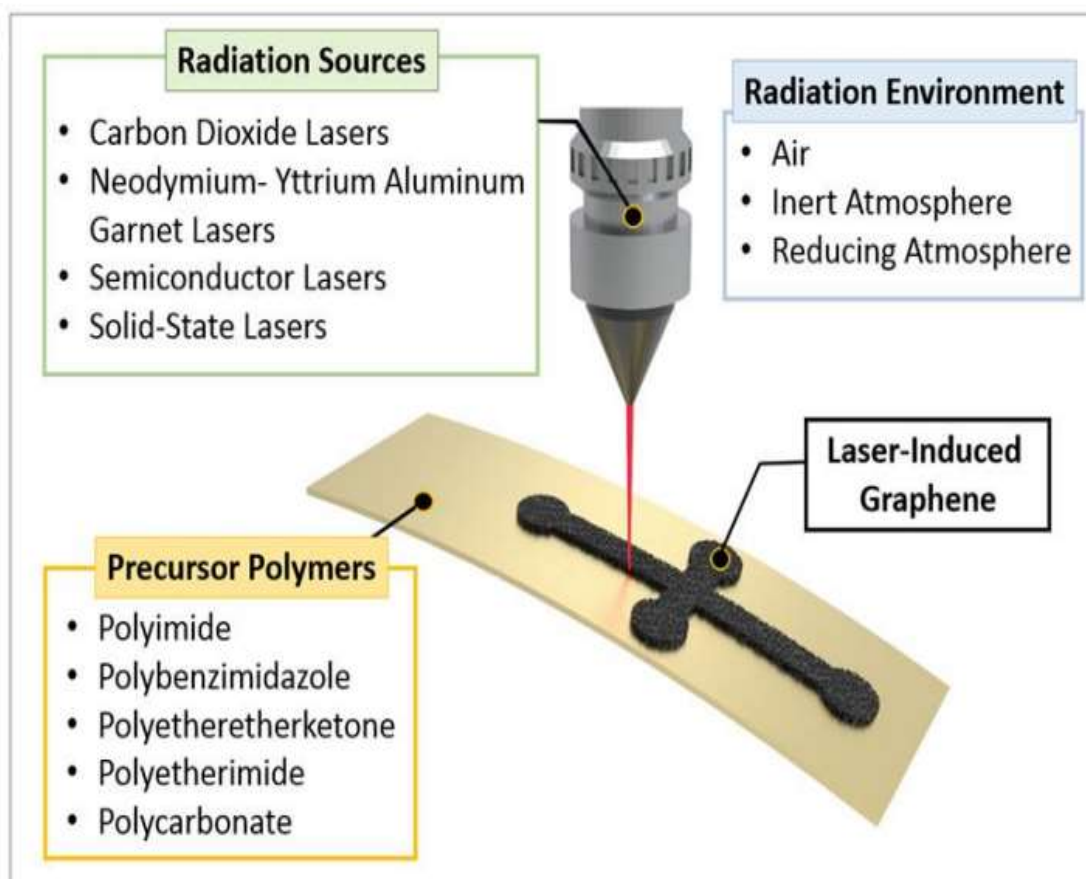


Fig 1.5 Fabrication of LIG with examples of possible laser types, polymers, and laser radiation environments [1]

1.3.1 Substrate

Many Known Carbon Substrates Such as Polyimide, Poly Urethane, Teflon, lignin, Bread potato etc. can give LIG on ablation with suitable laser power. Scribing LIG existing on the surface of the material containing a lot of lignin such as wood and paper needs to be prepared in nitrogen atmosphere to prevent oxidation and thus choice of substrate is crucial for preparation of LIG in ambient conditions. The use of precursor polymers made up of heteroatoms such as sulphur or fluorine or mixed with other compounds, permits one to obtain doped LIGs and further expands the surface chemistry and the possible applications, especially in electrocatalysis and sensing fields

1.3.2 Environment

An important factor determining the structure and composition of LIG is the processing environment. The Hydrophilic or Hydrophobic nature of the surface and internal structure of LIG may be altered by changing the atmosphere conditions. In a controlled atmosphere, high concentration of oxygen will make the adopted LIG contain more O atoms, which means that it becomes easier for edges to contact with water. These LIG materials are more hydrophilic and increase the energy density of energy devices such as supercapacitors. In contrast, when H_2 or SF_6 is used as the atmosphere during laser irradiating, the former could achieve higher hydrophobicity by reducing C-O bonds on the LIG surfaces the super-hydrophobic surface is obtained by forming C-F bonds with low surface energy on the LIG surfaces in the latter.

Multiple differences in LIG fabricated from the same PI precursor in air or under nitrogen atmosphere were observed by Mamleyev et.al.[4]. LIG formed in air was found to be thicker, had a slightly lower conductivity, a hydrophilic character and a higher porosity, whereas under N_2 a hydrophobic character, higher graphitic content and a different morphology were observed. The authors postulated that because of these characteristics the LIG prepared in nitrogen was suitable for applications in electronics thanks to its higher graphitic content, while LIG prepared in air due to its higher surface area was more apt in the sensor and biosensor field. Tour et.al. [5] also reported on the use of air assist and close chamber methods for the control of atmosphere. To control the specific atmosphere a special preparation space containing inert gas is required as depicted in the figure below. These arrangements are complex and may hinder further industrialization of LIG. In our work we will focus on LIG production in ambient conditions to show the simplicity and versatility of the process.

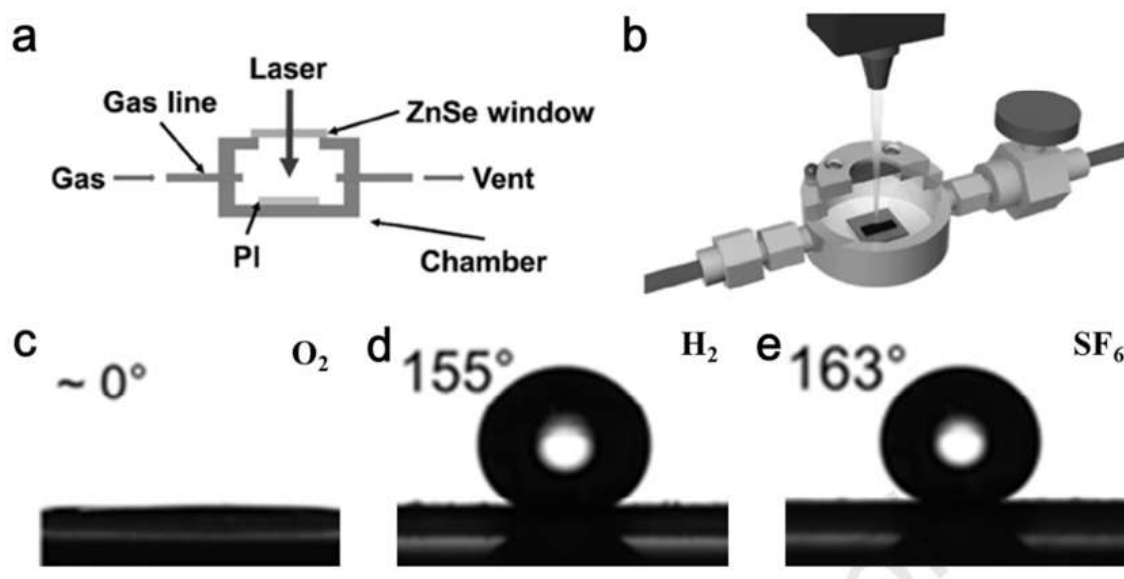


Fig 1.6 The influence of atmosphere on the LIG surface. (a-b) The controlled atmosphere chamber for fabricating LIG. (c-e) Contact angles of the water droplet on the LIG surfaces made in the atmosphere of (c) O_2 , (d) H_2 , (e) SF_6 Mamleyev et al. [3] and Tour et.al. [5]

1.3.3 Laser

Besides infrared CO₂ lasers for example Lin et.al. in 2014, successful synthesis of LIG by visible laser and ultraviolet laser have since been reported. In the case of the infrared laser, it was suggested that the photothermal effect accounts for the Kapton to LIG transition. The high energy density of the laser leads to instantaneous pyrolysis causing the breakdown of the chemical bonds in the precursor and subsequent recombination with the release of gas. It is theorized that a photochemical process is more likely to occur when using an ultraviolet laser. The closeness of the photo energy of the ultraviolet radiation to the chemical bonds in the precursor would allow direct absorption of photons and breaking of the chemical bonds to form LIG. The overall process may be classified as laser ablation.

1.3.3.1 Laser Ablation

Ablation is removal or destruction of something from an object by vaporization, chipping, erosive processes or by other means. Laser ablation is a method that utilizes a laser as an energy source for ablating solid target materials. In this process extremely high energy is concentrated at a specific point on a solid surface to evaporate light-absorbing material.

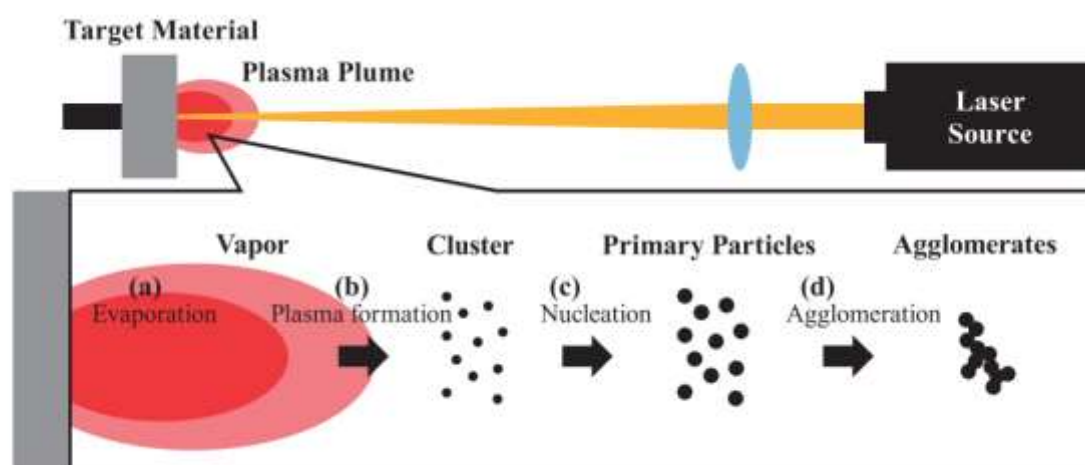


Fig 1.7 Ablation process [8]

The ablation mechanism is a complex interrelated system, where photochemical and photothermal reactions are very important. The pressure jump, which is associated with the creation of small molecules and originates from both types of reactions, is also important for ablation. The importance of each effect is strongly dependent on the type of polymer, the laser wavelengths, the pulse length, and the substrate. In the case of LIG formation majority of ablation products are gaseous.

1.3.3.2 Laser Fluence

Laser fluence **H** is the major factor controlling LIG morphology. It quantifies the laser energy deposited onto the substrate during LIG formation and is given by:

$$H = \frac{P}{v \times s \times PPI}$$

equation 1

where P is the power, v the scanning speed, s the spot size, and PPI the number of spots per inch set to 1 in our situation. Equation obtained from Vivaldi et al [2].

Mamleyev et [4] all noted threshold fluence of 1.3 J cm^{-2} using an IR laser. Above fluence of 3.5 J cm^{-2} carbon films begin to peel off and become unusable for device fabrication. After the conversion threshold is reached the carbon content is maximized and will decrease with higher fluence values. The oxygen content however, is increased with higher fluence values at the same time which results in a lower-grade LIG. Increasing the fluence has the benefit of improved depth of conversion allowing more LIG is formation and layering; this then causes the sheet resistance to grow up to a certain fluence value. By precisely varying the scanning speed v using a CNC setup and keeping spot size constant we can accurately vary the laser Fluence.

1.4 Apparatus

1.4.1 Polyimide or Kapton

For our study the material Polyimide (PI) branded ‘Kapton tape’ was the substrate of choice due to its easy availability, robust nature, flexibility, wide range of thickness available, thermal and insulative properties as well as chemical stability. Polyimide films represent the first and most popular precursor substrates for LIG manufacturing and are readily available on the market in the form of sheets, rolls, and even adhesive tapes with a wide range of thicknesses. The presence of aromatic Sp_2 carbons in PI are more prone to form hexagonal graphene structure making it an excellent substrate material. The presence of CN bonds which on ablation give gaseous by products further increase porosity of LIG which highly increases the surface area and is thus advantageous in applications such as supercapacitor. PI is also non-reactive to the human body and is promising for use as flexible skin sensors.

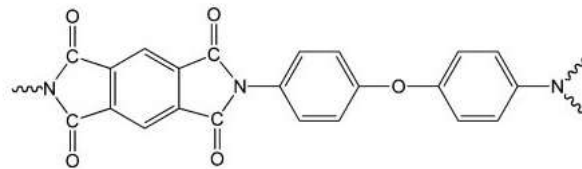


Fig 1.8 Kapton monomer T Lippert [4]

Kapton is a Polymer which are macromolecules, that can be synthesized from one or more different monomers using different types of polymerization techniques, it has the formula $C_{22}H_{10}N_2O_5$ and its monomer is shown in the above figure.

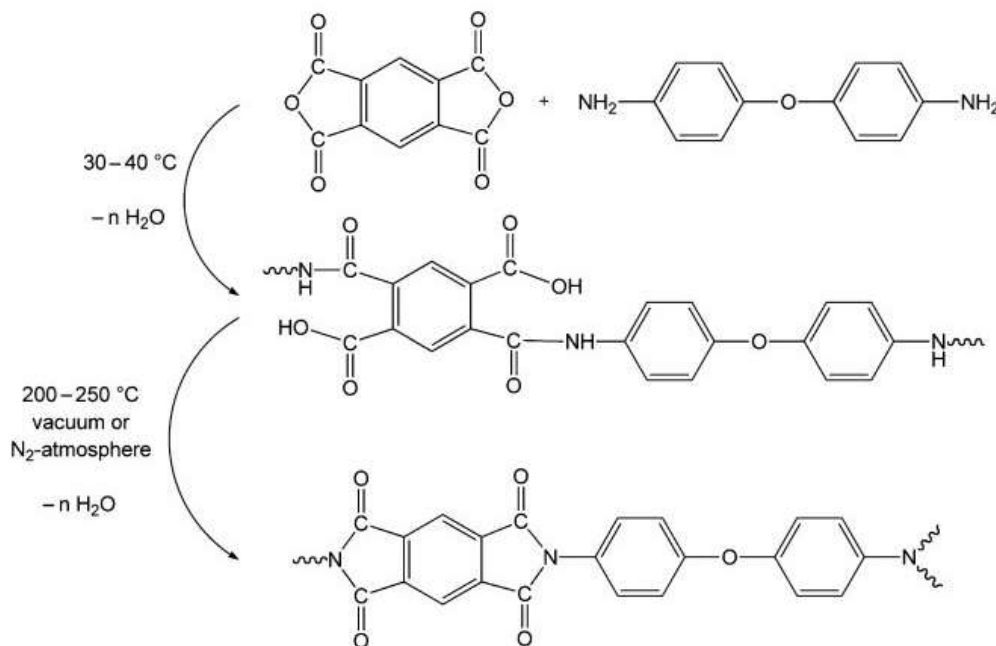


Fig 1.9 Polycondensation of PI T Lippert [4]

Kapton was pioneered in the 1950s by workers at Dupont who developed a successful route for synthesis of high molecular weight polyimide involving a soluble polymer precursor. Up to today this route continues being the primary method for the production of most polyimide. The polycondensation of pyromellitic dianhydride and 4,4'-oxydianiline used to prepare polyimide is depicted above.

Polymers produced by this method on decomposition by thermal or photochemical methods tend to show a pronounced fragmentation into various small molecules. The molecular differences in the polymer precursor affect the gases evolved during LIG formation. The large number of small decomposition products will result in a pronounced pressure increase inside the polymer matrix, which is important for ablation process. The decomposition products are depicted in the figure below all fragments have been detected by various analytical methods as seen in the literature.

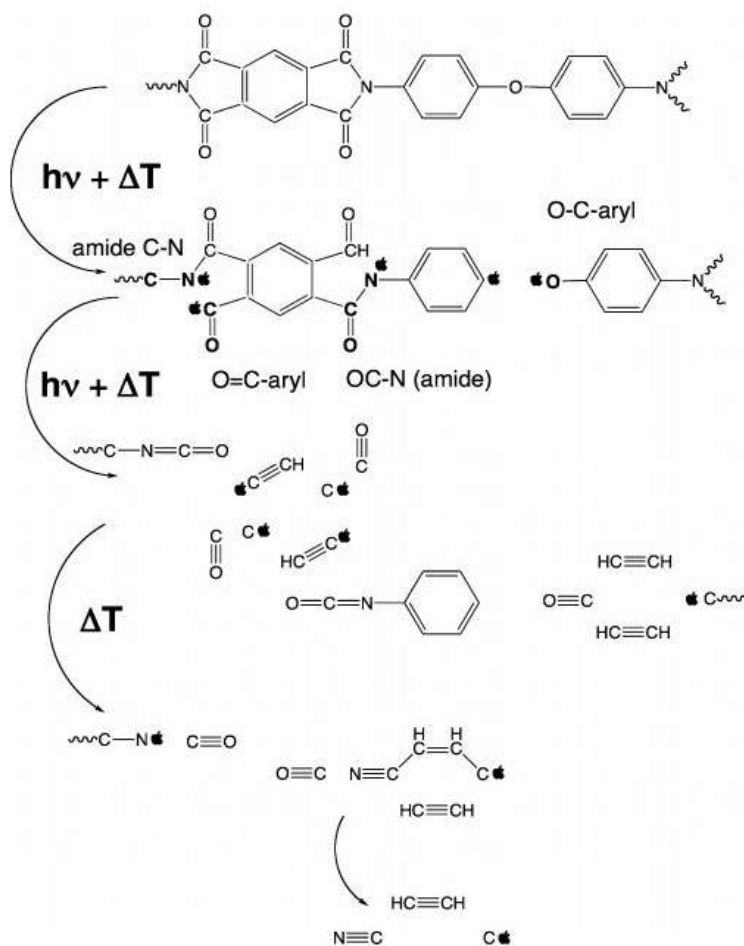


Fig 1.10 Laser-induced decomposition/fragmentation of Kapton T Lippert [4]

For our study we used Aadvay brand of Kapton tape from seller Aadvay Enterprises obtained on amazon. This brand was used as it has no adhesive and a thickness of 0.025MM. Do note that the use of the term Kapton tape in this document is with reference to the above and should not be treated in the literal sense as there is no presence of adhesive. We found that the Kapton had an additional coating of plastic on one side therefore LIG was obtained on ablation of the non-plastic side of the Kapton tape.

1.4.2 Diode Laser

Growing interest in Graphene along with the work of Chemist James Tour and the Rice University has created increasing research and experimentation in LIG technology, although the majority of published works employ a high-powered IR laser [5][14]. Recent work has also demonstrated the formation of LIG using a UV laser of lower power. Visible 405 nm lasers have been used to produce LIG from various carbon sources in papers by Tour et.al. [10], wang et.al. [11] and even semiconductor lasers were successfully employed in works by Huang et.al. [12] and Romero et.al. [13]. The theorised photochemical breakdown of bonds during the ablation process of the substrate caused by the interaction of UV light with C-C and C-N bonds makes the study of LIG formation and characterization by UV LASER a promising field.

Better understanding of the Photothermal and photochemical processes behind LIG may allow for better tuning of parameters for the production of specific and advantageous forms of LIG as well as further the industrialization of the process. In our work we wish to replicate the Success of the above authors using a low cost or easily available low power diode laser that has obvious advantages as compared to the large high powered and expensive IR and Excimer lasers in use today. It is our hope that a positive outcome may allow for increased industrial usage of this technology as well as more research due to the low cost, size and efficiency of the diode laser.

1.4.2.1 Working of Laser

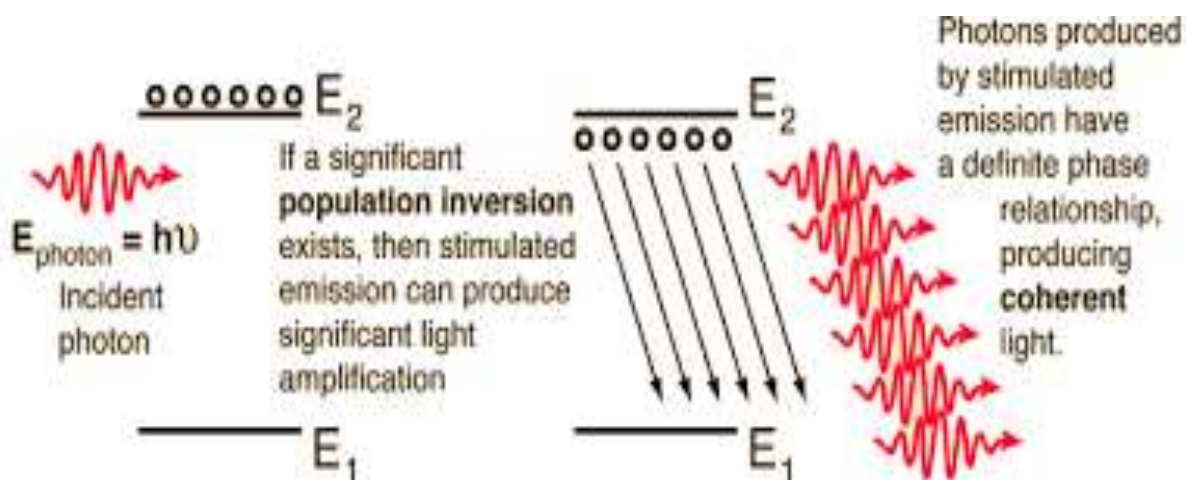


Fig 1.11 Principle of Lasing action

L.A.S.E.R. is an acronym for Light Amplification by Stimulated Emission of Radiation. Lasers work on the concept of Population inversion maintained by a pump that may be electrical or optical. Population inversion allows for continuous stimulated emission leading to the characteristic properties of monochromaticity, high intensity, high directionality, high coherence and small spot size shared by Lasers. Many classes of lasers exist such as Ruby lasers, gas lasers, Excimer lasers, etc. In our work we use a Semiconductor Diode laser whose working we will further explore in this section.

Semiconductor Lasers are unique when compared to other types of lasers. They are small, operate with relatively low power input and are very efficient. They require the merging of a p-type and n-type material between the interface of which the lasing action occurs as depicted below. Stimulated emission occurs when electrons in the higher energy of the conduction band recombine with holes in the valence band. The energy required to do so is termed the bandgap of the material. Different bandgaps thus emit different wavelengths of light. Diode lasers may be further classified into edge emitting and surface emitting lasers. Population inversion in Diode lasers is maintained through electrical pumping by providing a suitable forward bias voltage across the p-n junction to overcome the band gap. They generally have lower power than other laser types

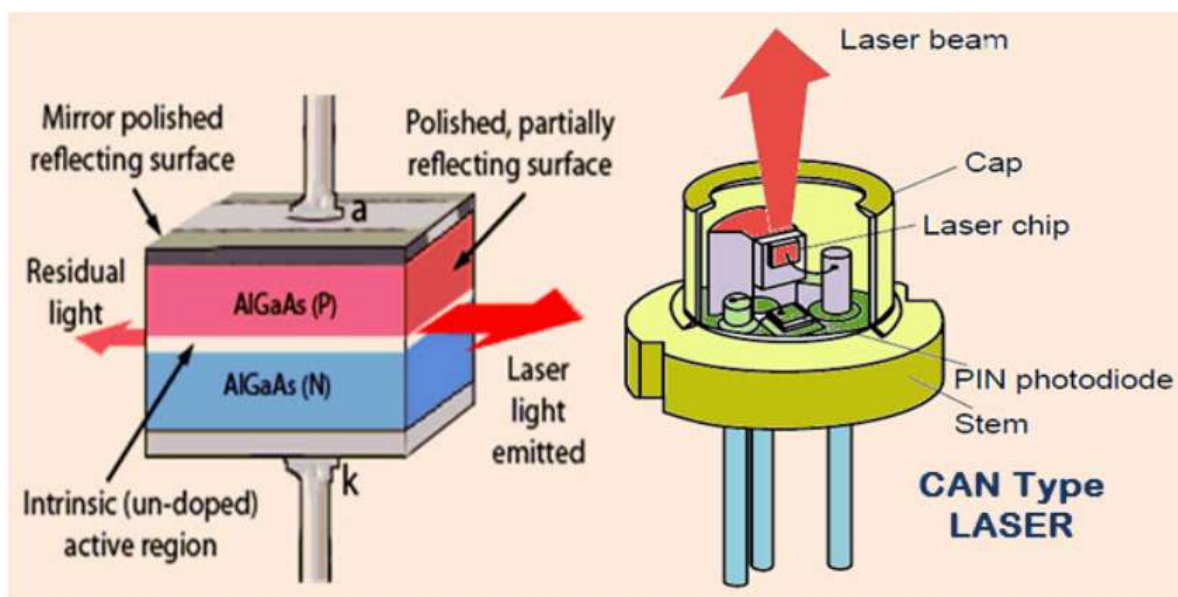


Fig 1.12 Laser Diode construction elprocus.com

1.4.2.2. Laser Properties

The laser used in this work is a 'WOL 3D CREALITY 3D high power laser' (Shenzhen, China) obtained from the Wol 3D store on amazon as seen in the figure below (right). It is a 1.6W, 500MW Diode Laser with operating Current 21000 mA at 12 volts (DC). It is a UV-Vis Laser with 405 nm wavelength and Class 3B safety rating requiring the use of safety goggles during its operation. The Laser can be optically adjusted by rotating the laser head containing a dedicated optical glass, ensuring proper focus at any vertical distance as well as control over the spot size. The laser can be pulsed using a compatible electronic interface. Laser spot size was recorded with the use of graphing paper.

1.4.2.3. CNC Lasing Setup

The low-cost laser comes as an add-on to a Computer Numerically Controlled (CNC) apparatus typically used for 3D printing under the brand name 'Ender 3 by Creality' sold by

Wol 3D store on amazon pictured in below(left). The total cost of the apparatus including CNC machine, laser, safety goggles and Kapton tape was less than 25,000 rupees.

This setup is advantageous as the Laser is fully compatible with the CNC machines software as well as hardware making it easy to mount, operate and troubleshoot.



Fig 1.13 CNC Apparatus(left) and diode laser used(right).(from Creality Ender 3 Manual)

The CNC apparatus allows accurate movement of the laser in 3 dimensions through the use of stepper motors and various sensors. It also ensures fine motor control over laser scan speed, path and accuracy. Laser scribing Process with Computer numerically controlled (CNC) Laser allows patterning of LIG on substrate with a fully customizable shape. The shape of LIG could be easily controlled by the computer design, which holds a great promise toward the development of printable electronics.

In order to create LIG of a particular shape or pattern we must first convert the desired shape into a bit map so it can be processed by a computer. This bit map is processed and converted into a suitable path that the CNC machine can follow. This can be achieved using a variety of imaging software. In our case we used the 'Inkscape project' software which is open source, and also allowed us to directly convert the file to the G-code (RS-274) CNC programming language used by the ender 3. It also allowed easy repeatability of the experiment by re-using the saved program file which ensures the same parameters are

maintained each time. The laser parameters such as laser path, scan speed, pulse duration as well as geometrical aspects such as line spacing and infill can be adjusted using the program.

1.5 Procedure

1.5.1 Experimental Setup

The experimental setup is fairly simple consisting of the laser mounted on the CNC machine onto which the Kapton is secured with double sided tape. The Ablation process takes place in natural atmosphere in ambient conditions.

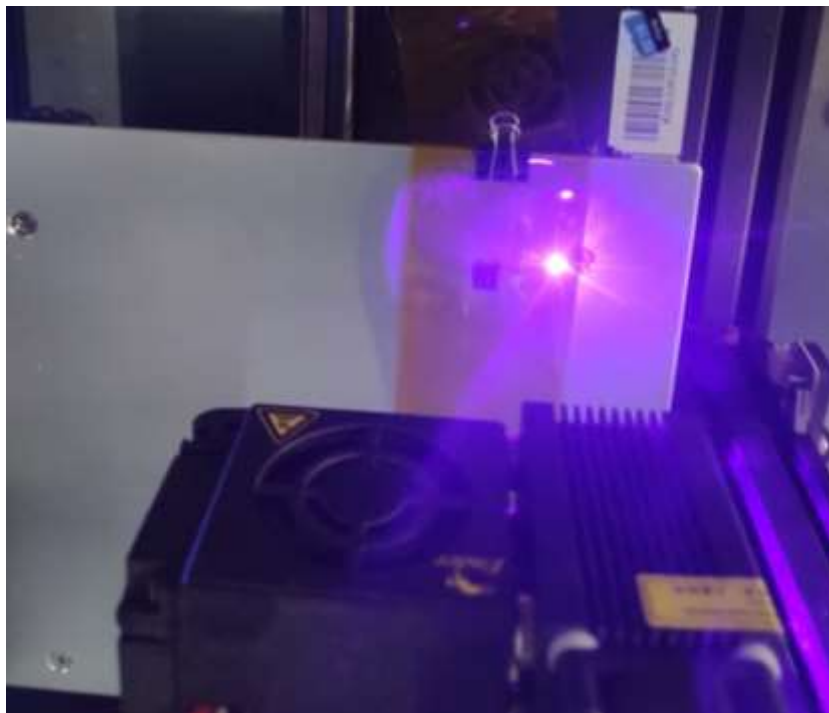


Fig 1.14 Laser Ablation of Kapton

1.5.2 Experiment

The Kapton tape and CNC bed are washed with ISO-propyl alcohol to remove contaminants and fingerprints. The z axis i.e., the vertical axis of the CNC is set to 10 centimeters as recommended in the manual. The Laser is turned on and focused. It is then moved above the Kapton tape. A program file is prepared depending on the experiment parameters and loaded onto the onboard processor of the CNC machine using a micro-SD card. The CNC machine then runs the program and the Direct Laser Writing process begins. Once complete LIG samples is transferred carefully onto scotch tape.

Chapter II

TiO₂ Nano-Structure Synthesis

by

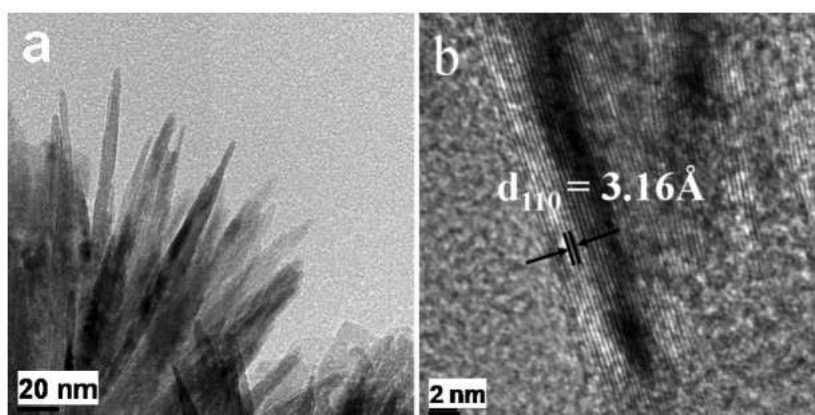
Anodic Dissolution

2.1 Introduction to Anodization

Anodization is a method for changing the surface chemistry of metals. It is an Electrochemical process by which natural oxide layer of metal is thickened, this increases resistance to corrosion and wear, therefore it is a type of passivation process. The process involves an electrolytic cell wherein the part to be treated acts as the anode, due to which the process gets its name. The microscopic texture of the surface and the crystal structure near the surface changes. In 1857 Buff Discovered that aluminum can be electrochemically oxidized to form an oxide layer thicker than the native one, this anodization process was later exploited in 1920s for industrial applications such as protection of sea planes from corrosive sea water.

Metals such as Aluminium, Tungsten, Titanium, magnesium, Zirconium, Niobium, have a thin layer of metal oxide that protect the material from further oxidation. The thickness of this

layer and its properties vary greatly depending the metal, for example in ambient temperatures aluminium is rapidly coated by a compact oxide 2-3 nm layer thick. gives aluminium



on

layer
This
good

corrosion resistance however local corrosion may occur in aggressive outdoor environments. The growth of this “**barrier oxide**” layer may be promoted under the anodization process with control on the thickness, density and uniformity, depending on the process condition.

Fig 2.1 TiO₂ Nanoneedles Synthesised using Anodic Dissolution Hyam et.al. [16]

In the case of TiO₂ nanotubes, electrochemical anodization due to its controllable, reproducible results has seen wide usage. It is a single process wherein tuning the size and shape of nanotubular arrays to the desired dimensions is feasible. Therefore, demands of specific applications employing specialized TiO₂ nanotubular structures may be met by means of controlled anodic oxidation of the Titanium substrate. In addition, the anodization parameters can be varied to control the morphology and thickness of TiO₂ films. To add to its merit, it is also a cost-effective method and good adherent strength has been attributed to tubes prepared via this method.

2.1.2 Anodization-cell

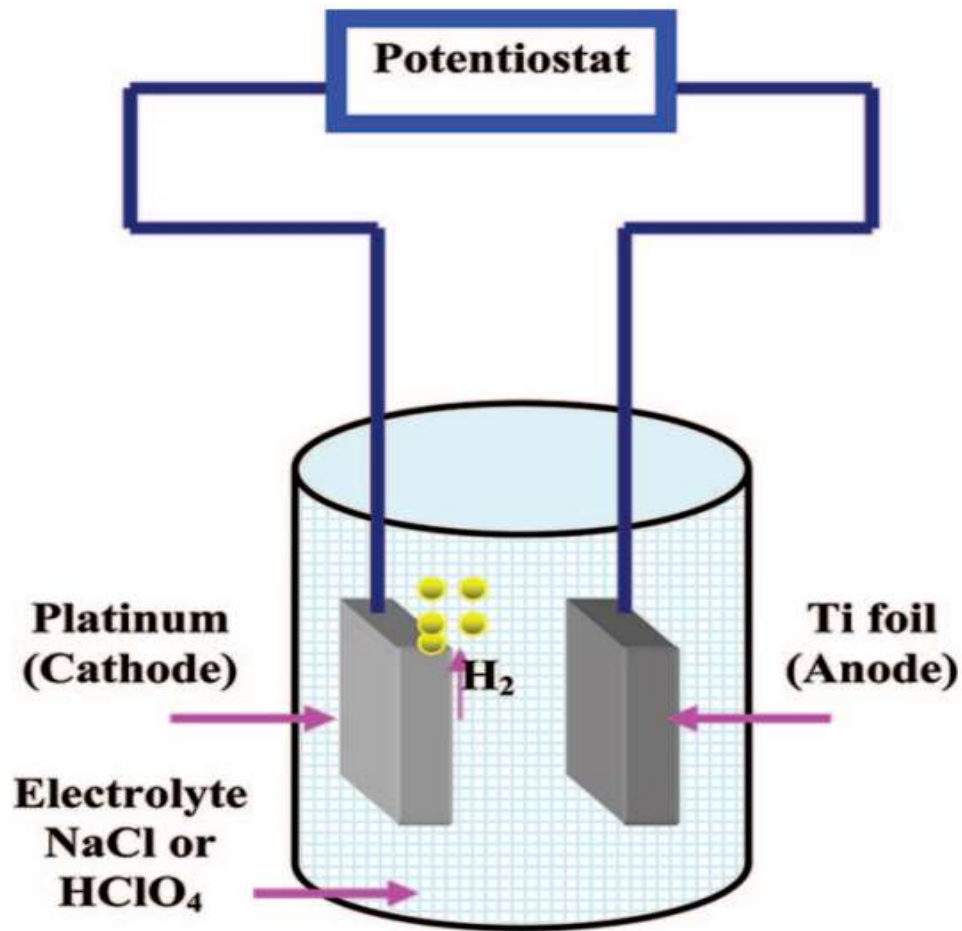


Fig 2.2 Typical Anodization cell Fahim et.al [20]

In an anodizing cell, the positive terminal of a dc power supply is connected to the workpiece making it the anode. The negative terminal of the supply is connected to the cathode which is a plate or rod of carbon, lead, nickel, stainless steel – any electronic conductor that is unreactive (inert) in the electrolytic bath. An electrolyte is a medium, containing ions that is electrically conducting through the movement of ions, but not conducting electrons.

When the circuit is closed, electrons are withdrawn from the metal at the positive terminal, allowing ions at the metal surface to react with water to form an oxide layer on the metal. The electrons return to the bath at the cathode where they react with hydrogen ions to make hydrogen gas. Anodizing is, therefore, a matter of highly controlled oxidation - the enhancement of a naturally occurring phenomenon.

2.1.3 Nanotube formation

A schematic showing the formation of TiO_2 nanotubes is shown below:

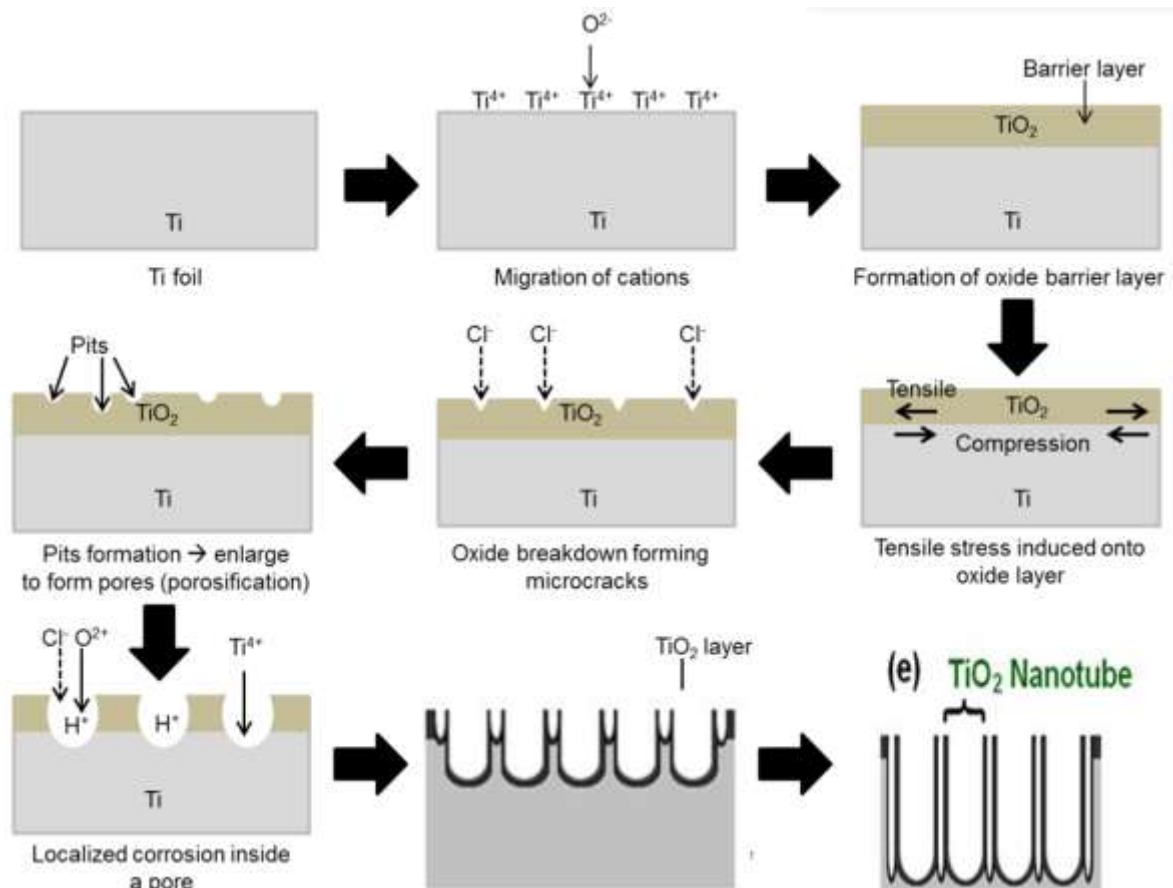


Fig 2.3 Nanotube structure formation, Ishibashi et al. [18]

Along with the generation of the TiO₂ film, the inward migration of O₂⁻ into Ti During anodization necessitates the expansion of the volume at the Ti metal surface. As the process continues the distortion of the lattice becomes greater due to this volume expansion and the release of reaction heat becomes more difficult. Therefore, a huge number of microcracks arise on the oxide/electrolyte interface in order to lower the internal stress. the electrolyte then quickly fills into these small cracks. The presence of chloride ions in the electrolyte will cause chemical etching to occur, further increasing the size of the cracks which will then develop into pits. With time, pits grow upwards forming larger and more stable structures called pores, the presence of which provides an easier pathway for more O₂⁻, OH⁻ or Cl⁻ to migrate through the barrier layer, leading to further metal oxidation. Furthermore, the electric field distribution within the oxide film changes because of the occurrence of microcracks. The field increases greatly especially at the bottom of the cracks and porosification process takes place due to the H⁺ ion accumulation inside the bottom of the pores. This causes the reduction of the electrolyte pH at the pore bottom, accelerating the chemical dissolution process. which will result in the inward growth of the pores thus forming the typical elongated tubular structure.

2.1.4 Current v/s time Characteristics

The current versus time diagram for a typical anodization process is shown below, the formation of TiO_2 nanotubes involves the following steps:

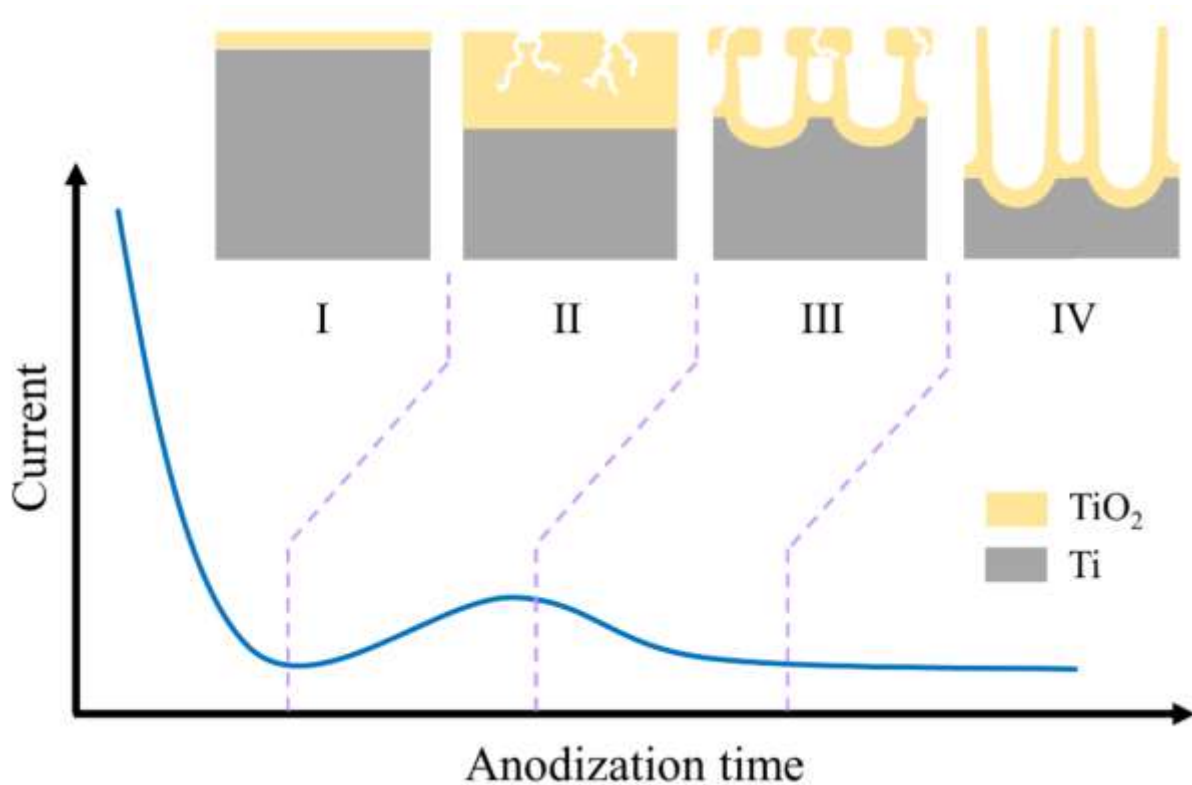


Fig 2.4 Current v/s Time diagram for Ti anodization Yoo et.al. [21]

- 1) Initially the current decreases rapidly due to the increasing resistance of the rapidly growing oxide layer.
- 2) In the second step, the current increases slightly due to the formation of nano-sized pits, which are formed due to attack by the Cl^- ions. The local electric fields are strengthened in these pits, thus attracting more anions to participate in the oxide formation and dissolution reactions.
- 3) As a tubular structure begins to form beneath the pits, the current decreases again.
- 4) When oxide formation and dissolution reactions reach equilibrium, the current converges.

If the oxide formation rate is faster than the oxide dissolution rate, the length of the TiO_2 nanotubes will increase as a function of anodization time. When the rates of these two competitive reactions are in a steady-state equilibrium, the growth of nanotubes is halted, and they maintain their length. However, longer anodization time causes the formation of nano-needles, which are produced by nanotubes splitting in the direction of the applied electric field of the Cl^- ions.

2.1.5 Factors affecting anodization

Effect of electrolyte

By controlling the electrochemical anodization parameters one can obtain different titanium oxide structures such as a disordered porous layer, a highly self-organized porous layer, a flat compact oxide, and/or finally a highly self-organized nanotubular layer. Another discrepant factor is the chemical dissolution rate of the oxide layer in different electrolytes. The quality of the tubular structure is strongly influenced by the nature of electrolyte used for the development of TNT.

Effect of Electrolyte pH

The pH of the electrolyte can affect the self-organization behaviour of TNT and is the key to achieve high-aspect ratio nanotube growth. the pH alters the thickness and diameter of the pores because of the pH dependence of the oxide dissolution rate, i.e., dissolution rate at higher pH is much lower than that at low pH. Therefore, the difference in the pH leads to significant variations in the pore diameter.

Effect of Applied Voltage

Properties such as the inter pore distance, pore diameter and film thickness in a wide range are strongly influenced by the applied voltage. Similarly, the applied voltage and anodization time is strongly correlated to the morphology of the layer. In the short-term anodization, the rings on the side walls of the individual tubes connected them with each other, whereas in the longer-term anodization, dissolution of these rings causes the tubes to be separated.

Effect of Temperature

At higher temperature, faster etching rates are observed due to reduction in the electrolyte viscosity. The faster etching increases the oxide layer dissolution rate and pore formation. At lower temperature, slower etching rates are observed as a result of the suppressed mobility of the electrolyte ions. Therefore, no regular pores were formed at lower temperatures because of the slower etching rate of the oxide layer.

Effect of Current Density

Different pore sizes are produced by different current densities, which impacts the electrochemical etching rate. An increase in the current density directly causes an increase in the electric field intensity, power and the electrochemical etching rate. Further increase in the current density of Ti foil results in the growth of TNT pore size. Consequently, different tube diameters could be produced by controlling the current density.

Effect of Anodization Time

The TNT formation mechanism is strongly influenced by the anodization time. If the anodization time is too short There is no TNT formation.

2.2 Properties of TiO₂

2.2.1 Physical and chemical properties.

Titanium dioxide (titania, TiO₂) is chemically inert, semiconducting material that also exhibits photocatalytic activity in the presence of light with an energy equal to or higher than its band-gap energy. TiO₂ in all its crystal forms is a wide-bandgap semiconductor with suitable band-edge positions that enable its use in solar cells and for photocatalytic reactions. Photogenerated electron– hole pairs can be used for splitting water into oxygen and hydrogen, or can be used for the remediation of hazardous wastes, such as contaminated ground waters, or the control of toxic air contaminants.

These characteristics offer a wide range of applications. For these reasons, and because of the relatively low price of the raw material and its processing, titania has gained widespread attention over recent decades.

TiO₂ has been classified in humans and animals as biologically inert, and is widely considered to be a “natural” material, which at least partially contributes to its relatively positive acceptance by the public. It is a white, water-insoluble solid, although mineral forms can appear black. TiO₂ has Three polymorphs Rutile, Anatase and Brookite, unit cells pictured below (Ti-red, O-pink)

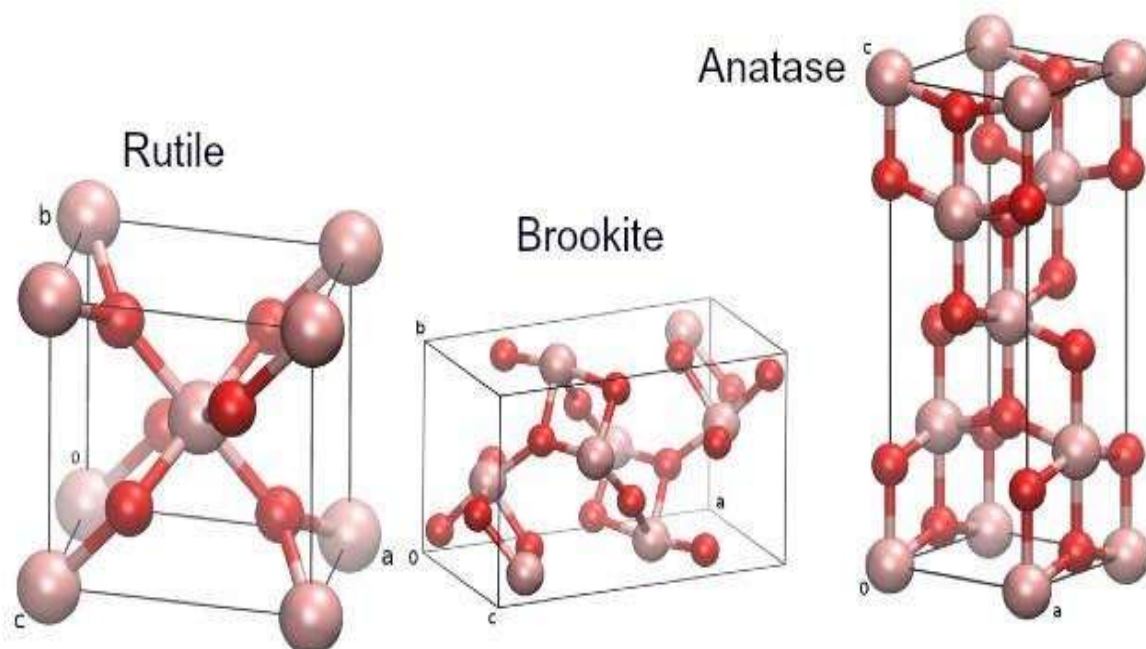


Fig 2.5 TiO₂ polymorphs

Titanium exhibits octahedral geometry in all three of its main allotropes, as it is bonded to six oxide anions. The oxides in turn are bonded to three Ti centres. The overall crystal structure of rutile is tetragonal in symmetry whereas anatase and brookite are orthorhombic. The anatase and rutile have higher stability and photoactivity properties and therefore have a wider application as compared to brookite.

2.2.2 TiO₂ Nanoparticles

Nanoparticles (NPs) are generally defined as particles having at least one dimension smaller than 100 nm. They are intermediate between microscopic and molecular structures. By diminishing dimensions to the nanoscale, not only the specific surface area increases significantly but also the electronic properties may change considerably (owing for example to quantum size effects, strong contribution of surface reconstruction, or surface curvature). These effects may also contribute to drastically improve the reaction/interaction between a device and the surrounding media, thereby making the system more effective (kinetics), or even allow for entirely novel reaction pathways.

Based on the dimensionality of their features TiO₂ nanomaterials can be classified into two-dimensional (2-D, nanobelt or nanosheet), one dimensional (1-D, nanowire, nanotube or nanorod) and zero-dimensional (0-D, nanoparticle). Among these 1-D or so called nanotubular structure is of great interest. Anodic oxidation of Titanium has been recognized as an efficient and facile approach to form vertically-oriented self-ordering nanotubular structures, that behave as room temperature conductors, and hence has gained wide interest and much attention. Different morphologies like nanotubes, nanospheres, hollow spheres, nanoneedles etc may also be obtained by suitably tuning the anodization parameters.

2.3 Anodic Dissolution

Anodic dissolution or Rapid breakdown Anodization (RBA) is a modified form of anodization in which metal dissolves from the anodic workpiece and various electrochemical reactions take place in the bulk electrolyte. It is a quick process that makes use of chloride and perchlorate ions in the electrolyte. When an oxidation voltage or current is applied, the electrode (anode) dissolves and consequently, the metal ions are rapidly released near the electrode surface. Gases are liberated at the cathode as well as at the anode surface and the gap between electrodes increase due to metal removal.

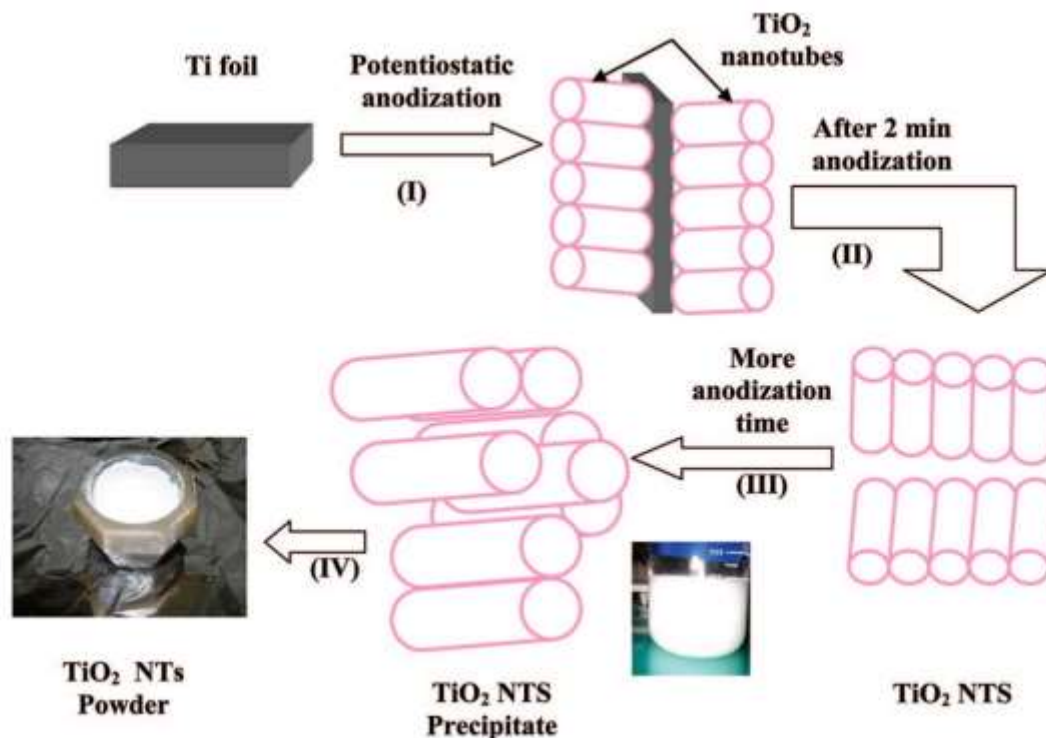


Fig 2.6 Stages of Anodic Dissolution. Fahim et.al. [20]

The metal ions may then form oxides having nanostructures depending on the anodization cell conditions. These nanostructures mix into the bath can be obtained from the bath using appropriate separation techniques. Titanium Anodization in chloride- or perchlorate-containing electrolytes, under breakdown conditions, leads to rapid formation of high aspect ratio Titanium nanotube (TNT) bundles.

Fabrication of TiO₂ nanotube powders by rapid breakdown anodization is summarized in the above figure and involves the following steps:

- I. TiO₂ NT bundles are synthesized on both sides of Ti foil.
- II. After anodization for more than 2 min, due to the vigorous nature and the ultrahigh speed of the reaction, tubes formed on the Ti surface start releasing into the electrolyte.

- III. The anodization process continues until the initial Ti metal foil is completely transformed into TiO₂ NTs, and a white precipitate has been formed.

2.4 Experimental Parameters

2.4.1 Electrolyte: Perchloric acid

Perchloric acid is a strong mineral acid commonly used as a laboratory reagent. It is a clear, colourless liquid with no odour. Most perchloric acid is sold as 60%-62% or 70%-72% acid in water. Above 70% when hot it's a powerful oxidizer but is comparable to strong mineral acids at aqueous concentrations below 70%.

Perchlorate ion is quite stable as compared to chlorate ion owing to larger degrees of freedom over which electrons may be distributed leading to a lower energy structure and thus higher stability. This allows for its use at higher current density and voltage range. The acid is also less likely to decay and hence the electrolyte does not have to be constantly regenerated.

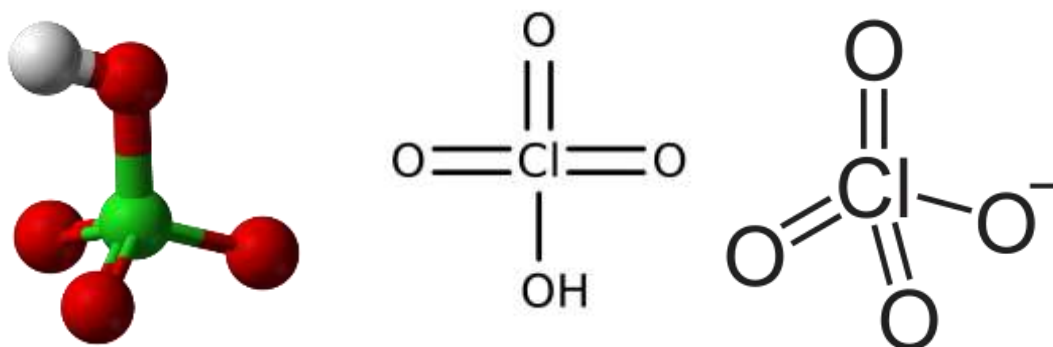


Fig 2.7 Perchloric acid 3d, bond structure and perchlorate ion [25]

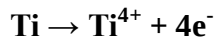
TiO₂ nanotubes can be obtained in electrolytes containing halides (ClO₄⁻, Br⁻, Cl⁻, F⁻), regardless of the electrolyte solvent. The use of F⁻ salts is favourable to prepare uniformly oriented TiO₂ nanotube arrays. When Cl⁻ or Br⁻ are added to the electrolyte, non-uniform bundle-like nanotubular structures are easily generated.

2.4.2 Mechanism

When the high voltage is applied, a thin layer of oxide is grown on the native oxide of the metal surface, which is quickly attacked by ClO₄⁻ ions which migrate to the positive anode while H⁺ ions move to the cathode. The aggressive environment created by these ClO₄⁻ results in the formation of localized pits on the Ti surface. After pitting, the oxide layer forms within the pits by the inward migration of O²⁻ ions from the electrolyte to the metal surface.

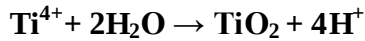
Oxidation of Ti:

(Hyam et.al)

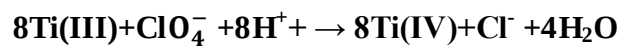


Formation of oxide layer:

(Hyam et.al)



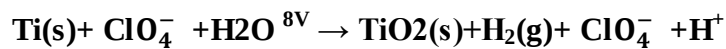
The perchlorate ions are not reduced directly but increase the anodic dissolution of titanium forming Ti(IV) ions from Ti(III) ions produced by corrosion: (Hyam et.al)



As Ti(IV) ions build up in the solution the anodization on the Ti surface occurs as if the current density for Ti(IV) reduction reaction then exceeds the critical current density the oxide layer breaks down exposing more of the Ti to the electrolyte and repeating the process. The oxidized metal ions (Ti⁴⁺) migrate outwards, and the formed TiO₂ layer is etched by the chloride ions to form water-soluble [TiCl₆]²⁻ ions.

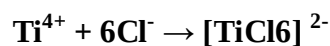
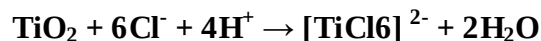
The overall reaction would be:

(Hyam et.al)



The electrochemical oxidation reaction of Ti occurs at the entire dipped surface of anode causing passivation by forming oxide layer and anodic dissolution starts only at pits where a high-density current flows. The chloride ions get adsorbed on the (110) plane of rutile TiO₂ suppressing further growth of this plane, resulting into anisotropic growth and hence TiO₂ nanoneedle formation.

The formation of soluble chloro-complexes (titanium hexachloride, [TiCl₆]²⁻) may result due to this electrochemical dissolution reaction and can be described as follows: (Fahim et.al.)



Despite the thermodynamically stability of TiO₂ within the pH range 2-12, a complexing ligand (Cl) leads to significant dissolution. This leads to the TNPs being highly hygroscopic in nature. The high stability of the [TiCl₆]²⁻ complex, which depending on the cation type has free energy of formation ranging from -5.12 to -10.90 kcal/mol further supports this.

Nanotubes/Nanoneedles are formed when the equilibrium is maintained in the oxide growth and chemical etching of oxide. The bundles of nanotubes grow around the pits in a random

direction within few seconds. After some time, the nanotube bundles fall into the electrolyte due to high stress between the metal and the oxide nanotubes.

2.4.3 Power supply

The 'Aplab High voltage dc power supply H1010' with a 100 to 1000 volts D.C rating (minimum 4 volts) was the chosen power supply due to its stable voltage and current output.



Fig 2.8 Aplab high voltage DC power supply [26]

2.4.4 Washing

TNTs obtained from the anodization process will contain trace amount of the perchlorate ion which increases the hygroscopic nature of the TNT powder. This prevents proper drying of the TNTs. The perchlorate ion may also be reactive to other compounds in the environment and thus multiple washing and even centrifugation is necessary to remove its presence from the TNTs. Care must be taken during the process so as to retain as much of the TNT powder as possible

2.4.5 Annealing

Annealing refers to any heat treatment process that changes the physical or chemical properties of a material for the better. The structure of the as-grown TNT obtained directly after anodization is amorphous in nature and therefore, non-photoactive. For a number of applications, it is necessary to transform this amorphous TNT into one of the crystalline polymorphs. This can be achieved by converting them into anatase or rutile phase through high temperature annealing which has been regarded as an effective route to induce crystalline formation in the as-prepared TNT.

At higher temperatures (at 280°C) in air the amorphous phase of TNTs can be converted into anatase phase. A mixture of anatase and rutile forms at temperatures higher than 450°C as shown by several studies. Near 480°C The rutile phase emerges above which the anatase phase transforms into rutile phase gradually. Annealing in air for 3 hours at a higher

temperature (greater than 600°C) resulted in collapse of nanotube bundles whereas Nanotubular integrity is maintained at below 600°C annealing temperature.

2.5 Procedure

2.5.1 Experimental setup

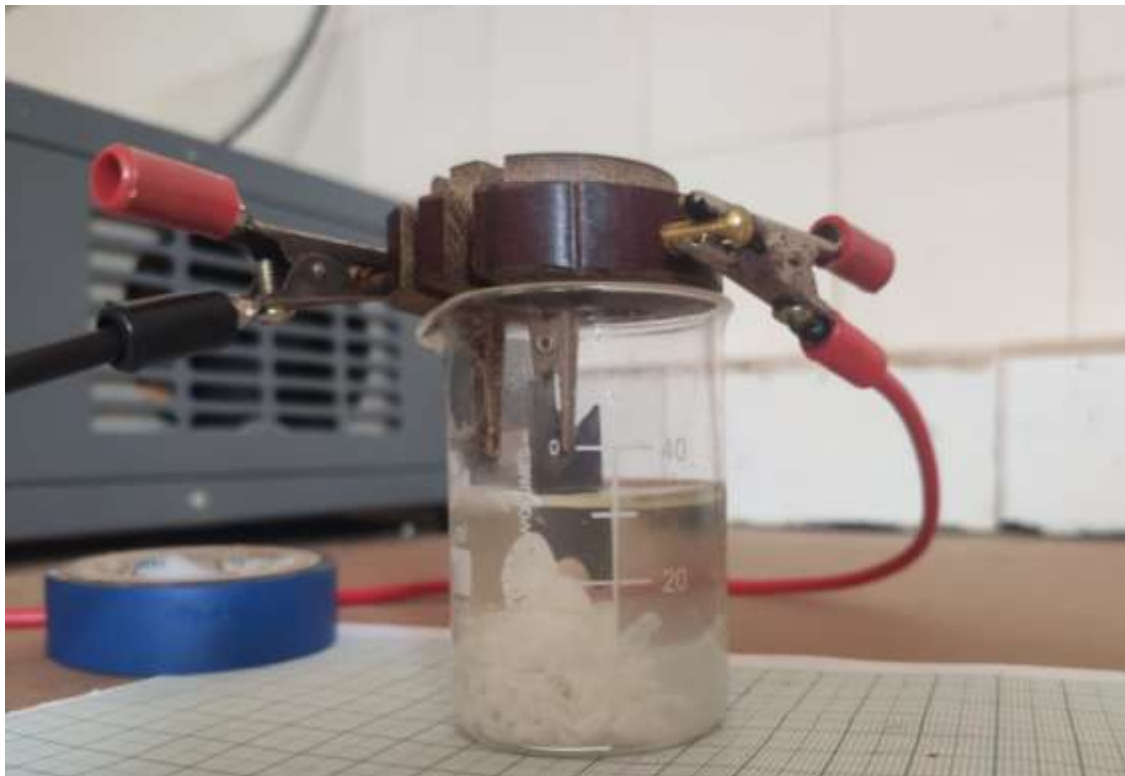


Fig 2.9. The experimental setup used

The experimental setup is fairly simple, it consists of a beaker and a holder made of Bakelite in order to be non-reactive to any chlorate fumes. The two electrodes were held in place by alligator clips adjusted to be well above the acid level in order to avoid any splashing due to bubbling. The electrodes were positioned parallel to each other with a distance of 0.8-1.0 cm and adjusted to give maximum dipped area. The Titanium electrode was positioned away from the walls of the container to prevent a build-up of anodised material which will slow down the process.

2.5.2 Preparation

Perchloric acid: 1.4 M Perchloric acid was prepared by diluting 5.7mL 70% perchloric acid (Rankem) in 43 mL of De-Ionised water (DI water). The freshly prepared solution was then carefully ultrasonicated for 30 minutes to ensure homogeneity of the solution.

2.5.3 Electrodes:

For the cathode a platinum electrode was chosen due to its inert nature in low concentrations of perchloric acid. Titanium electrodes were weighed and their dimensions noted.

Both electrodes were washed in acetone and D.I water in order to remove any residue such as fingerprints or oils used during the cutting process. Followed by ultrasonicated in D.I water, Acetone and Ethanol respectively for 10 minutes each. This ensures a clean surface of the electrodes along with the partial removal of oxide that has built up due to exposure to air, which will aid the formation of the etch pit.

All beakers, Pipettes, glass rod, etc used were washed and rinsed carefully in order to prevent contamination. Gloves, lab coat and protective eyewear were used at all times particularly during the handling of the perchloric acid. Cleanliness and safety were of utmost priority during the entire process.

2.5.4 Experiment

The electrodes are mounted onto the holder, a suitable level of perchloric acid is poured into the beaker and the holder is placed on top of The Beaker. The power supply is set to minimum voltage and current output. and the negative terminal connected to the Pt electrode (cathode) And positive terminal to the Titanium foil (anode).

The power supply is turned on and the voltage slowly increased to 8 Volts. The current is then slowly increased till bubbling around the cathode increases, this is accompanied by a drop in voltage and increase in current due to presence of Ti^{4+} ions in the electrolyte indicating the formation of the etch pit. The current is set to minimum and stable value of 140 mA and voltage of 7 volts is observed ,the experiment proceeds for 6-8 hours or until the complete dissolution of the dipped titanium area. The power supply is carefully monitored during the full duration of the experiment in case of any voltage spikes. If a large enough piece of titanium breaks off the electrode such that it may cause a short circuit the experiment must be stopped immediately.

Once a suitable amount of TNT nano powder is formed the experiment may be stopped by turning of the power supply and disconnecting the electrodes. The holder is then removed carefully and the electrodes are washed to remove any perchlorate ions. The supernatant bath is decanted and TNT powder is washed 3 times with DI water. The TNT-water solution is transferred to a clean beaker and stored in a desiccator. Depending on the experimental requirements the powder solution can then be centrifuged or annealed. The different samples and their parameters are noted in the observations table in the experimental results and discussion section.

Chapter III

Characterization Techniques

3.1 UV Visible Spectroscopy

UV-vis spectroscopy is a simple, non-destructive, inexpensive and fast analytical method applicable to a wide class of organic compounds and few inorganic species. UV-vis spectrophotometers are used to measure the absorbance or transmittance of light passing through a medium as a function of its wavelength. The UV-vis light spectral wavelength range is from 100nm to 200nm. The schematic for a double beam UV-vis spectrophotometer instrument is shown below. The D2 lamp generates ultraviolet light while the tungsten lamp emits visible light. The electromagnetic radiation can then be directed towards a monochromator that is used to choose the wavelength required to irradiate the sample.

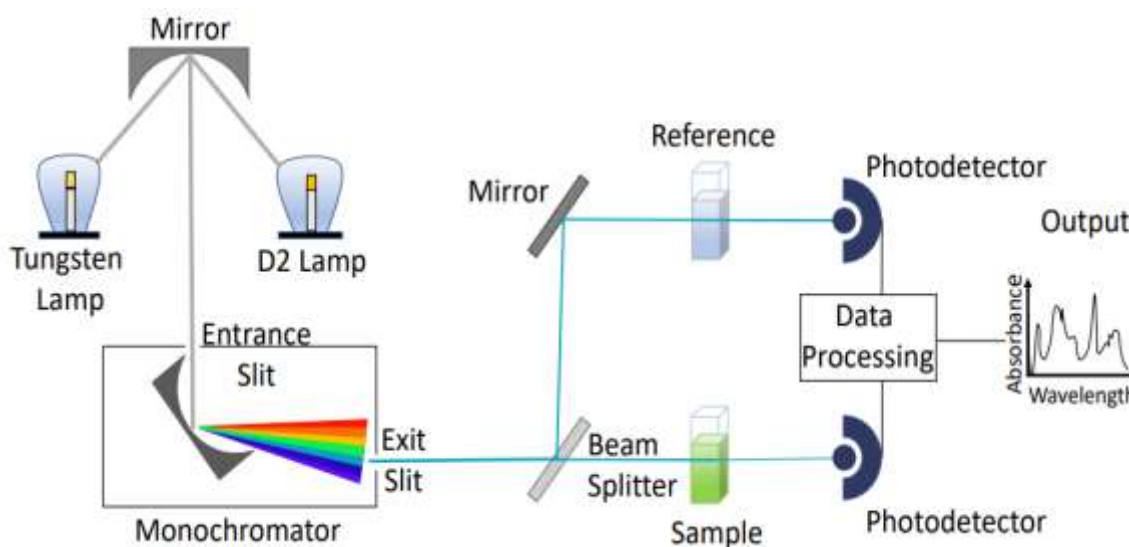


Fig 3.1 Schematic for UV-Vis spectrophotometer Rocha et.al. [27]

The light from the light source is directed through the sample and the transmitted light is recorded by a detector on the opposite side. The transmittance therefore represents the amount of light absorbed at each wavelength and this is termed as transmittance Spectroscopy. If instead the beam of light reflected off the surface of the sample is recorded it is termed as absorption spectroscopy.

The Beer-Lambert Law: states that the light absorbance (A) is proportional to the path length (B) of light passing through the sample, the concentration (C) and compound characteristic molar absorptivity (ϵ).

$$A = \log_{10} I_0 / I = \epsilon \cdot b \cdot C$$

(I) is the light intensity, which is measured with respect to a reference (I_0). The sample concentration as a function of the known parameters can be found by rearranging the above equation after calibration:

$$C = A \cdot 1/(\epsilon \cdot b)$$

The basis of UV-visible spectroscopy is the electronic transitions in organic molecules caused by absorption of light that leads to excitation of its electrons from a lower energy orbital; known as highest occupied molecular orbital (HOMO) to an unoccupied orbital of higher energy designated; lowest unoccupied molecular orbital (LUMO). To be absorbed the light must have a wavelength having energy equal to the energy gap ΔE of the HOMO-LUMO system shown schematically below.

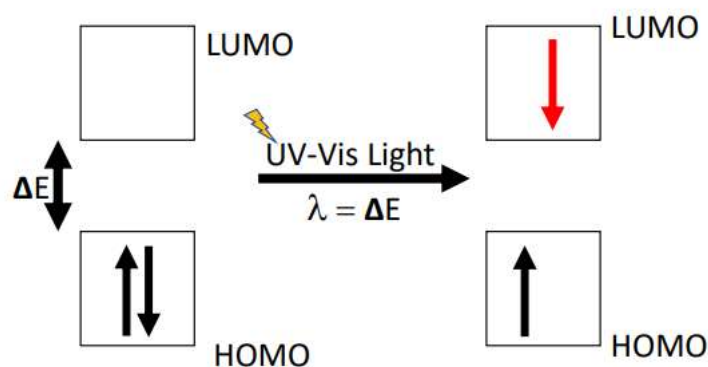


Fig 3.2. Visualization of molecular orbitals and energy required to excite electron energy state Rocha et.al. [16]

In the case of powdered samples, we may use diffuse reflectance spectroscopy (DRS) wherein the sample (usually a powdered solid) is placed in an integrating sphere, allowing addition of multiple reflections. The intensity of the reflected beam (R) can then be compared with a reference giving:

$$R_{\infty} = R_{\text{sample}}/R_{\text{standard}}$$

Making the approximation of an infinitely thick sample.

3.2 X-Ray Diffraction

X-ray diffraction (XRD) is a powerful, non-destructive characterization technique used for materials with crystalline nature. It can be used to provide information on phases, structures, preferred crystal orientations (texture) of a crystal as well as other structural parameters, such as strain, average grain size, crystal defects and crystallinity. In 1912, Max von Laue and co, discovered that crystalline substances act as three-dimensional diffraction gratings when X-ray wavelengths similar to the spacing of the planes in the crystal lattice are incident on them (Friedrich W, et al., 1912). Today, X-ray diffraction is a common technique used to study crystal structures and atomic spacing.

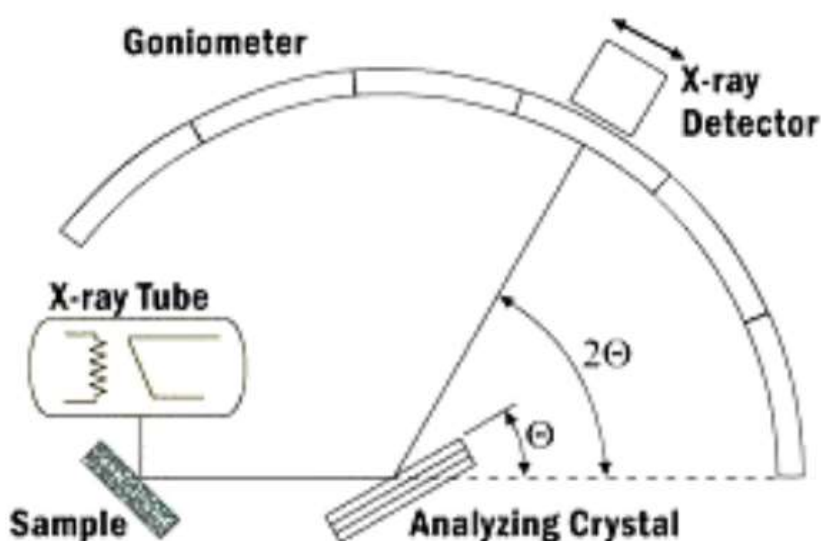


Fig 3.3 Schematic of a basic XRD setup Bunaciu et.al. [28]

The geometrical layout of a typical diffractometer system showing X-ray tube, sample, detector analysing crystal and the goniometer is shown schematically above. The X-rays are generated when a filament in the cathode ray tube is heated causing it to produce electrons. These electrons are accelerated towards a target by applying a voltage causing them to bombard the target material. Characteristic X-ray spectra are produced if these electrons have sufficient kinetic energy so as to dislodge the inner shell electrons of the target. Although several other components are produced, the $K\alpha$ and $K\beta$ components are the most common of this spectrum. The X-rays are then collimated and directed onto the sample. The intensity of the reflected X-rays is recorded continuously as the sample and detector are rotated. When the geometry of the incident X-rays incident on the sample satisfies the Bragg law, a peak in intensity occurs due to constructive interference. These X-ray signals are recorded by a device called the detector which processes and converts the signal to a count rate. The output can then be interpreted by a computer and displayed through a monitor or printer

The geometry of an X-ray diffractometer is designed in such a way that the sample rotates into the path of the collimated X-ray beam at an angle θ while the X-ray detector used to collect the diffracted X-rays is mounted on an arm and rotates at an angle of 2θ . The instrument known as the goniometer maintains the angle of the sample and rotates it as

required. For a typical powder scan, data is collected from 50° to 70° at 2θ , these angles come pre-set in the X-ray scan.

X-ray diffraction involves constructive interference of monochromatic X-rays and a crystalline sample. The basic Principle is based on the Bragg Law of Diffraction which relates the wavelength of any electromagnetic radiation to the diffraction angle and the lattice spacing. Due to the random orientation of the powdered material all possible diffraction directions of the lattice should be attained by scanning the sample through a range of 2θ angles. Bragg's Law is given by:

$$\lambda = 2d \sin\theta$$

- n is any integer
- λ denotes the X-ray wavelength
- d denotes the interplanar spacing that causes diffraction
- The diffraction angle is θ .

Bragg's law is depicted on the left side of the figure below. For reciprocal space the equivalent Laue condition in the reciprocal lattice for the 2-dimensional case is shown on the right. For 3 dimensions the law is given as: $G^2 = 2G \cdot k$

Where G and k are reciprocal lattice vectors and $G = 2\pi/d$.

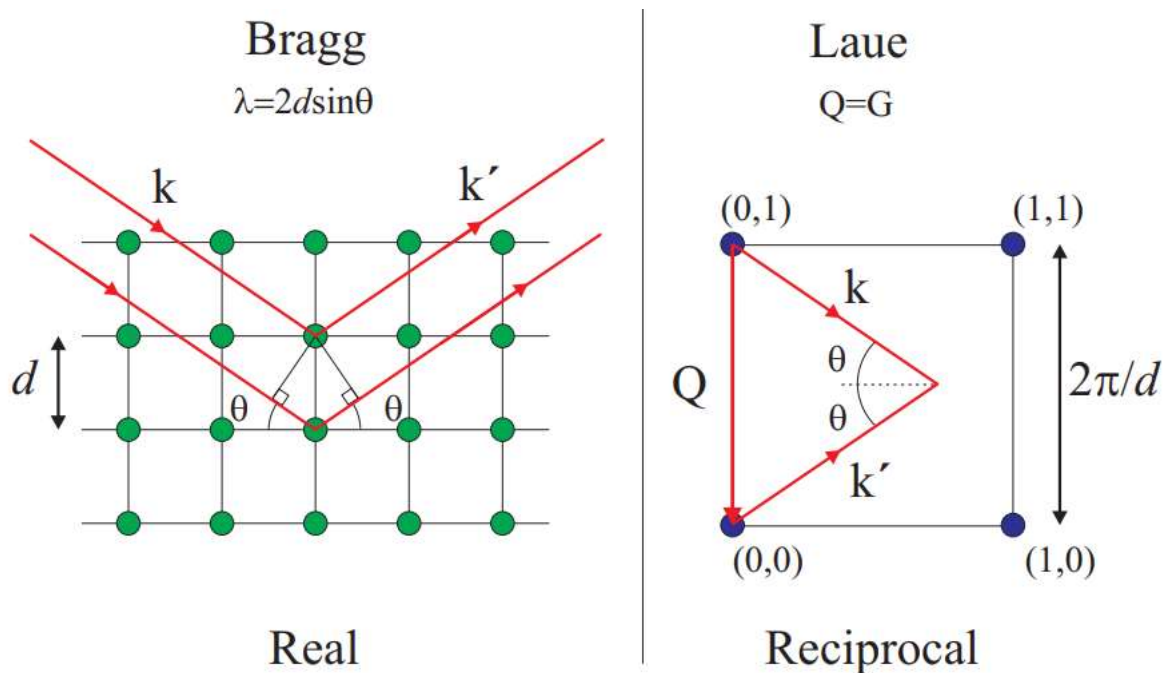


Fig 3.4 Bragg and Laue condition Als-Neilsen et.al [29]

The distribution of atoms within the lattice determines the peak diffraction intensities. Therefore, the X-ray diffraction pattern acts as a fingerprint of the periodic atomic arrangements in any given material. Since each compound has a set of unique d -spacings, conversion of the diffraction peaks to d -spacings using Bragg's law allows identification of the compound. Typically, this requires the comparison of d -spacings with various standard reference patterns.

The Powder X-Ray Diffraction or PXRD technique is employed widely for the characterization of unknown crystalline materials. Identification of unknown solids (minerals, inorganic compounds) is critical to studies in biology, material science, environmental science, engineering and geology. PXRD is invaluable in the measurement of sample purity; crystalline materials characterization and determining unit cell dimensions.

The powder method gets its name due to the fact that the specimen to be studied is typically in the form of a microcrystalline powder. Therefore, proper sample preparation is a key requirement in the analysis of powder samples by X-ray diffraction. Analysis of samples by PXRD requires them to be an extremely fine-grained powder to avoid fluctuation in intensity to achieve good signal-to noise ratio, avoid spottiness and minimize preferred orientation. Reduction of powders to fine particles also ensures enough particle participation in the diffraction process. An example of sample mounting onto the holder is shown below:



Fig 3.5 Sample preparation for PXRD

There are some strengths and some limitations of X-ray Powder Diffraction (XRD):

Strengths:

- Powerful and rapid (< 20 min) identification technique
- High certainty mineral determination in most cases;
- Minimal sample preparation required;
- XRD units are widely available;
- Relatively straight forward data interpretation.

Limitations:

- For the identification of an unknown material homogeneous and single-phase is best
- standard inorganic compound reference file is required
- Tenths of a gram of the material ground into a powder is required
- For mixed material samples there is a ~ 2% detection limit
- In case of unit cell determinations: pattern indexing of non-isometric crystal systems is complex.
- High angle "reflections" may cause the occurrence or worsening of Peak Overlay.

3.3 Raman Spectroscopy

Raman spectroscopy is a type of vibrational spectroscopy that uses unique vibrational characteristics or fingerprints of chemicals for their easy interpretation and highly sensitive structural identification even in trace amounts. It is a non-destructive spectral analysis technique specialized in the measurement of the frequency shift of light scattered inelastically from molecules in the sample when the photon from incident light strikes them. The scattered light will have a difference in frequency compared to the incident light due to its interaction with the phonon vibrations of the sample. This difference between the incident and the scattered light frequency provides information about the lattice vibrations. Therefore, the Raman vibration spectra is employed widely for providing a structural fingerprint for molecular identification. Information from the Raman spectra, namely: the intensity, the band position, band position shift and full width at half maximum (FWHM) is characteristic to a material. Thus, Raman spectroscopy provides a powerful, efficient, sample preparation friendly and non-destructive technique for the characterization of various materials.

A Basic Raman spectrometer setup consists of the following components: light source, monochromator, sample holder and detector. For example, consider a simple fibre-coupled Raman setup depicted below. Note that usually contaminant Rayleigh scattering is removed from the photons emitted by the sample by filtration before they enter the spectrometer. The Spectrometer typically consist of a high-quality imaging apparatus or line detector. The excitation source consists of suitable laser such as argon ion (488.0 ,514.5 nm), Nd:YAG (1064 nm , 532 nm), krypton ion (530.9 ,647.1 nm), He:Ne (632.8 nm), or diode laser (630 ,780 nm).

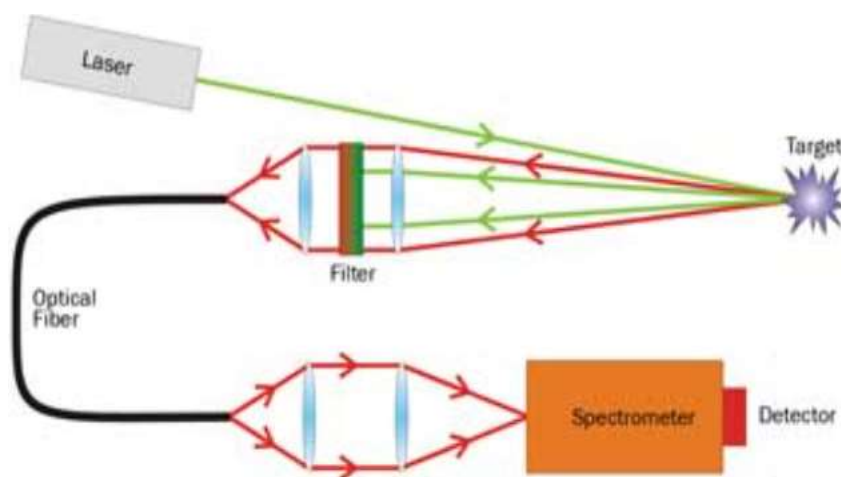


Fig 3.6 Raman Spectroscopy setup Foster et.al. [30]

Raman spectroscopy works based on the Raman Effect first discovered in 1928 by C.V. Raman. The principle of the Raman effect involves the inelastic light-scattering process between incident light and an irradiated substance. The interaction between the light and sample occurs as follows: the incident light excites the sample molecules distorting the electron cloud which forms a 'virtual level'. This 'virtual level' is not stable hence the photons are immediately scattered to another relatively stable state. We can see in the below figure there are three possible cases: (a) the excited photons fall back to their initial energy

level (or ground level) i.e., no transfer of energy between incident light and scattered light, and hence no change in photon frequency or wavelength. Thus, the collision process is elastic and is termed Rayleigh scattering.

However, there is a possibility that the photons may fall to a new energy level, different to the initial level. For this to take place the photon gains or loses some amount of energy resulting in a shift of the laser photons energy up or down which can give information about the systems vibrational mode. The inelastic scattering process is termed Raman Scattering which is further classified into two types: Stokes Raman scattering (b) where light scattered has lower frequency and anti-Stokes Raman scattering (c) where light scattered has a higher frequency than incident light. The higher frequency occurs when excited photons fall from the initial energy level to a lower energy level and vice versa the lower frequency occurs when excited photons fall from the initial energy level to higher energy level.

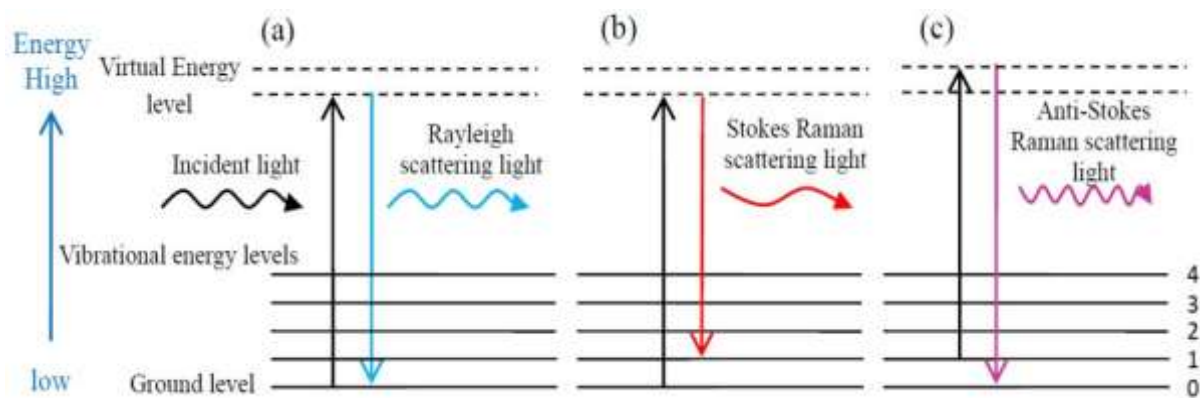


Fig 3.7 Raman scattering Xu et.al. [31]

The number of scattering molecules is directly proportional to the intensity of Raman scattered light. Using the Boltzmann distribution, we can find the number of molecules in each energy level as follows:

$$N_1 / N_2 = (g_1 / g_2) \exp [(-\Delta E) / KT]$$

N_1 and N_2 denote the number of molecules present in the higher and lower energy levels respectively, with degeneracy g_1 and g_2 . The change in energy before and after scattering is ΔE , K is the Boltzmann's constant and temperature T . At room temperature due to Thermal equilibrium the number of low energy level vibration molecules is always greater than the number of high energy level vibration molecules. Since the number of ground level molecules is the highest, the Stokes Raman scattering intensity is greater than the anti-Stokes Raman scattering intensity, therefore Raman scattered light is usually Stokes Raman scattering light i.e., having frequency lower than the frequency of the incident light.

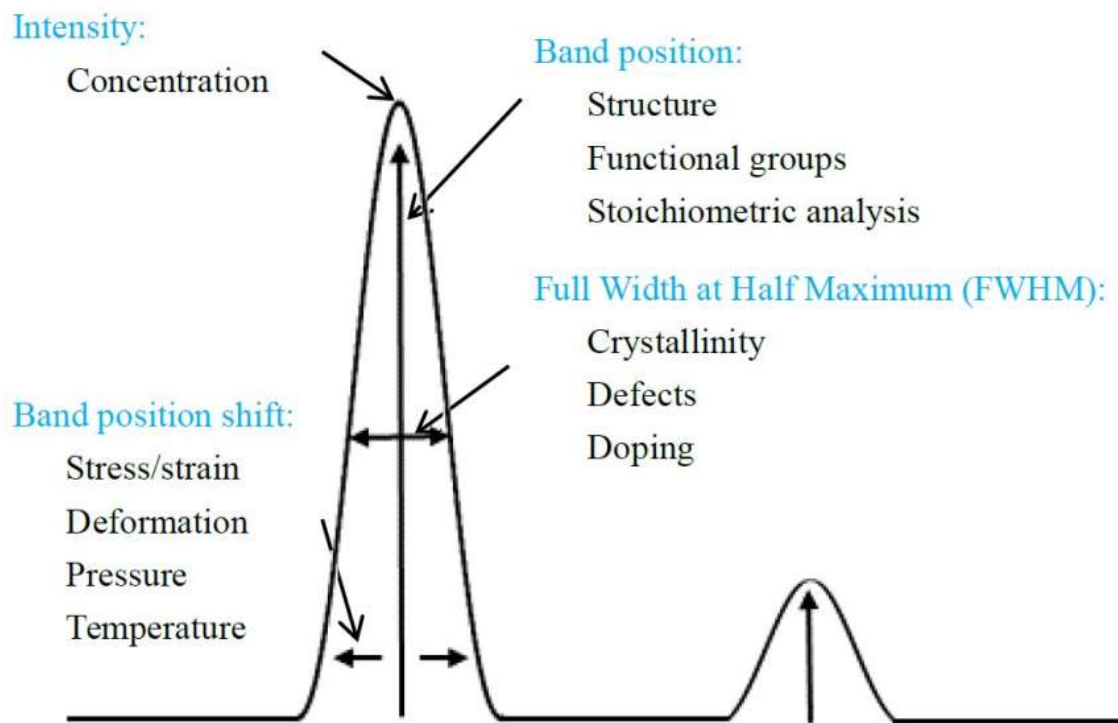
The Raman spectra shows the reciprocal of wavelength or wavenumber versus intensity of scattered light.

The distance to the y axis of Raman spectra or abscissa termed Raman shift, cm^{-1} is given by

$$\text{Raman shift} = \left(\frac{1}{\lambda_{\text{incident}}} - \frac{1}{\lambda_{\text{scattered}}} \right) \times 10^7$$

Here $\lambda_{\text{incident}}$ and $\lambda_{\text{scattered}}$ denote the wavelengths (nm) of incident and scattered light respectively. The wavenumber in particular is correlated linearly with the incident light and scattered light energies therefore, the Raman shift of materials depends on the incident wavelength of the light source and choice of laser is important.

Characterization by Raman Spectroscopy involves the collection of Raman scattered light from the tested sample and producing the corresponding Raman spectra which carries material information on crystal structure and molecular vibration. Typical Raman spectra information is shown in the figure below along with the corresponding material information.



*Fig 3.8 The typical information of Raman spectra and corresponding material information
Xu et.al. [31]*

Penetration depth into the sample surface usually varies with laser wavelengths. Therefore, different wavelength lasers can be used to acquire information from different depths into the sample surface. Information closer to the surface can be obtained by shorter laser wavelength. However, if the selected laser wavelength is too small the material information far from the surface may be concealed and vice versa if the wavelength is too long surface information will be missed. Hence the accuracy of the Raman characterization result is highly dependent on an appropriate choice of laser wavelength. The Raman scattering cross sections may be very small resulting in a difficulty in detecting the Raman signal this is the main disadvantage of Raman spectroscopy.

Chapter IV

EXPERIMENTAL RESULTS AND DISCUSSIONS

4.1 Laser Induced graphene

4.1.2 Index of Samples

Table 1: LIG Samples

Sample Name	Scan speed	Fluence	Substrate
LIG700	700 mm/min	3.1 J cm ⁻²	Kapton
LIG500	500 mm/min	3.5 J cm ⁻²	Kapton
LIG300	300 mm/min	4.2 J cm ⁻²	Kapton
LIG300 Scotch	300 mm/min	4.2 J cm ⁻²	Scotch tape

The major experimental parameter for this experiment is the laser fluence. Since the fluence is directly dependant on the scan speed (equation 1) it can be easily varied using the CNC setup. All the above samples were prepared one after the other without any change to the laser focusing keeping a fixed height of 10 cm (z axis) LIG begins to break off at 300 mm/min scan speed and hence no slower variations were taken. Above this the LIG is well bonded to the to the substrate as supported by the literature. Hence only the 300 mm/min scan speed variation was used for characterization with the Scotch tape. To prevent warping due to the heat generated during laser ablation the Kapton was secured to the laser bed using

double sided tape. Scotch tape is an adhesive tape by brand Scotch TM widely available in the market.

4.1.3 XRD Data

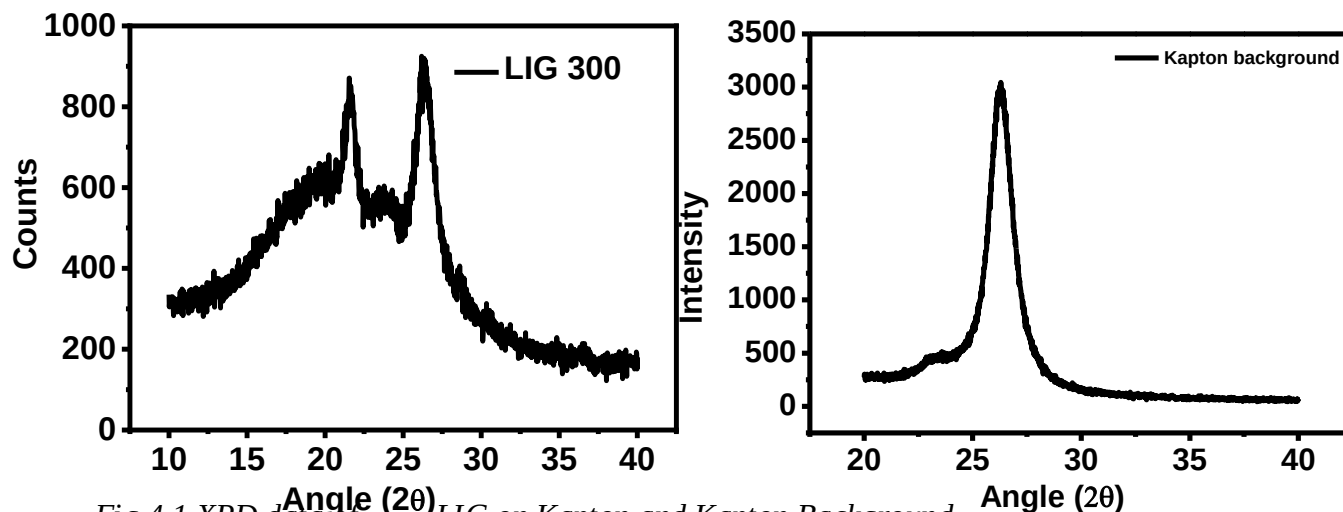
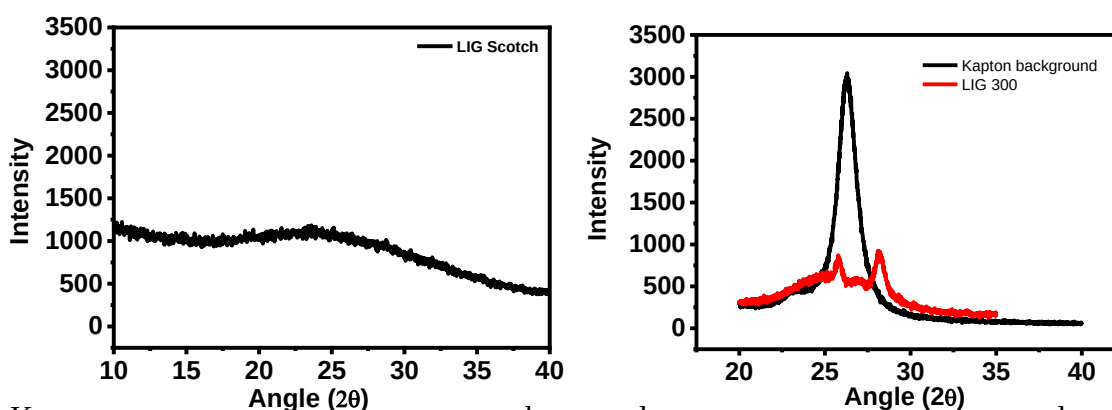
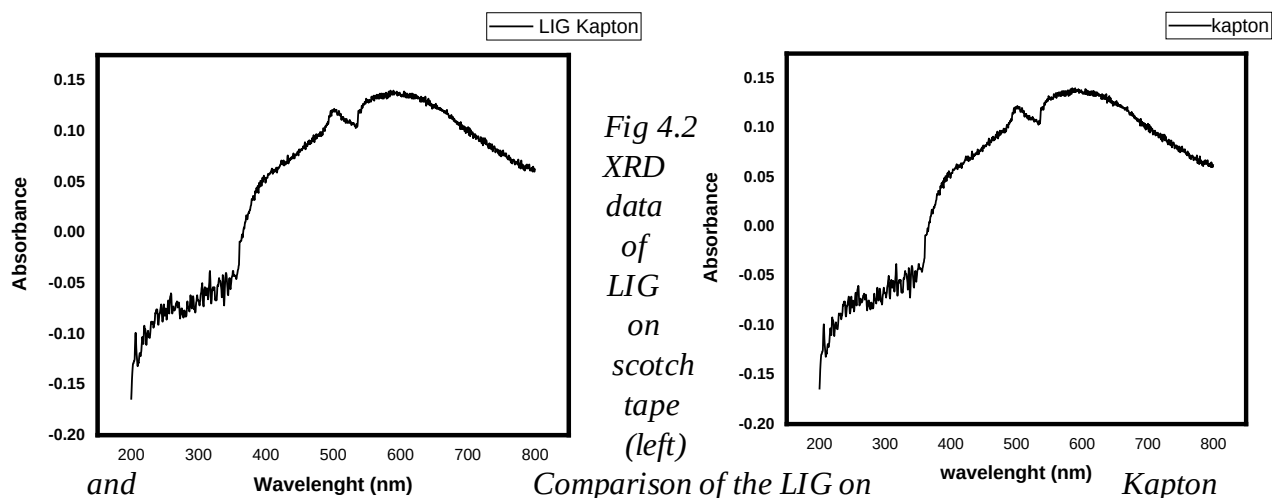


Fig 4.1 XRD data of LIG on Kapton and Kapton Background respectively

Due to its amorphous nature LIG does not show characteristic crystalline peaks. The random orientations of the porous LIG surface do not allow for the constructive interference. The

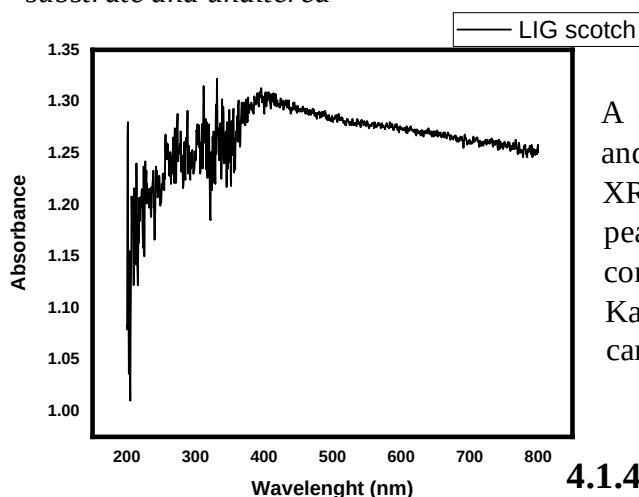


Kapton substrate also warps due to the laser ablation of the surface, this combined with the ridged structure of the LIG further exemplifies this problem. Thus, the two peaks observed are attributed to Kapton surface that was not ablated. The amorphous graph in the case of the scotch tape is in agreement with this.



and substrate and unaltered

Kapton tape (right)

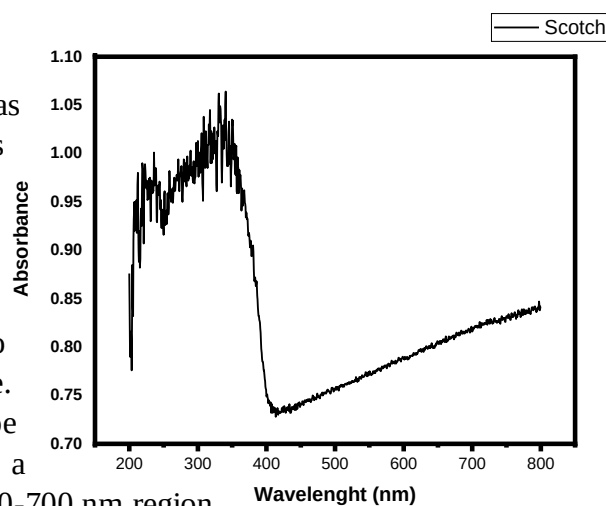


A comparison of the unaltered Kapton sheet and LIG clearly shows a large change in the XRD intensities going from a strong singular peak to two smaller low intensity peaks. This confirms the transformation of the ordered Kapton polymer to an amorphous carbonatious material.

4.1.4 UV-vis Data

Fig 4.3 UV-vis data of LIG on Kapton substrate, unaltered Kapton, LIG on Scotch tape and unaltered Scotch tape.

The UV data of LIG on Kapton substrate was inconclusive as the same absorption pattern was observed for both unaltered and laser scribed Kapton. This is not completely unexpected due to the previously mentioned light absorption characteristics of Kapton especially in the near UV region. To combat this the LIG was transferred onto scotch tape kept secure by the adhesive on the tape. The side-by-side comparison of unaltered scotch tape and scotch tape with LIG shows the presence of a substance with a relatively high absorption in the 400-700 nm region. Typically, Graphene oxide shows no absorbance in this region but graphene does and this may indicate its presence.



4.1.5 Raman Data

Raman spectroscopy is a very helpful technique for the characterization of Laser Induced Graphene samples in a non-invasive way and constitutes the main characterization technique. The Raman spectrum of the treated surface provides a large amount of information about its structure, as well as a quantification of the disorders and defects introduced by the ablation process.

The laser incidence on the LIG surface creates two main peaks, the so-called D located at $\sim 1350\text{ cm}^{-1}$ (D-band; A_{1g} breathing mode of the hexagonal rings at the K-point initiated by disorder), and G peaks $\sim 1580\text{ cm}^{-1}$ (G-band; E_{2g} mode at the Γ -point, responsible for the stretching vibrations in all sp² carbons). These peaks are present in disordered graphitic materials. In particular, the D peak reveals the presence of defects in sp²-hybridized carbonous systems, while the G peak indicates a graphite-derived structure.

The 2D peak $\sim 2700\text{ cm}^{-1}$ (characteristic of all sp² carbons) is due to a second-order resonance, and gives information about the number of layers of the graphite structure. The formation of graphitized carbon is indicated by the presence of a distinct 2D peak, and the single Lorentzian fit of the peak indicates the formation of graphene. The bent graphene sheets in the LIG foam resulting from defects such as 5 and 7 membered rings cause the D-band and D + D' band.

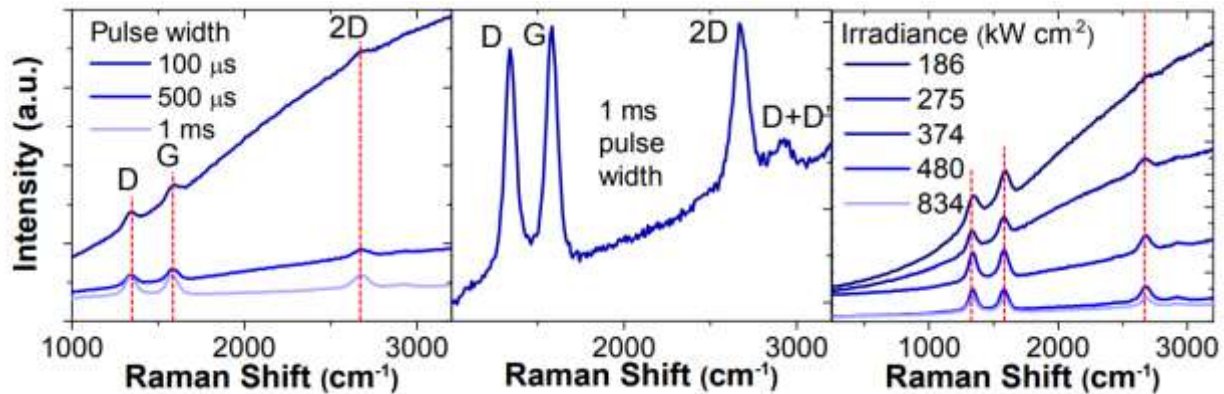


Fig 4.4 Example of Raman data for LIG Tour et al[10]

Note that the above images the image in the centre corresponds to data corrected for the Raman shift of Kapton tape that creates an upward slope visible in the images on the right and left. This interference caused by the Kapton led to reduced intensity of the D and G peaks as well as the 2D peaks. To overcome this the LIG formed on the Kapton was once again transferred to a Scotch tape substrate. However only LIG 300 samples would peel off the Kapton and so the characterization in that regard was limited.

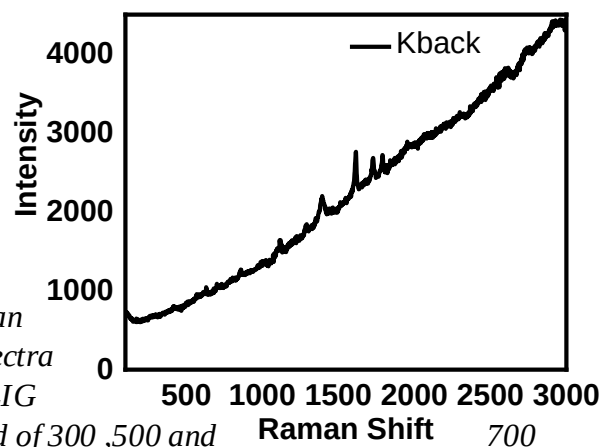
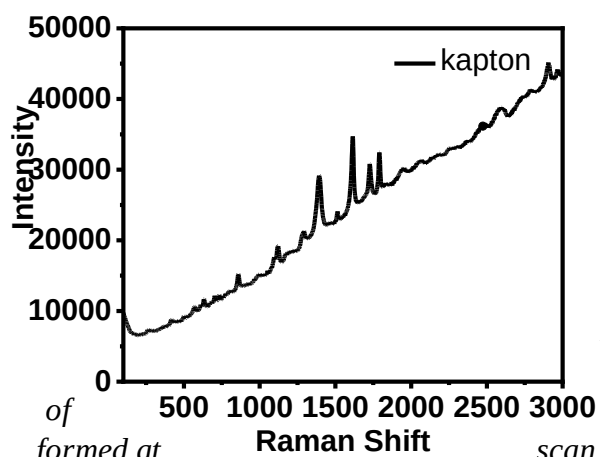
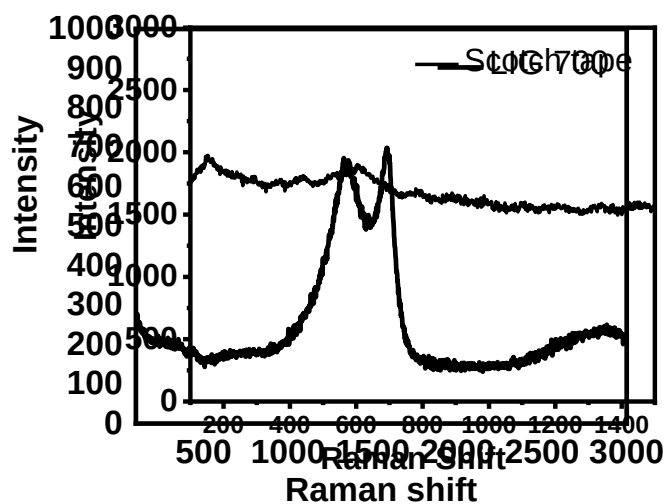
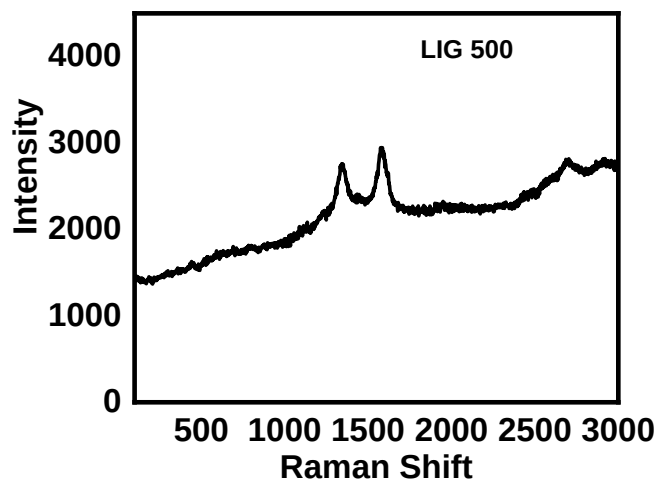
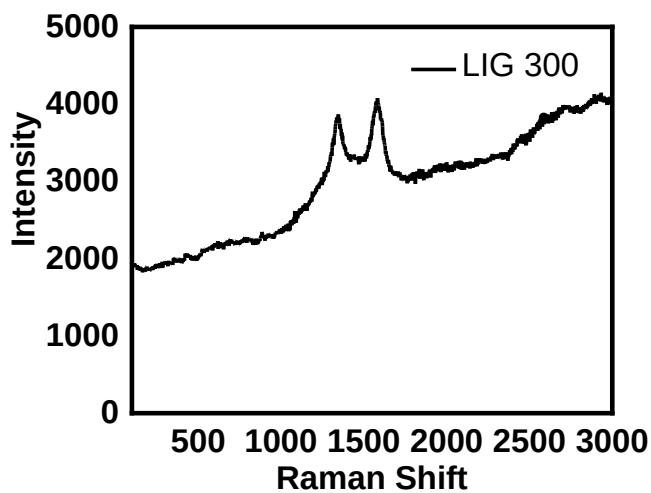


Fig
4.5
Raman
Spectra

of
formed at
scan speed of 300 ,500 and 700
mm/min and also plain scotch tape and front and back of Kapton tape

The choice of Laser is important while measuring the Raman spectra because a UV laser may interact with the Kapton substrate as discussed previously. The Raman data obtained in this work was under the illumination of a 532-nanometre laser at 10% intensity. A comparison of the Raman data of unaltered Kapton tape and laser scribed tape shows vastly different peaks confirming the transformation into LIG as inferred by the XRD data. Further examination of the spectra shows an increasing trend as laser scan speed is decreased with the intensities of the peaks seen in LIG 700, LIG 500 and LIG 300. This corresponds to the increase in fluence and hence the increased ablation of the Kapton substrate. The first peak is the D peak corresponding to graphene and the second the G peak corresponds to graphite. In all 3 cases the D peak is lower than the G peak indicating a higher graphitic nature and layering of graphene characteristic of LIG

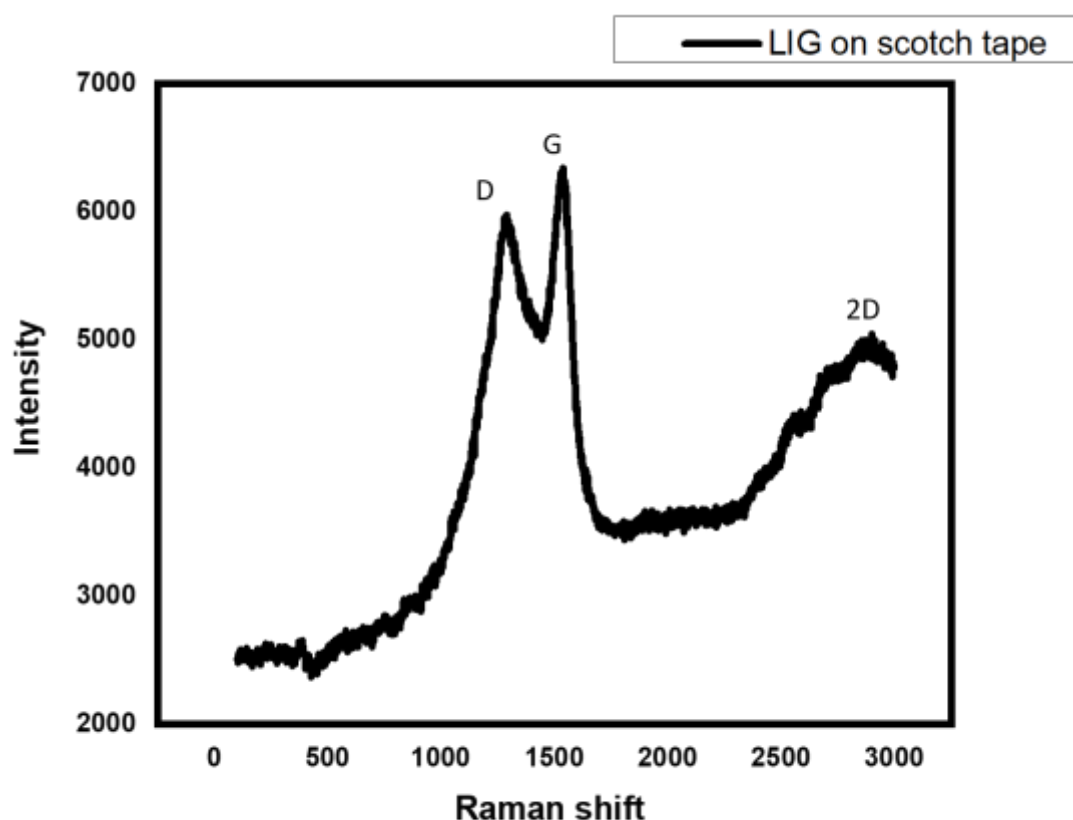


Fig 4.6 Raman spectra of LIG transferred onto Scotch tape showing clear D, G and 2D peaks

A cursory glance on the Scotch tape spectra reveals a lack of sharp peaks making it a noteworthy substrate emphasising its use by Geim and Novoselov in their Nobel winning graphene exfoliation experiment. As is simply evident by the above graph Scotch tape has much less interference than Kapton and gives us much clearer data of the LIG Raman spectra to investigate. The D and G peaks are much more defined clearly showing the presence of graphene although in a lower concentration to graphite.

The graph also reveals the 2D peak, a broad hump indicating the inhomogeneity of the graphite and its multi stacked porous nature confirming the presence of LIG

4.1.6 Observations and discussion

It is noteworthy to mention here that during the experimentaion it was noticed that LIG would form only on one side of the kapton. This should not be the case as Kapton is a homogeneous polymer however it was theorized that there could be a plastic coating on one side of the PI sheet the presence of which was not mentioned by the manufacturer. A side by side comaprison of the Ramn data of the LIG producing side of the kapton designated the “front” side and of the Kapton and non LIG produing side designed the ‘back’ side is shown in the bottom two panels of the fig 26 on page 33 . The subdued peaks confirm this hypothesis. LIG can be produced on this back side despite the presence of this coating given sufficently low scan speed i.e., a high fluence. However, the lines produed by the laser are uneven and inferior compared to the front side.



Fig 4.7 Image showing LIG on kapton substrate (left) kapton transferred onto Scotch tape (centre) and Kapton afer removing the LIG (right)

The Physical properties of the LIG scribed on the Kapton substrate were quite promising showing a strong binding to the substrate enough to partially withstand removal through the use of the Scotch tape adhesive as can be seen in the above figure. The sample used in this case was LIG300 samples formed at lower scan speeds i.e., higher fluence rates. Samples formed at lower fluence were much more resistant allowing only miniscule or no amounts of the material to be removed. This made them flexible and durable as reported in the literature. This is both advantageous and disadvantageous the Scotch tape substrate is evidently more

desirable in the characterization process and thus hindered any further attempts to better understand the relationship between the fluence and the LIG properties

The Raman Setup also has a microscope which allowed us to see magnified images of LIG pictured below.

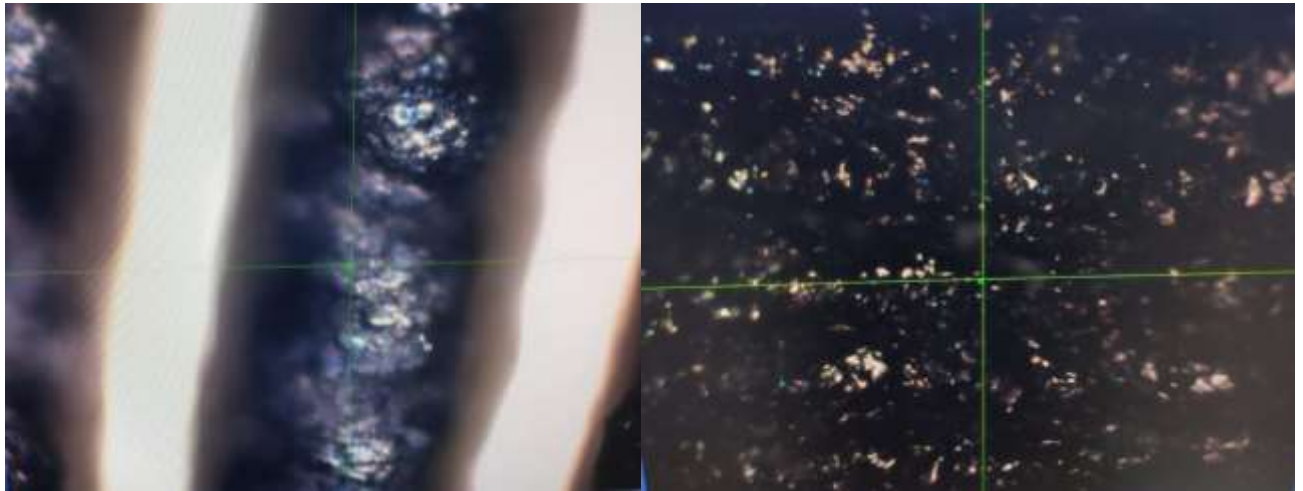


Fig 4.8 Magnified images of LIG on Kapton (left) and scotch tape (right)

On the left we can see the clear distinction of the non-reflecting Amorphous LIG and the highly reflective Kapton surface as indicated by the UV-Vis and XRD data. The line of LIG is approximately 100 micro meters thick which is possible because of the low wavelength of our diode laser (405nm). This is a highly desirable quality for a multitude of Chemical and Electronic sensors. We can see the porous nature better in the right image. It is also less reflective indicating why Scotch tape is considered an advantageous substrate for characterization of LIG. The pinkish colouration dimly noticeable in parts of the images is attributed to graphene. Intricate patterns, such as the one below were produced using the CNC lasing setup

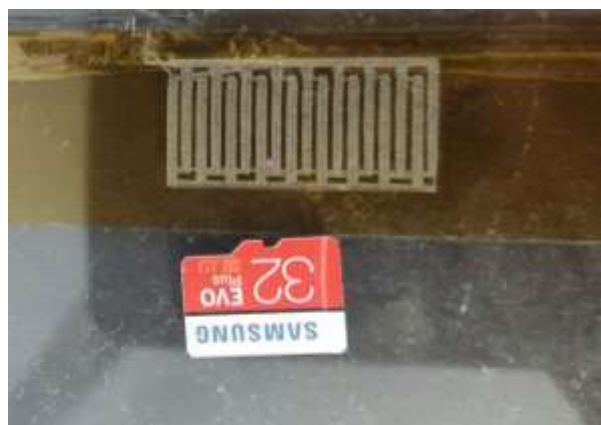


Fig 4.9 LIG patterned in the form of interdigitated electrodes with a micro-SD card for scale.

4.2 TiO₂ Nanostructure Synthesis by Anodic Dissolution

4.2.1 Index of samples

Table 2

Sample Name	Anodization time	Washing	Annealing
A	8 hours	3 times with DI + centrifuged 3 times	100°C
B	8 hours	3 times with DI water	Ambient
C	4 hours	3 times with DI water	450°C
D	6 hours	3 times with DI water	250°C
E	6 hours	3 times with DI water	300°C
F	6 hours	3 times with DI water	300°C
G	6 hours	3 times with DI water	120°C

Experimental parameters were varied in a way so as to replicate the works of Hyam et.al. [16][17]. In the case of all samples an electrode separation of 0.9-1.1 cm was maintained. A lot of TNT powder from sample A was lost during washing therefore there was not enough material to perform UV-vis spectroscopy. Similarly for sample C the experiment had to be stopped early due to fluctuations hence the short anodization time lead to a lack of powder for use in UV-vis spectroscopy. Sample B failed to dry ambiently, after 30 days it was washed and centrifuged but still highly hygroscopic and so the sample was lost. Sample E was also lost during annealing when the Borosilicate Glass containing it cracked. The final samples prepared were A, C, D, F and G.

4.2.2 XRD Data

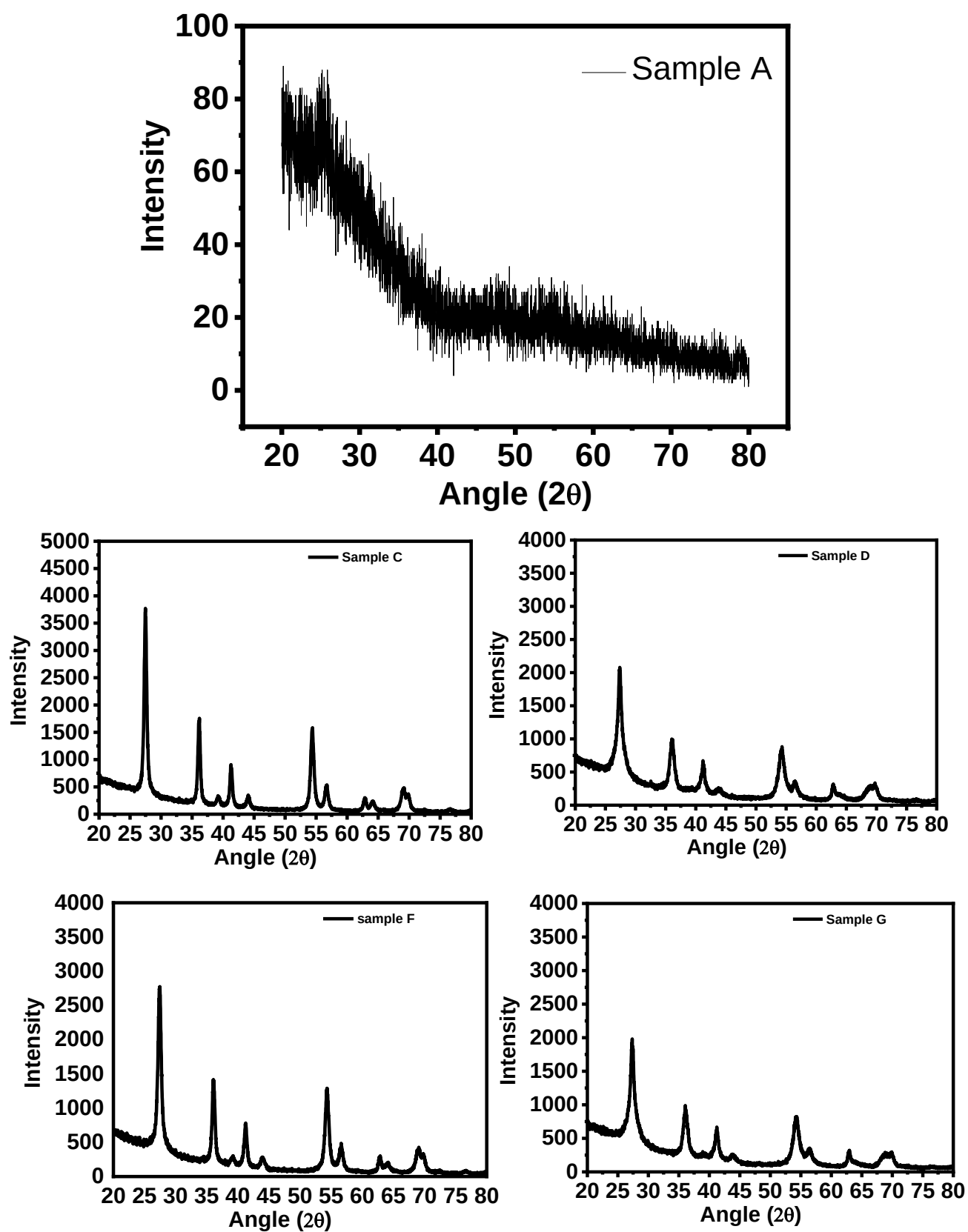


Fig 4.10 XRD data of samples A, C, D, G and F

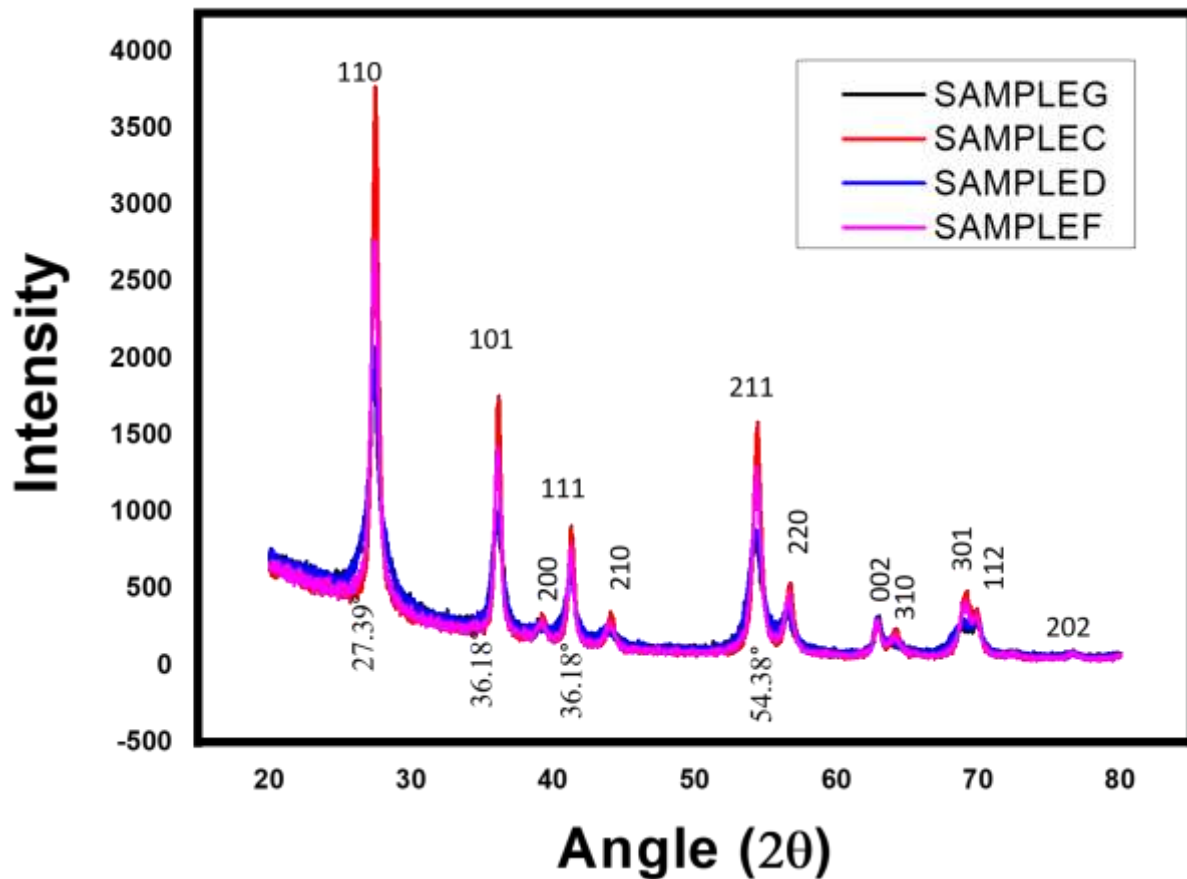


Fig 4.11 Comparison of XRD data w.r.t samples C, D, F and G (left)

The X-Ray diffraction peaks for all samples was measured at a rate of two degrees per minute from 20 degrees to 80 degrees. Rutile TiO_2 has major diffraction peaks at 2θ values of 27.39° , 36.18° , 41.20° and 54.38° assigned to the (110), (101), (111) and (211) plane reflections. Anatase TiO_2 shows 2θ values of 25.3° , 37.8° , 48.0° , 53.9° , 55.1° . From the XRD data we see that samples C, D, F and G all show Rutile nature with major diffraction peaks matching those in the literature. Sample A shows amorphous nature with non-distinct peaks. The amorphous nature may indicate a mixture of Rutile and Anatase phase. As both samples A and G were annealed at 100°C a comparison between them would indicate that the perchlorate ion absent in sample A plays a major role in the formation of Rutile phase at low temperature annealing. This was theorized by Hyam et al. [16].

A comparison of the XRD data of samples C, D, F and G shows a trend of higher intensity of the Rutile peaks with temperature. The higher temperature would provide the necessary energy required for any amorphous TiO_2 nanostructures to undergo a phase change to the Rutile phase, increasing phase purity of the nanostructures

4.2.3 Raman Data

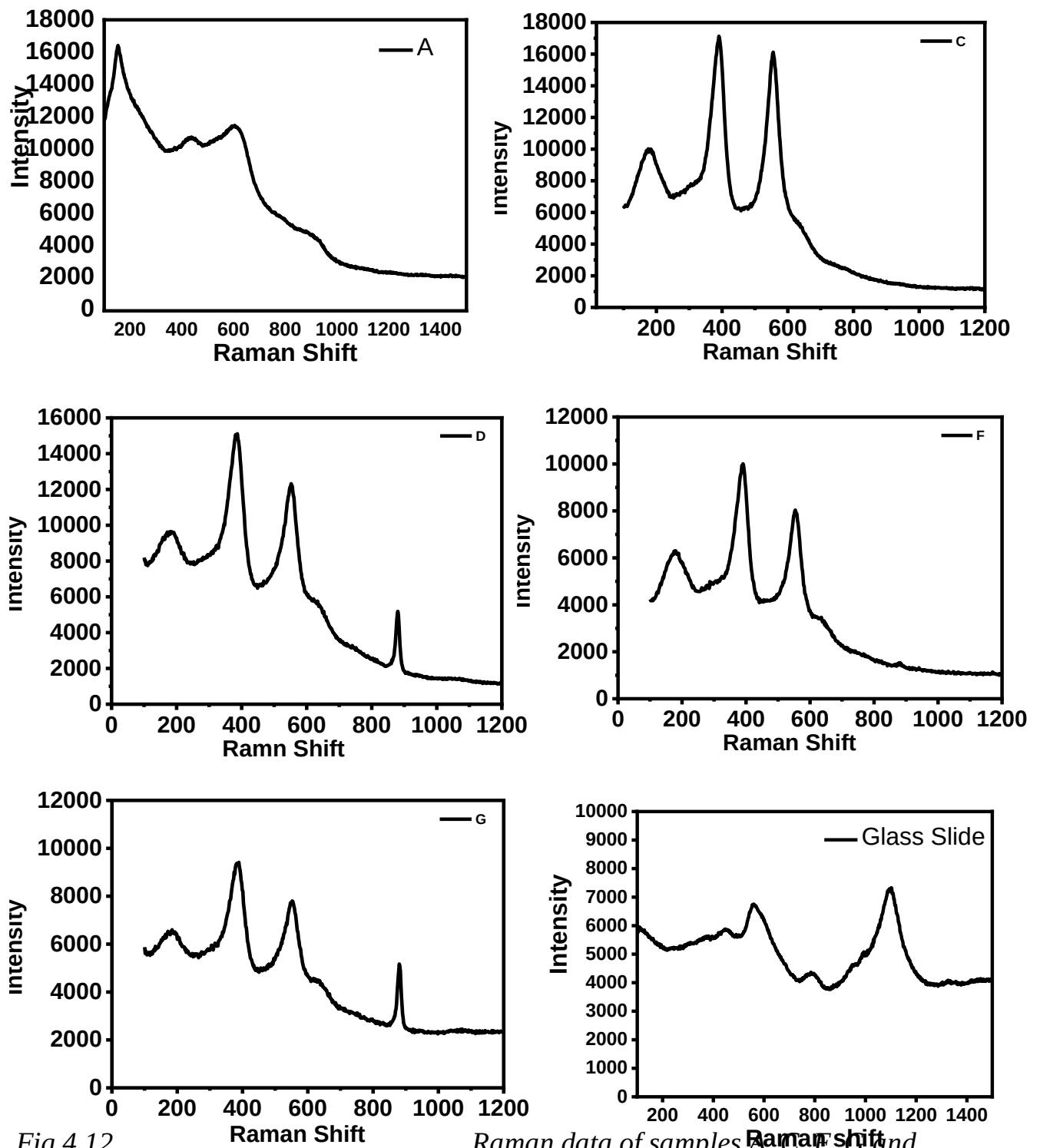


Fig 4.12

Raman data of samples A, C, D, F, G and the glass slide

The Raman Spectra for all samples was measured under the illumination of a 532 NM laser at 10% intensity. The glass slide carrying the samples had a bio coating present on it which is seen in the Raman data. However, the impact of this on the sample data was observed to be low.

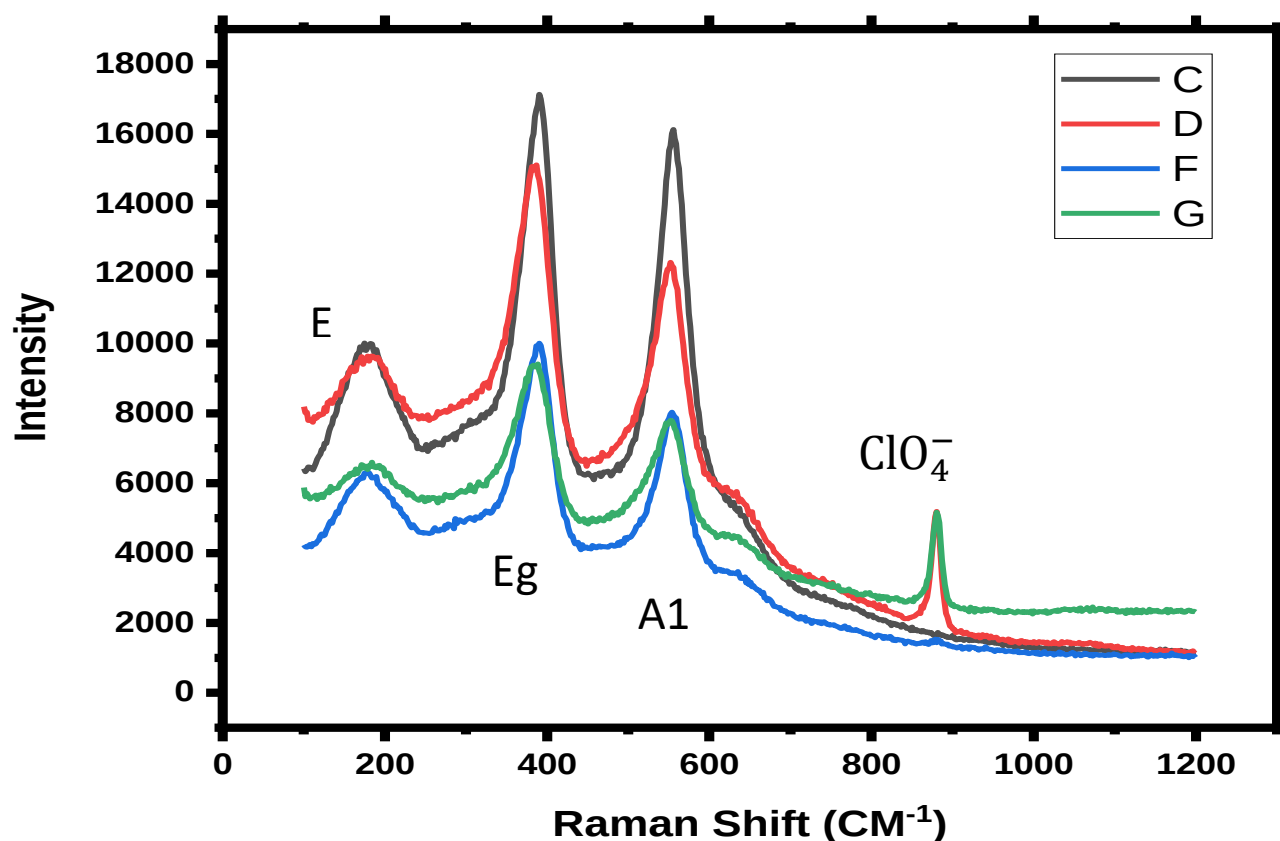


Fig 4.13 Comparison between Raman data of samples C, D, F and G

The Raman data confirms that samples C, D, F and G are Rutile having the sharp E_g peak characteristic to Rutile TiO₂. The breadth of this main anatase peak (E₁) and its lower intensity signify a tiny particle size as can be seen in samples F and G. Once again, the Raman spectra of sample A was inconclusive showing a mixed phase and broad peak. This confirms the importance the perchlorate ions in the formation of crystal phase in TiO₂.

The low intensity peak present around ~900 cm⁻¹ in samples G and D is attributed to the presence of the perchlorate ion. Due to the higher annealing temperatures used in the preparation of samples C and F, 450°C and 300°C respectively the perchlorate ion would evaporate as indicated by the absence of this peak. This peak is also absent in sample A. once again a direct comparison between samples A and G both annealed at approximately 100°C confirms that the perchlorate ion is the cause of this peak as multiple washings would remove all trace of perchlorate ion in sample A.

4.2.4 UV-vis Data

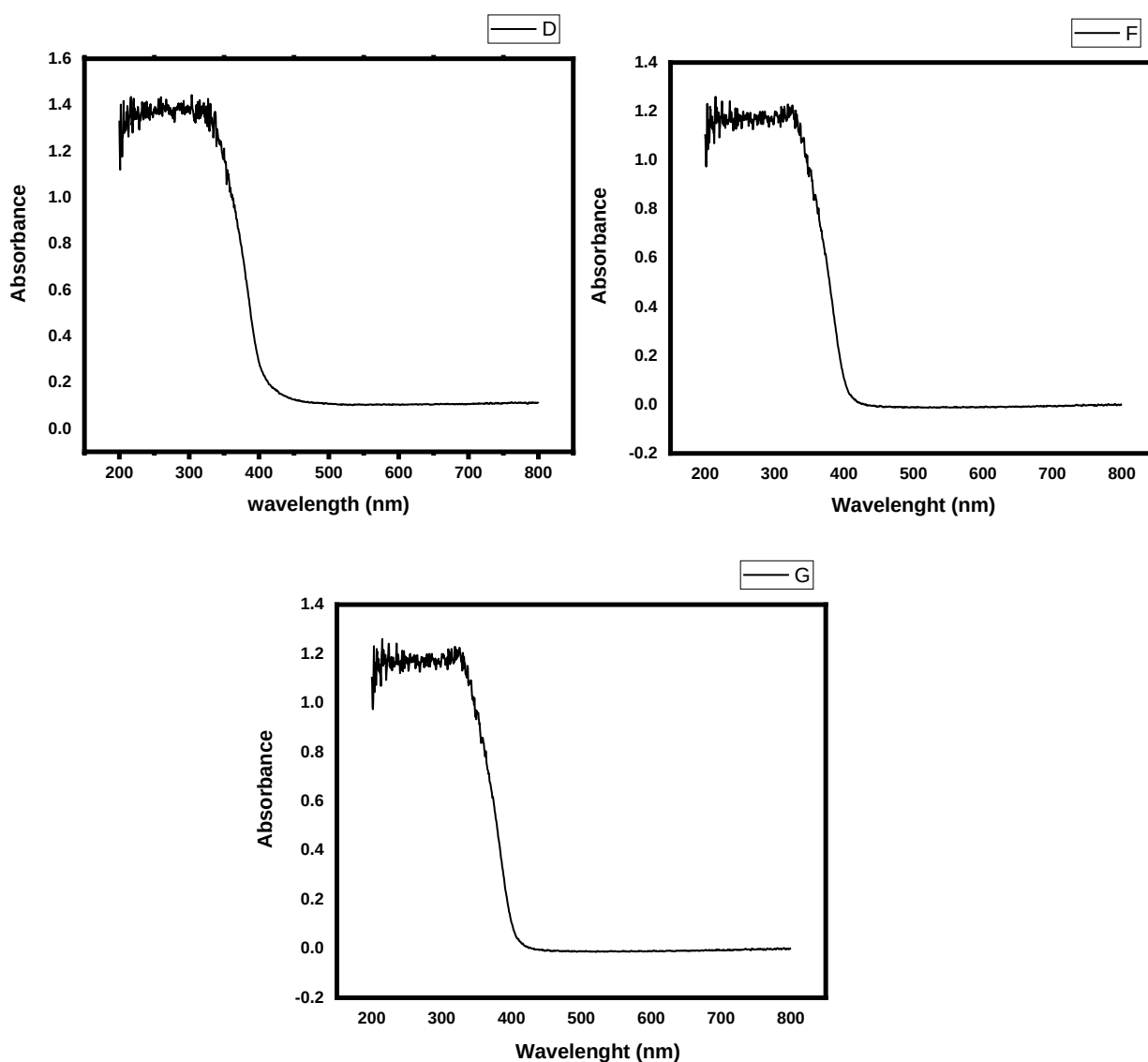


Fig 4.14 UV-vis data of samples D, F and G

Samples A and C could not be analysed as there was not enough material. From the UV-vis data available we can infer that the TiO_2 nanoparticles in samples D, F and G show high electromagnetic radiation absorption in 200-400 nano meter range. This is in agreement to the UV-Vis absorption spectrum of Rutile TiO_2 . This would imply that the samples would have decent photo-activity.

Conclusions

The Laser Ablation of Kapton (PI) for the production of Laser Induced Graphene was studied. The Ablation product was studied using X-Ray Diffraction showing a clear change from Kapton to an amorphous Carbonations substance. After Transferring the Substance onto Scotch tape, UV-Vis Spectroscopy showed the absorption characteristics of Graphene. Both the above observations were reinforced using Raman Spectroscopy. The Presence of D and G peaks in the Raman Spectra confirmed the presence of Laser Induced Graphene. Using the CNC Lasing setup, the effect of variation of Scanning speed was quantitatively analysed using Raman Spectroscopy and the linear relation between LIG formation and Laser fluence was observed. The change in LIG-Kapton substrate bonding strength was also noted. Microscopic imaging helped further the understanding of the surface nature of LIG. An interdigitated electrode was printed using the patterning ability of the CNC machine. The production of Laser Induced Graphene using a low-cost laser was Successful.

The formation of Nanotubes during Anodic Dissolution Process was studied and used to synthesise TiO_2 Nanoparticles. The mechanism and effects of perchlorate ions in the electrolyte were observed. The as-Anodized Nano-structures were washed and annealed at varying parameters to understand the effect of these parameters on them. The Nano-structures were studied using X-Ray Diffraction which indicated the Rutile phase of most of the samples. XRD data showed that the sample with majority of perchlorate ions removed due to washing had amorphous nature. This was reinforced using Raman Spectroscopy, along with a linear relation of Rutile phase transition with Annealing temperature. This was in Agreement to the observations by Hyam et al [16][17] whose work we tried to replicate. The Narrow and short E_g Raman peaks confirmed the presence of nanostructures. The Raman data also gave insight into the role of perchlorate ion in producing phase pure TiO_2 nanoparticles, as its presence was observed in low temperature Annealed samples. The UV-vis spectroscopy gave information with regards to the band structure of the TiO_2 Nanoparticles and was in Strong agreement with Rutile phase. It also gave insight on the possible photoactivity of the Rutile nano-structures.

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