Sulphur Doped Graphene: Synthesis, Characteristics and Applications

A Thesis

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in

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Submitted By

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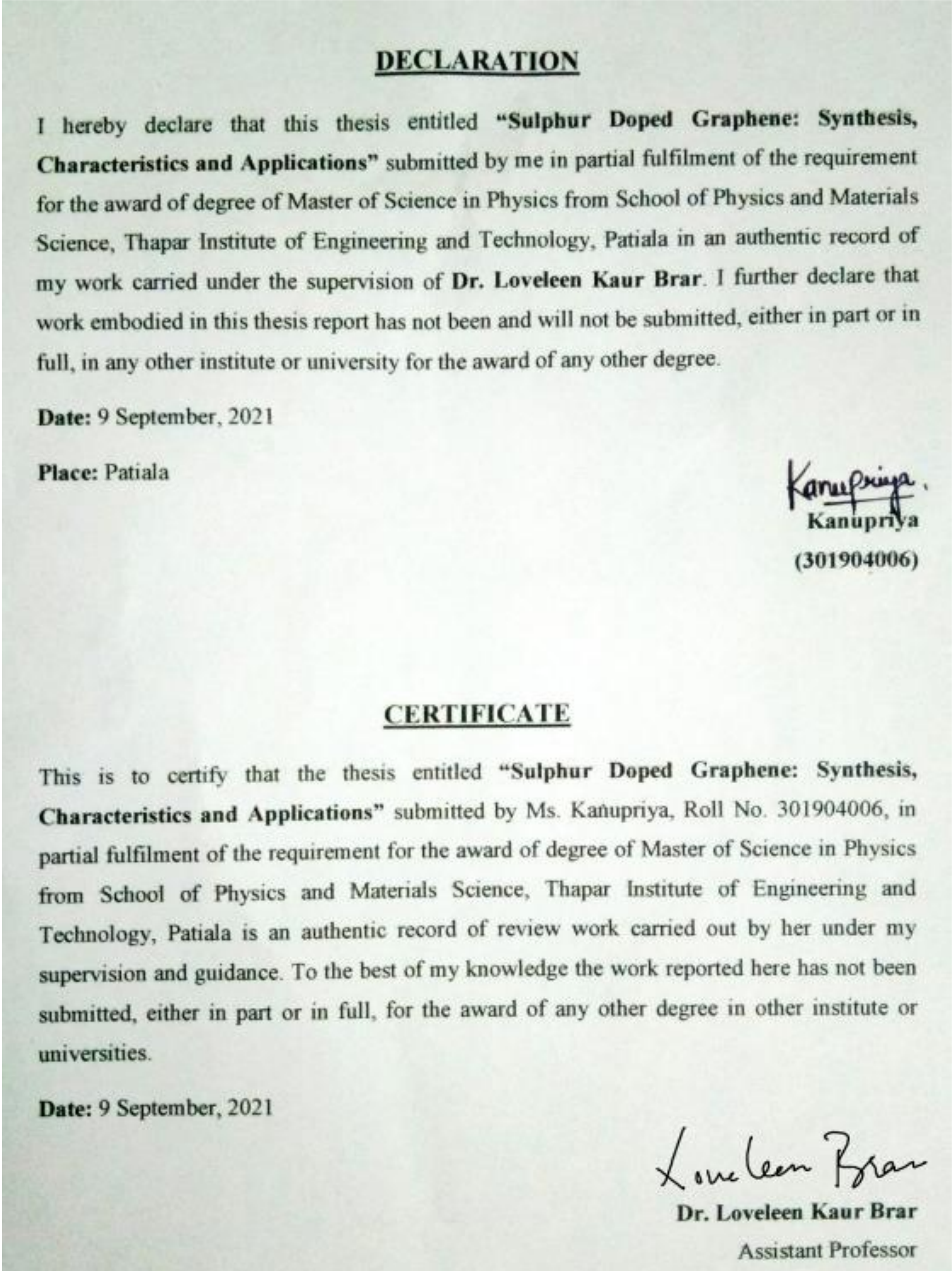

DECLARATION

I hereby declare that this thesis entitled **"Sulphur Doped Graphene: Synthesis, Characteristics and Applications"** submitted by me in partial fulfilment of the requirement for the award of degree of Master of Science in Physics from School of Physics and Materials Science, Thapar Institute of Engineering and Technology, Patiala in an authentic record of my work carried under the supervision of **Dr. Loveleen Kaur Brar**. I further declare that work embodied in this thesis report has not been and will not be submitted, either in part or in full, in any other institute or university for the award of any other degree.

Date: 9 September, 2021

Place: Patiala

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CERTIFICATE

This is to certify that the thesis entitled **"Sulphur Doped Graphene: Synthesis, Characteristics and Applications"** submitted by Ms. Kanupriya, Roll No. 301904006, in partial fulfilment of the requirement for the award of degree of Master of Science in Physics from School of Physics and Materials Science, Thapar Institute of Engineering and Technology, Patiala is an authentic record of review work carried out by her under my supervision and guidance. To the best of my knowledge the work reported here has not been submitted, either in part or in full, for the award of any other degree in other institute or universities.

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ABSTRACT

Graphene is a two-dimensional sheet of carbon atoms with outstanding properties such as high electrical conductivity, mechanical strength, thermal conductivity and electron mobility. These properties lead to its multiple applications, including energy storage devices, sensors, optics and in medical field. There is a tendency of stacking between the graphene sheets because of weak van der waals interaction, resulting in reduction of specific surface area. It has zero band gap which is not suitable for switching applications. Doping is an effective approach to increase the specific surface area and widen the graphene band gap. Sulphur atom is an attractive choice for doping of graphene among the different heteroatoms since the resulting materials are expected to have wide band gap due to electron withdrawing character of sulphur. Also, the size difference from carbon will result in breaking the planar structure and reduced stacking. C-S bonds present at the edges enhance the charge storage capacity and electro-catalytic activity of the sulphur doped graphene. Oxidized rich-S doped graphene has relatively low conductivity, while thiophene rich-S doped has better conductivity and charge transfer ability. Sulphur doped graphene has been widely used in various applications such as super-capacitors, biosensors, batteries, fuel cells etc. It can be prepared by using different methods such as chemical vapour deposition, thermal annealing, electrochemical deposition and hydrothermal method. Out of the four synthesis methods, hydrothermal method is simplest, low cost, green technique with low processing temperature. However, hydrothermal method is applicable only for small scale synthesis whereas other three methods can be adapted for large scale synthesis. In hydrothermal method, sulphur doping in graphene can be done by using different precursors such as Na_2S, sulphur powder and thioacetamide. Products synthesised by different precursors show variation in properties. Na_2S not only acts as sulphur dopant but also a highly efficient reducing agent. Sulphur may or may not be incorporated into the synthesis of sulphur doped graphene when it is employed as a precursor in hydrothermal conditions. Both Na_2S and thioacetamide emerged as good precursors for the hydrothermal production of sulphur doped graphene.

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CHAPTER 1

INTRODUCTION TO GRAPHENE

Graphene is a two-dimensional structure made up of a single layer of sp^2 bonded carbon atoms arranged in a hexagonal lattice which resembles a honeycomb-like pattern (Fig 1.1). It is one of the multiple possible allotropic forms of carbon. The C-C bond length in the graphene sheet is 0.142 nm, while the thickness of the graphene sheet is roughly 0.35 nm. Konstantin Novoselov and Andre Geim were the first to discover graphene in 2004, and both were awarded by Nobel Prize in Physics in 2010 [1].

1.1 STRUCTURE OF GRAPHENE

Carbon atoms in a single layer graphene sheet form a σ-bond with the carbon atoms around them. The σ-bond in graphene is formed by the sp^2(2s, $2p_x$, $2p_y$) hybridized orbitals as shown in Fig 1.1. The unbonded $2p_z$ orbitals hybridize together to form the π-band (filled) and π^*-band (empty). The majority of graphene's electronic characteristics are determined by these bands [2].

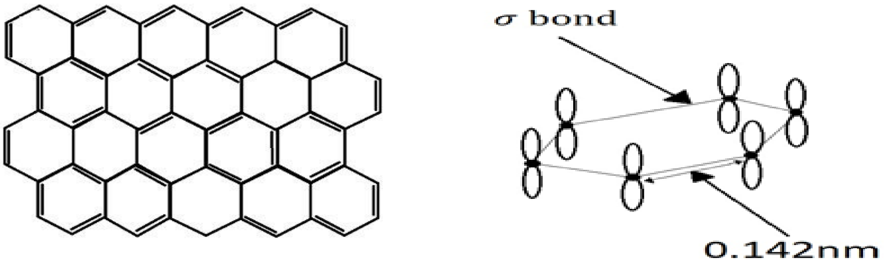

Fig 1.1: Structure of graphene

1.2 PROPERTIES OF GRAPHENE

- **Mechanical Properties:** The tensile strength of graphene is 130 GPa, while Young's Modulus is 1TPa. Graphene is a flexible material that can be stretched to 20% of its original size without breaking [4, 5]. The high mechanical strength ($\sim$ 40 Nm^{-1}) is due to the strength of sp^2 carbon bonds.

  Electronic Properties: Graphene has high electrical conductivity ($\approx 10^6$ S/m) and electron mobility ($\approx 10^5 cm^2 V^{-1} s^{-1}$) due to its band structure [5]. Because of the overlapped π-electrons in graphene, the band gap is zero, allowing electrons to travel freely without any energy input (Fig 1.2) [2].

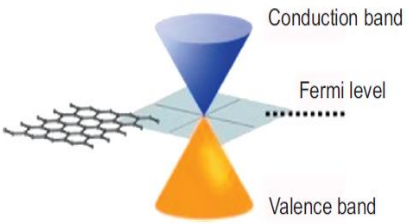

Fig 1.2: Energy band diagram of graphene [2]

- **Thermal conductivity:** It has a high thermal conductivity of about 5×10^3 W/mK at normal ambient temperature. It is an isotropic conductor because it conducts heat equally in all directions. Carbon nanotubes, graphite, and diamond all have lower heat conductivity than graphene.
- **Chemical Properties:** Graphene is a non-reactive material that means it does not react with other atoms. Adsorption of different atoms and molecules on the surface of graphene can cause variations in its electronic properties. Charge transfer between adsorbed molecules/atoms and graphene modifies the electronic profile of the graphene. By substituting the carbon atoms, the electrical property of graphene can be changed as well. This property of graphene allows it to be used in a variety of fields including sensors and super-capacitors. Even helium atoms cannot travel through graphene because it is highly impermeable. Graphene can be functionalized with a variety of chemical groups, resulting in a variety of compounds such as graphene oxide [3]. Functionalization of graphene requires harsh chemical/thermal conditions.

- **Optical properties:** Graphene has a high absorption capacity at the wavelength of 660nm and its transparency is 97.7% due to its single atomic thickness [5].

Table1.1: Comparison of some key properties of graphene with other common materials

	STRENGTH	**THERMAL CONDUCTIVITY**	**ELECTRON MOBILITY**	**ELECTRICAL CONDUCTIVITY**
GRAPHENE	130 GPa	5 $\times 10^3$W/mk	2$\times 10^5 cm^2$/Vs	$\approx 10^6 Sm^{-1}$
OTHER MATERIALS	STEEL 841MPa	COPPER 401W/mk	SILICON 1400cm^2/Vs	SILVER 2.7$\times 10^7$Sm^{-1}

1.3 APPLICATIONS OF GRAPHENE

- **Biosensors:** Graphene can improve the sensitivity as well as the performance of graphene-based biosensors by enhancing the electron transfer between graphene and biomolecules because of its excellent electron transport capabilities [6].
- **Photovoltaic devices:** Graphene is often used for low-cost, flexible, and highly efficient solar systems because of its outstanding electron-transport properties and very high carrier mobility [5].
- **Super-Capacitors:** Graphene has high electrical conductivity and high electron mobility resulting in low diffusion resistance enhances the power and energy density which is responsible for designing graphene based super-capacitors. Graphene based super-capacitors are capable of storing nearly the same amount of energy as nickel-metal hydride (Ni-MH) batteries [5]
- **Batteries:** Graphene has excellent flexibility, high surface area (2630 m^2g^{-1}), high thermal conductivity and mobility due to which it is used in batteries. Graphene-based batteries provide a longer lifetime and better safety compared to the other batteries [5].
- **Transistors:** Graphene is a key component in the development of new generation transistors because of its high electron mobility. Because of the high electron mobility of graphene, it is used for making FETs known as Graphene-based Field Effect Transistor (GFET) [5].
- **Medical Applications:** Graphene has a wide range of medical applications including medicine transport, cancer therapy and sensors due to its huge surface area, high conductivity and outstanding biocompatibility [5].

1.4 DERIVATIVES OF GRAPHENE

Graphene oxide and reduced graphene oxide are two common graphene derivatives that offer excellent electrical, mechanical, and electrochemical properties.

Graphene Oxide (GO): It is the heavily oxygenated form of graphene as shown in Fig 1.3. Oxygen is present in the graphene basal plane as a several functional groups such as hydroxyl, epoxide, and carboxyl groups as shown in Fig 1.3 [7]. GO is hydrophilic due to the presence of functional groups. Because of its high surface area and oxygen content, GO can form better nano-composites [8]. This leads to better enhancement of mechanical and electrical properties for various applications.

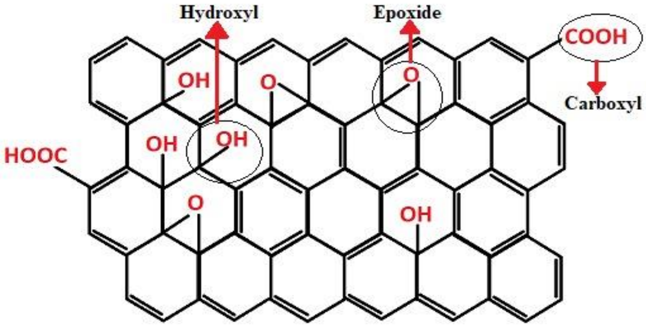

Fig 1.3: Structure of graphene oxide

The oxidation of graphite produces graphene oxide as shown in Fig 1.4. It has special characteristics such as high convective heat transfer, insolubility and low density. It is the greatest interest of the researchers due to low cost and extensive capability to convert to RGO [8].

Reduced Graphene Oxide (RGO): It contains lower amounts of oxygen-functioned groups as compared to GO (Fig 1.5). RGO is primarily synthesised by reducing GO with different techniques such as thermal, chemical, electrochemical reduction as shown in Fig 1.4 [7]. GO is insulating in nature whereas RGO can be either insulating or conducting depending on the percentage of oxygen present on the graphene sheet after reduction. RGO has a strong optical absorption cross-section as compared to GO [9]. The thermal reduction requires a high cost since it involves high temperature. Thus, the chemical reduction is preferred by most researchers [7].

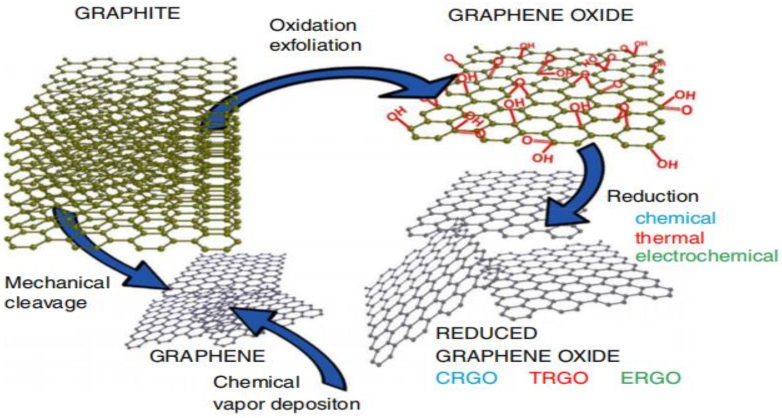

Fig 1.4: Oxidation process of graphite and reduction process of GO [8]

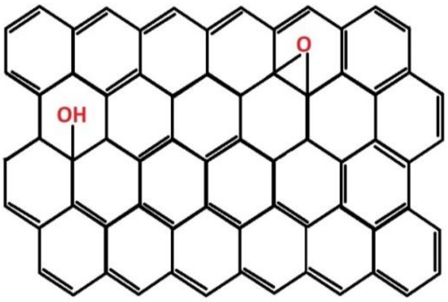

Fig 1.5: Structure of reduced graphene oxide

Properties

- GO has a high young's modulus which varies from 380 to 470 GPa and tensile strength of ∼ 120 MPa whereas RGO has a young's modulus of 1 TPa and tensile strength of 130 GPa which is analogous to graphene [10, 11].
- GO behaves as an insulator or semi-conductor, but RGO has a high electrical conductivity. The difference in conductivities between GO and RGO allows for a variety of applications including biosensors and super-capacitors [11].
- GO shows hydrophilic behaviour while RGO shows hydrophobic behaviour due to increase in C/O ratio [11].

Table1.2: Comparison of the main properties of GO and RGO

	Young's modulus	**Tensile strength**	**Specific Surface area**	**Behaviour**
Graphene oxide	380 – 470 GPa	120 MPa	890 $m^2 g^{-1}$	hydrophilic behaviour
Reduced graphene oxide	1 TPa	130 GPa	2600 $m^2 g^{-1}$	hydrophobic behaviour

Applications

- **Energy storage:** Because of high surface area of reduced graphene oxide, it is used in lithium-ion and lithium sulphur batteries for energy storage [12].
- **Solar cells:** GO and RGO has a large specific area which is attractive for solar cell applications. Due to its semiconducting property, graphene oxide is used as a holes transport and electron blocking layer [12].

- **Sensors:** RGO is used in sensing applications because of its large surface area and electrical conductivity. Due to the active surface and large surface area, GO has excellent sensing capacities [12].
- **Super-Capacitors:** Because of their huge specific surface area, electrical conductivity, and cyclic stability, RGO is an excellent candidate for super-capacitor application. The capacitance of these super-capacitors increases up to 33.80 F/g which results in high power (442.5 W/Kg) and energy storage (1.66 Wh/kg) [13].
- **Biosensors**: Electrochemical, optical, and field-effect transistor (FET) biosensors can be made from GO and RGO composites. These are biocompatible and widely used to detect biomolecules such as DNA, glucose, and micro RNA. The fluorescent property of GO allows it to be used in optical biosensing applications to detect various molecules such as metal ions and cancer biomarker glucose [13].

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CHAPTER 2

DOPED GRAPHENE

2.1 NEED FOR DOPING GRAPHENE

Graphene is made up of a single layer of sp^2 hybridized carbon atoms with s, p_x and p_y atomic orbitals on each carbon atom, which form three σ bonds with the other three surrounding atoms. Overlapping of leftover p_z orbital on each carbon atom with neighbouring atoms, resulting in a filled valence band and an empty band of π^* orbitals called a conduction band [1]. Six points are situated at the corners of the first brillouin zone in the honeycomb arrangement. These six points are divided into two groups, each of which contains three identical points. These points are called Dirac points are denoted by K and K$'$ as shown in Fig 2.1 [2].

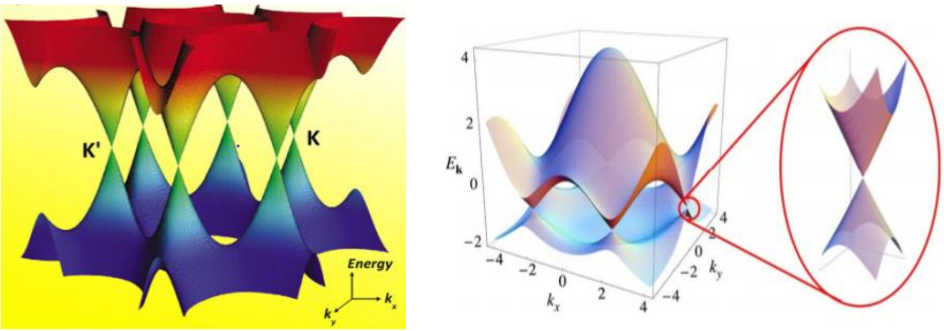

Fig 2.1: Band structure of graphene in the honeycomb lattice [1]

The valence and conduction band touch at the Dirac point positions, resulting in a zero energy gap as shown in Fig 2.2. Hence, graphene is popularly known as zero band gap semiconductor or semimetal [2].

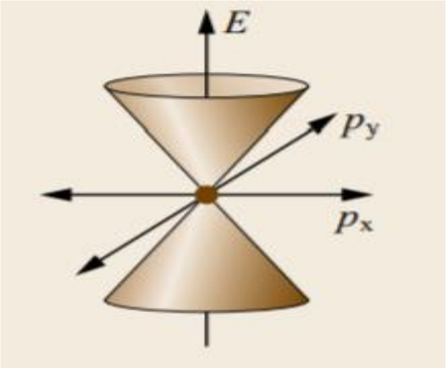

Fig 2.2: Energy band diagram of graphene[2]

There is need to develop band gap in graphene because of the following reasons:

- A band gap must be opened to increase the electronic properties of graphene in semiconductor devices such as field-effect transistors. To open the band gap, doping is an effective method of altering the electric and magnetic properties of the materials [3].
- Graphene has various fascinating aspects such as high electrical conductivity, electron mobility, thermal conductivity. On the other hand, because of the weak van der waals interaction, there is stacking between graphene sheets, resulting in the reduction of specific surface area. To solve this issue, doping with heteroatoms is considered to be an effective way [4].

2.2 TYPES OF DOPING

Graphene doping is divided into two categories:

- <u>Electrical doping:</u> Electrical doping occurs when the gate voltages of graphene devices change. An electrostatic potential difference between the graphene and gate electrode is formed when a gate voltage is provided and the addition of charge carriers causes a shift in the fermi level. This causes the modification of the band structure in graphene materials.
- <u>Chemical doping:</u> Chemical doping occurred when there is a change in the lattice structures of graphene lattice through chemical methods. Chemical species like substitutional atoms and organic molecules are present in this process. Dirac point is shifted in comparison to the fermi level by chemical doping. Graphene’s electronic properties can be altered by this method [1].

Chemical doping is further divided into two categories:

<u>Surface transfer doping</u>:

Charge transfer between the adsorbed dopant and graphene is used to achieve surface transfer doping. It is also known as adsorbate-induced doping. Charge transfer can be calculated using the density of states of the dopant's highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), as well as the fermi level of graphene. If a dopant's HOMO is higher than graphene's fermi level, the charge is transferred from the dopant to the graphene layer, and the dopant acts as a donor. When the LUMO is below the fermi level of graphene, there is a charge transfer from the graphene layer to the dopant and the dopant acts as an acceptor as shown in Fig 2.3 [1].

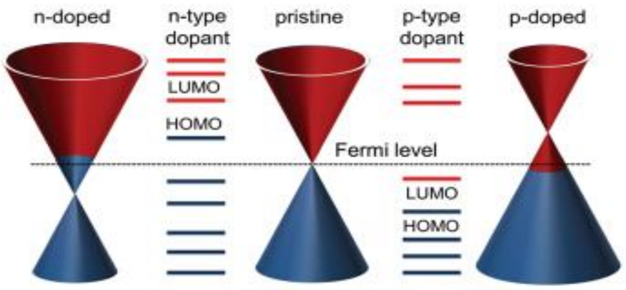

Fig 2.3: Surface transfer doping [5]

Substitutional doping :

In graphene, substitutional doping refers to the substitution of heteroatoms for carbon atoms in the hexagonal lattice, causing sp^2 hybridization to be disrupted and hence dramatic changes in electrical characteristics. Substitution of heteroatoms such as nitrogen (N), phosphorous (P), boron (B), sulphur (S) etc. can improve the surface and bulk properties of graphene thereby extending its applications in varied fields such as lithium-ion batteries, super-capacitors, biosensors etc. Heteroatoms create defects in graphene that are responsible for changes in the properties of graphene [3]. Doping with acceptor impurity atoms (e.g. Boron) causes the fermi level to shift below the Dirac point, favouring p-type doping, whereas doping with donor impurity atoms (e.g. Nitrogen) causes the fermi level to shift above the Dirac point, favouring n-type doping of graphene as shown in Fig 2.4 [6]. Doped graphene shows better conductivity.

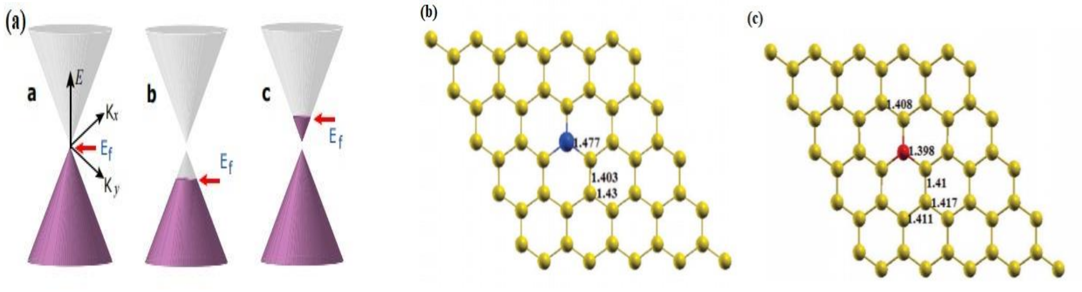

Fig 2.4: (a) Band diagram of graphene (i) Undoped (ii) Hole doped (iii) Electron doped [6] (b) Substitutional doping of boron [7] (c) Substitutional doping of nitrogen [7]

2.3 ADATOM DOPING

Substitutional doping is achieved when the carbon atom is substituted by a heteroatom such as boron (B), nitrogen (N), phosphorous (P), sulphur (S) etc. which improves the surface and bulk properties of graphene. The doping of heteroatoms into graphene's hexagonal carbon sheet creates structural and electrical distortions. This leads to altering of the graphene properties such as thermal stability, band gap, fermi level, optical and magnetic properties. The type of dopants and their bonding arrangement improve the properties of graphene, which are helpful for specific applications. Because of their resemblance to carbon atoms, heteroatoms like B, N, P, and S are better dopants for graphene [8].

Table2.1: Comparison of different dopants

Element	Covalent radius (pm)	Electronic configuration	Number of valence electrons	Electro-negativity	Bond length X-C (Å)
Carbon	75	$1s^2 2s^2 2p^2$	4	2.55	1.42
Boron	85	$1s^2 2s^2 2p^1$	3	2.04	1.50
Nitrogen	71	$1s^2 2s^2 2p^3$	5	3.04	1.41
Phosphorus	111	$1s^2 2s^2 2p^6 3s^2 3p^3$	5	2.19	1.77
Sulphur	103	$1s^2 2s^2 2p^6 3s^2 3p^4$	6	2.58	1.78

Boron: Boron (2.04) has less electronegativity than carbon (2.55). This results in electron transfer within the bond in the direction from boron to carbon. Doping of boron atom in graphene sheet causes the Dirac point to shift below the Fermi energy, resulting in holes doping. This turns graphene into an electron-deficient system, increasing its electrophilic character and allowing for more Li-ion adsorption. The improvement in lithium storage occurred due to defects created during boron doping in graphene [8]. The boron atom creates sp^2 hybridization in the carbon lattice, which preserves the planar structure of graphene [9]. The electrochemical activity of boron doped graphene is enhanced due to its large surface area, open porous structure, and high electrical conductivity. On comparing with pristine graphene, boron doped graphene exhibits excellent electrocatalytic activity [10].

Nitrogen: Nitrogen is an electron-rich element that distinguishes nitrogen doped graphene from boron doped graphene. The C-N bond length (1.41 Å) is similar to the C-C bond length (1.42 Å). Nitrogen (3.04) has a higher electronegativity than carbon, so charge transfers from carbon to nitrogen along with the bond which is beneficial for the electrical conductivity of the material. In carbon lattices, nitrogen atom creates sp^2 hybridization which retained graphene in the planar structure. The surface oxygen containing group in nitrogen doped graphene is reduced, which improves graphene's corrosion resistance. Surface imperfections in graphene caused by nitrogen doping improve Li-ion storage for Li-ion battery applications [11]. At a current density of $1\,Ag^{-1}$, the super-capacitor based on the nitrogen doped graphene has a high specific capacitance of 242 $\mathrm{F}g^{-1}$ [12]. Nitrogen doped graphene has high biocompatibility, a high electrocatalytic activity which is used for making biosensors [13].

Phosphorus: Phosphorus has a larger size than carbon which causes structural distortion within graphene. Phosphorus atom overhangs the graphene plane by 1.33, resulting in a pyramidal shape [13]. In pure graphene, the P-C bond (1.77 Å) is longer than the C-C bond. The electronegativity of the phosphorus (2.19) atom is lower than that of carbon. Lower electronegativity results in the formation of positive charge on P-atom which in turn is favourable for the transfer of charge [9]. Structural distortion and charge density variation upon phosphorus doping in graphene enhance the capacitive performance. Phosphorus doped graphene enhances the density of charge carriers in the material because phosphorus electrons contribute to the graphene π-system [14]. Phosphorus has high donor capacity than nitrogen. As a result, phosphorus doping provides a superior n-type nature in graphene than N-doping [15]. It donates its extra unbounded valence electron while doping resulting in enhancement of chemical reactivity and electrical conductivity of graphene based devices [16].

Sulphur: Sulphur (2.58) has electronegativity similar to carbon (2.55) atom, resulting in negligible polarization of C-S bonds. Sulphur atom doping in graphene sheet causes structural distortion, results in a pyramidal structure in which sulphur atom is elevated up to 0.7 Å from the graphene plane. After sulphur doping, the C-S (1.78 Å) bond length which is 25% longer than the C-C bond, causes the creation of defect sites in graphene [13]. Sulphur doped graphene exists in two configurations i.e. thiophene-S and oxidized-S. For electro-catalysis and electro-analysis applications, thiophene-S doped graphene is a promising material [17]. The misalignment of S and C outermost orbits results in non-uniform spin density distribution which is useful for the catalytic properties [13]. The doping of sulphur atoms in graphene sheets enhances the electrical conductivity, which aids charge transport and is thus used in high-power applications [17].

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CHAPTER 3

INTRODUCTION TO SULPHUR DOPED GRAPHENE

3.1 SULPHUR DOPED GRAPHENE BONDING CONFIGURATION

- Sulphur has a larger atomic radius (1.80 Å) compared to carbon (1.70 Å) which induces structural distortion when sulphur atoms are substituted into graphene lattice. The wrinkling and overlaying of the graphene sheets leads to open edged sites and defects within the sample which behave like active sites [1].
- S-doping occurs preferably at the site of the oxygen-functional group in GO which results in more efficient GO reduction [2]. The S bonding configurations in sulphur doped RGO samples are thiophene-S (Fig 3.1) and oxidized-S (Fig 3.2).
- Sulphur doping in graphene occurs at the surface and edge as follows:
  i. In graphene, sulphur atoms replace some carbon atoms and form -C-S-C bonds.
  ii. Sulphur atoms create S=O bonds at the graphene structure's edge [3].

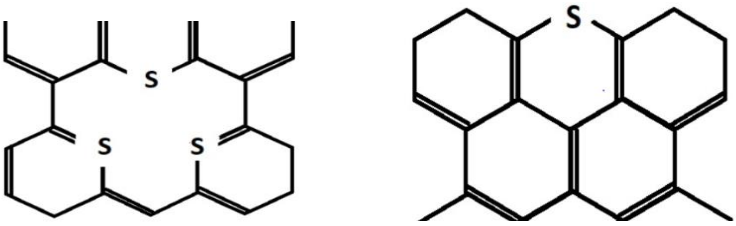

Fig 3.1: Structure of thiophene-S at basal planes and edges

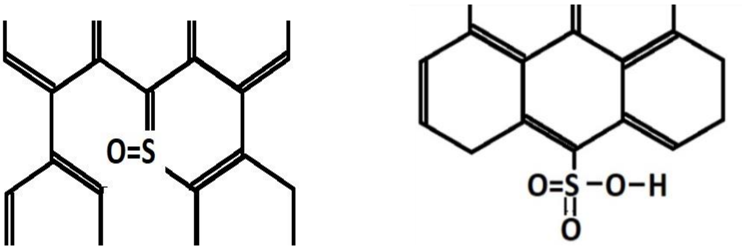

Fig 3.2: Structure of oxidized-S at basal planes and edges

- The average electron transfer numbers of S-doped graphene increase thiophene-S content indicating better electrocatalytic activity of the sample [4].

- Chemical reactions between sulphur and oxygenated groups such as –OH, C=O, and COOH can occur at the surfaces and edges of graphene sheets due to thiophene sulphur and oxide sulphur. Thereby making the system more reactive. The hydroxyl and carboxyl functional groups of S-RGO as well as the GO sheets are dehydrated intramolecularly or intermolecularly, resulting in tight S-RGO linkage by π-π stacking and covalent bonds [4].
- C-S bonds present at the edges provide active sites which are beneficial for the charging of electrical double-layer and are conducive to supercapacitive performance. S-doped graphene prefers a curved carbon nanostructure because of longer C-S bond [6, 7].
- Open edge sites and defects at the surface of S-doped graphene with high sulphur content as well as C-S-C sulphurated species are favourable for increased ORR (oxygen reduction reaction) catalytic activity [1].
- Sulphur forms only a double bond with carbon, resulting in S doping sites at the graphene layer's edges or defects [5]. C-S bonds are mostly found at the edge sites, which causes the activity to increase due to the changed spin density and charge distribution. This increases the electrocatalytic activity and electrochemical sensing [2].
- Doping of graphene edges with sulphur atoms and sulphur oxides (O=S=O) improves electrocatalytic activity and electronic spin density [5]. At higher annealing temperatures, oxidized-S groups such as sulphate (SO_4^{-2}) and sulphonate (R-SO_3^-) can be converted into sulphide (S^{2-}) groups [5]. Thiophene-S has higher charge and spin densities than oxidized-S bonding configuration because oxidized-S bonding configuration decreases the conductivity of carbon materials [8].

3.2 BAND STRUCTURE OF SULPHUR DOPED GRAPHENE

Substitutional doping is the simplest method for opening the bandgap and changing the band structure of graphene. The band structure of the graphene can be altered by controlling the degree of heteroatom doping. Sulphur atom (EN=2.58) is the attractive doping material due to similar electronegativity with the carbon atom (EN=2.55). The 3S-graphene exhibits a downshift of the band energy below the Fermi energy which results in n-type character as shown in Fig 3.3 [9].

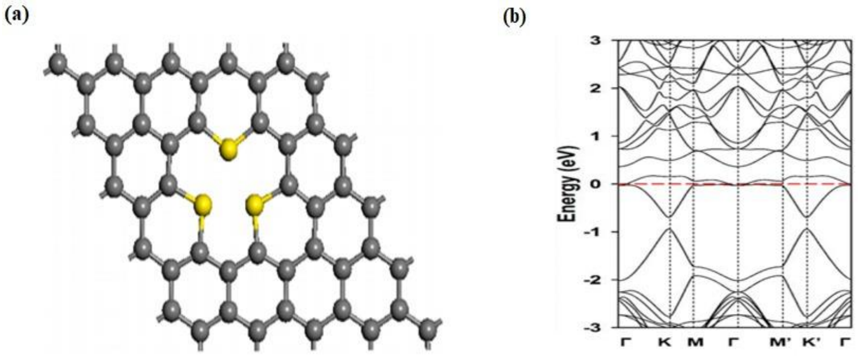

Fig 3.3: (a) Structure and (b) Band structure of 3S-graphene system [9]

The structural changes originated by the substitution of sulphur atom in sulphur doped graphene are significant as shown in Fig 3.4. The second row of atoms is too big to fit into the sp^2 framework, thus it protrudes from the sheet. Also the carbon atom surrounding the sulphur in sulphur doped graphene are lifted. Three carbon atoms bonded to sulphur atom are raised to 0.7 Å. This results in a structural modification which is suggested for the graphene reactivity because variation from complete sp^2 hybridization makes these atoms more reactive. Doping with sulphur atoms opens a band gap while also increasing the reactivity of the graphene [10].

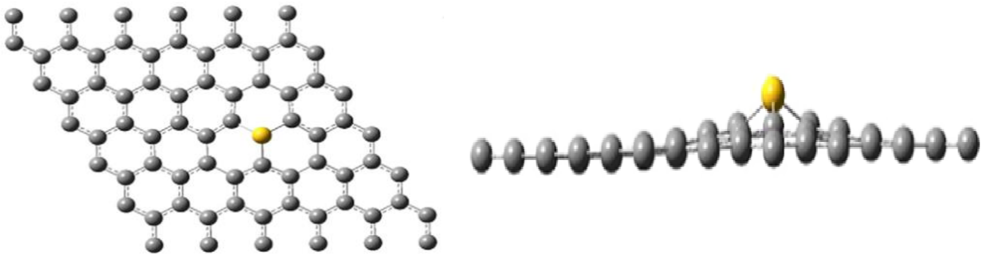

Fig 3.4: Structure of 1S-graphene system [10]

3.3 IMPORTANCE OF SULPHUR DOPED GRAPHENE

- Doping of graphene with sulphur atom is of particular interest among the different heteroatoms because resulting materials are expected to have a wide band gap due to the electron withdrawing character of Sulphur [11].
- Sulphur-doped graphene is a novel nanomaterial based on graphene. Doping of sulphur atom into pure graphene enhances the activation region on its surface which enhances its catalytic ability and opens the band gap, giving it numerous applications in fuel cell chemistry, semiconductor devices, sensors, and other technologies [6].

- Distribution of non-uniform spin density on S-doped graphene is caused by a mismatch between the outermost orbitals of sulphur and carbon, which improves the catalytic characteristics suitable for various applications [6].

3.4 APPLICATIONS

Batteries: Lithium-sulphur (Li-S) batteries have a high specific capacity (1672 mAhg^{-1}) and energy density (2600 Wh Kg^{-1}) as compare to lithium ion batteries [11]. Sulphur is considered as an active material in cathode for lithium-sulphur batteries which is cost effective and environment friendly. Sulphur doped graphene based batteries have high biocompatibility, low cost and high capacity of energy storage [12].

Super-Capacitors: Super-Capacitors have been intensively researched as energy storage devices because of their high power density and long lifecycle. Graphene has a large specific surface area, so it has high electric double-layer capacitance. Hence, doped graphene materials are attractive for super-capacitors because they have better sheet-to-sheet separation, lower charge transfer resistance, and greater conductivity. It also enhances the electrochemical activity of the capacitance [11]. At a current density of 0.2 Ag^{-1}, a sulphur doped graphene based super-capacitor has a high specific capacitance of 343 Fg^{-1}. Sulphur doped graphene based materials are produced and employed as electrodes for double layer electric capacitors which enhances the capacitance performance. The presence of oxidised sulphur compounds like sulfones and sulfoxides affects the capacitive behaviour of such systems.

Biosensors: Sulphur doped graphene has low toxicity because of that it is used for sensing in cells and living organisms. Biosensors based on sulphur doped graphene are used for the detection of antibodies, proteins, DNA, RNA etc. in living cells. Low cost, great stability, and a wide range of clinical diagnostic applications are all advantages of these biosensors. Sulphur doped graphene based biosensors have excellent catalytic activity because of a high density of active sites which is used in the manufacturing of biosensors. Sulphur doped graphene quantum dots are also employed for making biosensors due to their excellent aqueous dispersibility, tiny size, narrow size distribution and low toxicity [13]. On combining the high electroactivity and biocompatibility of sulphur element with large surface area and electrochemical property of graphene, sulphur doped graphene has excellent performance as electrochemical biosensor used for detecting dopamine, hydrogen peroxide (H_2O_2), 8-

hydroxy-2-deoxyguanosine molecule (biomarker for cancer) with high selectivity and sensitivity [14, 15, 16].

Fuel cells: Graphene lacks catalytic activity towards oxygen reduction reaction and is inefficient in electron transfer. Doping graphene with sulphur improves the catalytic activities. The formation of spin density due to misalignment of orbitals between heteroatoms and carbon, improves the catalytic ability. Tolerance to methanol and CO, long-term stability, and selectivity are all improved by sulphur doping graphene [11].

Sensors: Sulphur doped graphene can increase the performance of electrochemical sensors by introducing electrochemically active sites that can enable charge transfer and adsorption. Heteroatom doping changes the graphene from semimetal to semiconductor which is advantageous for electronic detection. Sulphur has a high electron-donating capacity which enhances the electrochemical sensing capabilities of the sensors. Sulphur doped graphene based sensors are used to distinguish NO_2 from other gases such as NH_3, CH_4, SO_2 and CO [11].

3.5 SYNTHESIS METHODS

Chemical vapour deposition: One of the most promising approaches for producing doped graphene is chemical vapour deposition (CVD). Doping can occur in this procedure by introducing solid or liquid precursors as shown in Fig 3.5. Chemical vapour deposition is the direct synthesis method that produces homogeneous doping effects. It has specific advantages including high-quality, large-scale and easy transfer of the material. This method requires high temperature and special instrumentation for the synthesis of doped graphene [17].

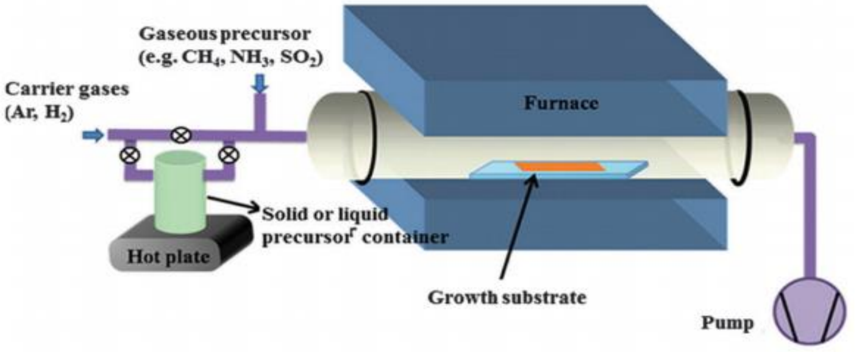

Fig 3.5: Experimental setup used for chemical vapour deposition [18]

Thermal annealing: Thermal annealing method involves heating of the material to an elevated temperature for an appropriate amount of time and then allowing the material to slowly cool to room temperature. The elevated temperature requires during the synthesis of sulphur doped graphene ranges from 600 -1000°C. It is a simple, effective and widely used method for the production of large-scale sulphur doped graphene at high temperature as shown in Fig 3.6. This method requires a high temperature and longer time for the synthesis of doped graphene [17].

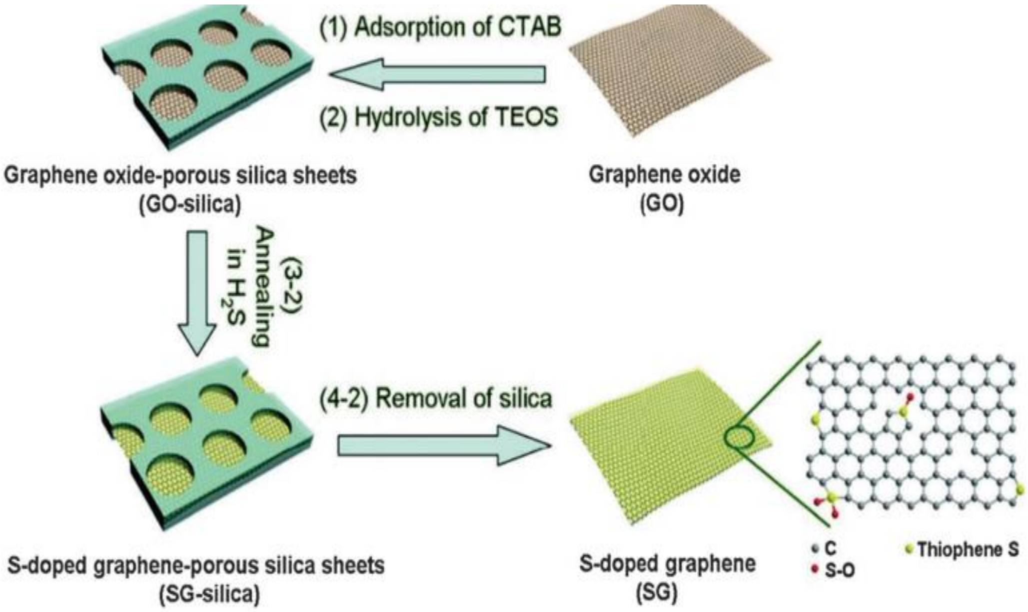

Fig 3.6: S-doping on graphene oxide porous silica sheets by thermal annealing method [11]

Electrochemical method: Electrochemical method is related to the preparation of chemical compounds in an electrochemical cell. It consists of two electrodes i.e. anode and cathode. The graphite rod is used as both anode and cathode electrodes in an electrochemical cell. This method involves the transfer of electrons between the electrode and the electrolyte. Sulphur doped graphene is synthesised using a simple one-pot electrochemical technique which improves the electrochemical storage as shown in Fig 3.7. This method is environmentally friendly and it involves cheaper synthesis with high production efficiency but consuming a longer time in order to make doped graphene [11].

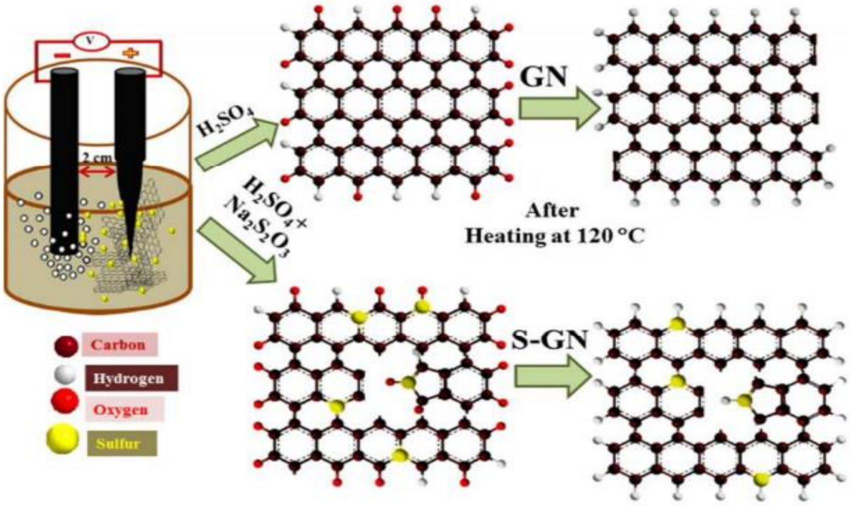

Fig 3.7: Schematic diagram for the synthesis of graphene and sulphur doped graphene by electrochemical method [11]

Hydrothermal method: Synthesis carried out by using the hydrothermal method, involves high temperature and pressure. The aqueous solution is used as a reaction system in a special closed vessel in this method as shown in Fig 3.8. This closed reaction vessel is known as autoclave which is used to establish high temperature and high pressure reaction environment. The hydrothermal method's general preparation steps are shown in Fig 3.9 [19]. Synthesis of sulphur doped graphene by hydrothermal method results in the production of the high conductive sheet which offers many promising applications including metal-free electrocatalyst in oxygen reduction reactions for fuel cells and supercapacitor electrode material for high performance batteries [21]. This method involves several advantages such as simplicity, low cost, low processing temperature, environmental friendly etc. However, this approach is employed to make sulphur doped graphene on a small scale [20].

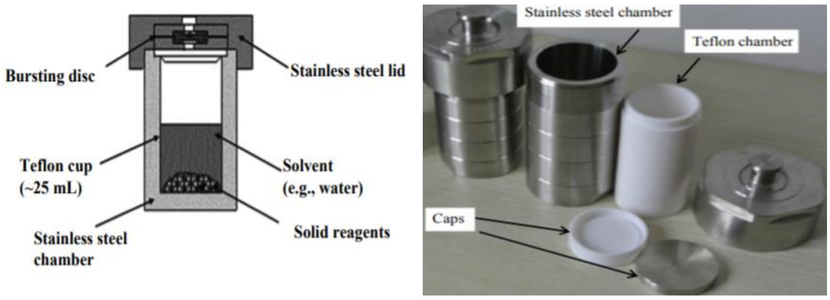

Fig 3.8: Hydrothermal autoclave [20]

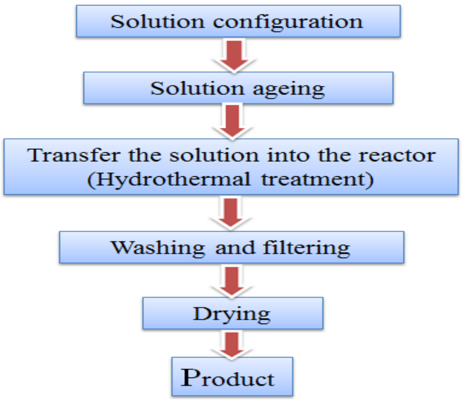

Fig 3.9: General steps for hydrothermal method [19]

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CHAPTER 4

LITERATURE REVIEW FOR SULPHUR DOPED GRAPHENE SYNTHESIS

4.1 Synthesis of Sulphur doped graphene by the CVD method

Wang, Jiacheng, et al 2015 [1] synthesised SG by using Na_2SO_4 and magnesium powder as a precursor and reducing agent respectively. These powders were mixed and put onto an alumina boat and then heated up to 700°C for 1 hour under argon atmosphere. After that, the furnace was brought to normal temperature. Then the product was filtered and purified three times using distilled water and ethanol.

Hassani, Fahimeh, et al 2016 [2] To make sulphur doped graphene by chemical vapour deposition, all of the growth factors must be investigated. 0.2g of prepared nanocatalyst was placed on an alumina boat and 1.4g of sulphur powder was placed on another alumina boat in a CVD instrument. The first zone was heated to a temperature of 450°C, while the second zone was heated to a temperature of 600°C. The produced sulphur doped graphene was collected and purified by HCl solution. The product was dried at 120°C overnight before being washed with deionised water.

Zhou, Jinhao, et al 2017 [3] prepared sulphur doped graphene by using the CVD method. Firstly, Cu foil was cleaned in HCl solution and washed with DI water to remove the residual acid solution. Before placing the Cu foil in the tube furnace, dried it with nitrogen gas and then placed ceramics container with 20mg thianthrene outside the hot zone. Cu foil was annealed with H_2 and argon at 1020°C. Then Cu foil temperature was lowered to 800°C. Finally, the product was rinsed with DI water before being dried at 50°C overnight.

Zhou, Jinhao, et al 2018 [4] synthesised sulphur doped graphene by chemical vapour method. Initially, with the help of dilute HCl, the nickel form was cleaned and then dried with nitrogen. It was then placed into a tube furnace on a quartz boat. After that, a ceramics container containing 200mg thianthrene was placed in the tube furnace upstream. The nickel form was annealed for 30 minutes at 800°C with H_2 and Ar. The tube was then heated to 140°C to introduce thianthrene vapours. Finally, the sulphur doped graphene product was washed three times with deionised water before being dried.

Zhou, Jinhao, et al 2018 [5] prepared sulphur doped graphene by using thianthrene as a precursor. The nickel form was washed with DI water and then placed into a tube furnace. It was then annealed with H_2 and argon at 900°C for 30 minutes. After that thianthrene vapour was introduced from the upstream of the tube furnace. The furnace was then switched off and cooled down to room temperature. The produced sulphur doped graphene was rinsed with deionised water and then dried.

4.2 Synthesis of Sulphur doped graphene by thermal annealing method

Yang, Zhi, et al 2012 [6] synthesised sulphur doped graphene by thermal annealing method using graphene oxide and benzyl disulphide. These products were dispersed in ethanol for 30 minutes. The mixture was then placed in a quartz tube and heated in an argon atmosphere from 600 to 1050°C. The prepared sample was removed from the quartz tube after cooling to room temperature.

Shahzad, Faisal, et al 2015 [7] synthesised sulphur doped reduced graphene oxides by thermal annealing at different temperatures. The annealing process was divided into two stages. In the first stage, doping of S on graphene carried under H_2S gas atmosphere for 30 minutes. The second stage takes 30 minutes of annealing in an argon atmosphere. The prepared graphene oxide powder was then placed in a quartz tube. To collect the S-doped graphene sample, it was heated to the reaction temperature and then cooled to room temperature.

Li, Mingjie, et al 2015 [8] prepared S-RGO by thermal annealing method. Initially, under magnetic stirring, graphene oxide aqueous suspension was combined with $MgSO_4$ solution, sonicated for 30 minutes at room temperature, and then dried. After that, the prepared mixture was heated at 700°C for 1 hour. The product was then washed multiple times with HCl solution and dried at 60°C.

Shahzad, Faisal, et al 2016 [9] prepared S-RGO by mixing reduced graphene oxide powder with lenthionine (1: 2.5) and then sonicated for 30 minutes. For 1 hour, the mixed product was heated to 400°C in an argon atmosphere. The sample was again synthesised with a 1:5 RGO to lenthionine ratio at 400°C. Sulphur content in S-RGO (1: 2.5) sample is 1.36 atom percent, which increases to 2.65 atom percent when heated at 400°C for S-RGO (1: 5).

Manna, Bhaskar, and C. Retna Raj et al 2018 [10] synthesised S-RGO using graphene oxide with dibenzyl disulphide as a sulphur doping agent by thermal annealing method. 50mg of GO was disseminated in water and sonicated for 1 hour. Evaporation was used to remove the water from the mixture and obtained product was mixed with dibenzyl disulphide. The resulted mixture was then annealed under an argon atmosphere for 5 hours at 900°C. The product was repeatedly washed in HCl and then dried.

4.3 Synthesis of Sulphur doped graphene by electrochemical method

Parveen, Nazish, et al 2015 [11] synthesised sulphur doped graphene by the method of electrochemical. The graphite rod was used as both anode and cathode material and $Na_2SO_4 + H_2SO_4$ was used as an electrolytic solution. Then the electrolytic solution was dissolved in water. These two graphite rods were separated by $\sim 2cm$ throughout the electrochemical process. The process was carried out by applying positive voltage of 5V to the graphite electrode and under ultra-sonication bath conditions. After 3 hours of filtration and washing with water and ethanol to eliminate impurities, the graphite sheet was doped with sulphur to prepare sulphur doped graphene. The prepared sulphur doped graphene was then dried at 80°C.

Li, Shuhua, Ling Ding, and Louzhen Fan et al 2015 [12] prepared S-doped graphene sheets by using dimethyl sulfoxide as a solvent. The graphite rod was used as both anode and cathode material, placed in the 5ml of electrolyte solution in an electrochemical cell with Pt foil which acts as a counter electrode. After that, a constant current of 10mA was applied for 2 hours. After that, the product was centrifuged and rinsed multiple times with ethanol. To obtain sulphur doped graphene sheets, the product was dried for 24 hours.

Gürsu, Hürmüs, et al 2020 [13] prepared sulphur doped graphene using graphite rod by electrochemical method. Graphite rod electrodes were placed in sulphuric acid solutions in the electrochemical cell. As auxiliary and reference electrodes, Pt wire and Ag/AgCl were utilised. The process was carried out by applying different voltages. In a 5M of the sulphuric acid solution, 1.2 g of S-GO powder was produced from the graphite rod. After that, the resultant was filtered, washed with deionised water and then dried.

4.4 Synthesis of Sulphur doped graphene by hydrothermal method

Chen, Yi et al 2014 [14] synthesised S-GO by hydrothermal treatment of graphene oxide and Na_2S as a precursor. Graphene oxide of 40mg was first ultrasonically dispersed in 70ml of deionized water. Then 40mg of Na_2S was added and agitated for 15 min. Then the mixture was placed in an autoclave at 120°C to 180°C for 6 hours. The resulted S-GO has 4.19at% sulphur and 4.73at% oxygen content.

Tian, Zhengshan et al 2016 [15] prepared sulphur doped graphene by using graphene oxide and Na_2S as a precursor by hydrothermal reaction. Firstly, GO aqueous solution (3mgml^{-1}) was obtained by ultra-sonication in deionized water. Then a given amount of Na_2S was transferred into an 80ml GO aqueous solution under magnetic stirring. Then above mixture was transferred into an autoclave and heated for 10 hours at 200°C. The resulted content of sulphur in SGO was 2.22 at%.

Zhang, Zhian, et al 2016 [16] prepared S-GO by using thioacetamide as a sulphur source. Under magnetic stirring for 12 hours, 0.3g of thioacetamide powder was added into 40 ml of graphene oxide solution. The solution was then placed in a stainless steel autoclave lined with Teflon and allowed to react for 12 hours at 185°C. After that, the solution was washed three times with deionized water then dried for 12 hours at 80 °C.

Raghavan, Nivea, et al 2018 [17] prepared S-GO by using graphene oxide as starting material. To make a homogeneous solution, sulphur was first dissolved in 2ml of CS_2 solvent. This combination was then sonicated for an hour with the GO solution. The solution was then placed in an autoclave and kept for 18 hours at 180°C. After that, the product was rinsed numerous times with deionized water and dried for 12 hours at 80°C.

Li, Fei et al 2018 [18] synthesise S-GQD by hydrothermal treatment using sulphur powder. A 1500 mg graphene quantum dot was dissolved in 300 ml water, then different amounts of sulphur powder were added and mixed to produce a homogeneous solution. The resulting product was then sealed and heated to 180°C for 12 hours in a Teflon-lined autoclave. After cooling the autoclave to normal temperature, the solution was filtered and dried at 80°C.

Siddiqui, Ayesha Saleem, et al 2019 [19] synthesised S-GO by hydrothermal method. GO of 50mg and pluronic F-127 of 50mg were sonicated separately for 30 minutes and then added together. Sodium sulphide of 24.3 mg was then added to this mixture and diluted up to

150ml. Mixture was sonicated for 1 hour and then placed in 200ml of autoclave which was heated for 7 hours up to 180°C. The product was collected after being washed in deionized water and dried for 24 hours at 45°C.

Wang, Yiting, et al 2019 [20] synthesised sulphur doped graphene by hydrothermal method using thioacetamide as a precursor. 20 mg thioacetamide was added to 80 ml graphene oxide solution and agitated for 30 minutes with magnetic stirring. In a 100ml of autoclave, the resulting solution was heated for 12 hours at 180°C. The hydrothermal result was centrifuged, then washed with deionized water and ethanol before being dried.

Liu, Yanxia, et al 2019 [21] sulphur doped graphene was prepared by hydrothermal treatment. Sonication was used to dissolve 15 mg of graphene oxide in 15 ml of deionized (DI) water. To make a homogenous solution, 10 mmol of thioacetamide was gently added to the mixture while stirring for 1 hour. The resulting product was then placed in an autoclave and sealed for 24 hours at 160°C. The product was centrifuged and rinsed numerous times with DI water and anhydrous ethanol. Finally, the product was dried for 12 hours in the air at 60 °C.

Tarimo, Delvina Japhet, et al 2020 [22] synthesised S-RGO by mixing 1g of sulphur, 3g of RGO and 3g of sodium sulphide into 100 ml of deionized (DI) water. The resulted mixture was then sonicated for 2 hours and transferred into stainless steel autoclave lined with Teflon for 12 hours at 180°C. The product was washed repeatedly with deionised water and then dried.

Vulcu, A, et al 2021[23] synthesised S-RGO by dissolving 100mg of graphene oxide in 100 ml ethylene glycol for 1 hour. Then 160 mg of sodium sulphide was added and sonicated for another 45 minutes. The solution was then sealed at 180°C for 12 hours in an autoclave.

Zhang, Qian, et al 2021 [24] prepared sulphur doped graphene by using $Na_2S_2O_8$ and $C_{12}H_{10}S_2$ as a precursor. The graphene oxide solution was ultrasonicated for 30 minutes after these precursors were added. The solution was then transferred into an autoclave under 140°C for 1.5 hours. The solution was then filtered, cleaned with DI water and then dried.

Zhang, Mingmei, et al 2021 [25] synthesised sulphur doped graphene by using sodium thiosulphate ($Na_2S_2O_3$) as a precursor. In 50 ml of GO solution, 350 mg of $Na_2S_2O_3$ was added and ultrasonicated for 30 minutes. After that, the mixture was placed in an autoclave at 220°C for 6 hours. The solution was then filtered, cleaned and dried.

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CHAPTER 5

MOTIVATION

For the synthesis of sulphur doped graphene, hydrothermal method is often preferred because it is simple, economical and requires low temperature. In the hydrothermal method, sulphur doping in graphene can be done by using multiple precursors. Based on the precursor, the properties of the sulphur doped graphene change. An in-depth review of the literature was undertaken to review the precursor and synthesised product property correlation. Three main precursors used for hydrothermal sulphur doping of graphene are: sodium sulphide (Na_2S), sulphur (S), thioacetamide (C_2H_5NS). Sodium sulphide is a chemical compound which is yellow in colour and smells like rotten eggs. Usually, Na_2S is available as flakes [1]. Sulphur is an odourless chemical element and exists as a pale yellow colour powder [2]. Thioacetamide is an organo-sulphur compound which is a white crystalline solid, soluble in water [3]. This compound provides an opportunity for nitrogen and sulphur co-doping using a single precursor. The structure for Na_2S, sulphur and thioacetamide are shown in Fig 5.1. The role/effect of these three precursors are discussed based on morphology, sulphur incorporation, and Raman analyses of the synthesised sulphur doped graphene.

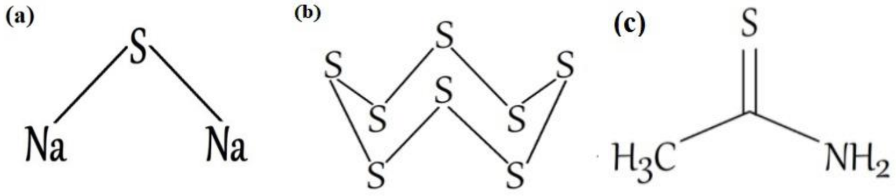

Fig 5.1: Structures of (a) sodium sulphide (b) sulphur (c) thioacetamide

5.1 MORPHOLOGY

Scanning electron microscopy (SEM) and transmission electron microscope (TEM) can be used to study the detailed nanoscale morphologies of GO and sulphur doped graphene. Table 5.1 shows the comparison of the morphology of sulphur doped graphene using different precursors. Some of the main features of the morphological differences which arise due to individual precursors are as follows:

Na_2S: As prepared GO has distinct folds and wrinkling on its surface because of oxygen-containing functional group present on the surface. Sulphur doped graphene synthesised using Na_2S as a precursor has more folds and distortions on the surface of S-RGO as shown in Fig 5.2 [4]. When sulphur atoms are substituted into the hexagonal lattice of graphene, they have a large radius compared to carbon which can induce structure distortion. Surface wrinkling and overlapping of the graphene sheets leads to open-edged sites and defects within the sample which behave like active sites [5].

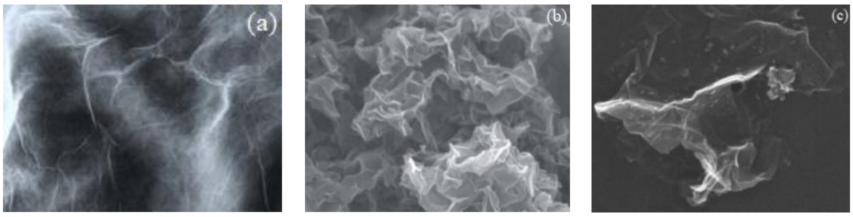

Fig: 5.2 (a), (c) SEM images of sulphur doped graphene (b) FE-SEM image of sulphur doped graphene using Na_2S as a precursor
(a) [4] (b) [5] (c) [6]

Sulphur: The morphology of S-GO shows an uneven distribution of sulphur when sulphur is used as a precursor as shown in Fig 5.3(a) [9]. It has been observed the formation of nanorod and nanosheet like morphology from SEM image of S-RGO because of the contribution of sulphur as precursor and additive as long-chained L-ascorbic acid as shown in Fig 5.3(b) [8]. There is a uniform size distribution in S-GQD when sulphur is used as a dopant for GQD as shown in Fig 5.3(c) [10].

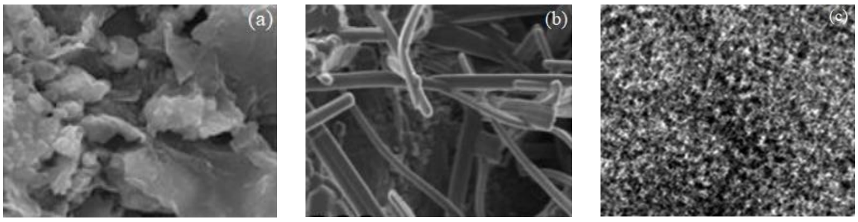

Fig: 5.3 (a), (b) SEM images of sulphur doped graphene (c) TEM image of sulphur doped graphene quantum dot using sulphur powder as a precursor (a) [9] (b) [8] (c) [10]

Thioacetamide: When sulphur doped graphene sample is prepared by using thioacetamide as a precursor, it exhibits a partly folded surface as shown in Fig 5.4 (a). The distinct porous structure has been observed using high resolution when thioacetamide is used as a sulphur precursor because gas released creates pores during the hydrothermal process [11]. Sulphur doped graphene prepared by using thioacetamide as a precursor and VS_4 as additive results well-defined voids on wrinkled graphene oxide sheet as shown in Fig 5.4 (c) [12]. Fig 5.4 (b) shows the FESEM image of sulphur doped graphene by using thioacetamide as a precursor and $FeSe_2$ as additive results in the formation of $FeSe_2$ particles with microspheres in shape which is embedded into the sulphur doped graphene sheet [13].

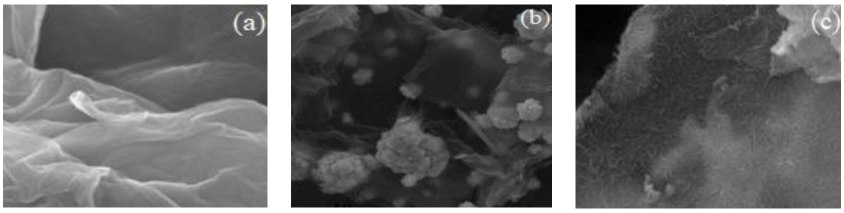

Fig: 5.4 (a) SEM images of sulphur doped graphene (b) (c) FE-SEM image of sulphur doped graphene using thioacetamide as a precursor (a) [11] (b) [13] (c) [12]

Table 5.1: Comparison of morphology of sulphur doped graphene using different precursors

S. No	References	Precursor Used	Ratio (GO : Precursor)	Morphology
1.	**Tian, Zhengshan, et al.[4]**	Na_2S	1: 0.1	Folds and wrinkles on the surface
2.	**Chen, Yi, et al.[5]**	Na_2S	1:1	Wrinkled surface
3.	**Vulcu, A, et al.[6]**	Na_2S	1:1.6	Wrinkled sheet structure
4.	**Siddiqui, Ayesha Saleem, et al.[7]**	Na_2S	1: 0.49	Distinct folds and waviness
5.	**Tarimo, Delvina Japhet, et al.[8]**	S, Na_2S	1:0.33: 1	Formation of Nano-rods and Nano-sheet
6.	**Raghavan, Nivea, et al.[9]**	S	1: 0.5	Uneven distribution of sulphur
7.	**Li, Fei, et al.[10]**	S	1: 0.08 1: 0.4 1: 0.1	Uniform size distribution
8.	**Wang, Yiting, et al.[11]**	C_2H_5NS	1:0.25	Partly folded structure
9.	**Liu, Yanxia, et al.[12]**	C_2H_5NS	1:0.5	Well defined voids with wrinkle surface
10.	**Zhang, Zhian, et al.[13]**	C_2H_5NS	1:1	Microsphere like structure with some wrinkles

Table 5.2: Comparison of amount of sulphur incorporation in graphene using different precursors

S. No	References	Precursor used	Additive	Ratio (GO : Precursor)	C (at%)	S (at%)	O (at%)
1.	**Tian, Zhengshan, et al.[4]**	Na_2S	-	1: 0.1	88.17	2.22	9.61
2.	**Chen, Yi, et al.[5]**	Na_2S	-	1:1	91.8	4.19	4.73
3.	**Vulcu, A, et al.[6]**	Na_2S	-	1:1.6	80.55	1.72	14.47
4.	**Tarimo, Delvina Japhet, et al.[8]**	S, Na_2S	L-ascorbic acid, HCl	1:0.33: 1	76.99	6.73	16.30
5.	**Raghavan, Nivea, et al.[9]**	S	CS_2	1: 0.5	76.64	12.45	10.91
6.	**Li, Fei, et al.[10]**	S	-	1: 0.08 1: 0.4 1: 0.1	36.74 32.29 33.51	12.79 15.06 19.53	48.64 51.28 45.43
7.	**Wang, Yiting, et al.[11]**	C_2H_5NS	-	1:0.25	57.42	2.1	3.4
8.	**Zhang, Zhian, et al.[13]**	C_2H_5NS	$FeSe_2$	1:1	-	2.4	-

5.2 SULPHUR INCORPORATION

The chemical compositions and status of elemental sulphur in S-RGO is investigated using XPS. The XPS survey spectra of sulphur doped graphene show the presence of oxygen, carbon and sulphur. In the XPS spectra, oxygen peak (for graphene oxide) shows an apparent decrease after the sulphur doping. Table 5.2 gives the comparison of hydrothermal synthesised sulphur doped graphene materials and atomic percentage of sulphur incorporated in graphene sheets.

Na_2S: When sulphur doped graphene is prepared by using Na_2S as a precursor then the C/O ratio increases from GO sheet to S-RGO sheet which shows that Na_2S is a high reducing agent in the hydrothermal process. XPS results show that when GO sheets react with Na_2S, sulphur gets incorporated to form C-S bonded groups and removes oxygen containing functional groups [4, 5]. Formation of -C-S-C bond dominated the sulphur atom in the sulphur doped graphene sheet. Therefore most of the sulphur atoms are directly doped into the carbon backbone of the graphene based devices [4, 6].

Sulphur: When sulphur is doped in graphene by hydrothermal method using sulphur powder as a precursor then sulphur may or may not get incorporated [8, 9]. So we have to test synthesised samples for sulphur incorporation: intercalation or doping or sulphur which gets removed on washing. Sulphur is a good doping reagent for graphene quantum dots [10].

Thioacetamide: XPS analysis of sulphur doped graphene shows four peaks for C-C bond, C-S bond, C=C bond, and C=O bond [11]. Sulphur doped graphene prepared by thioacetamide as a precursor shows the existence of a C-S bond at the edge which provides active sites [12]. Two major peaks are observed for the XPS spectrum for sulphur doped graphene at 161.44eV and 167.04eV which corresponds to C-S-C and C=S respectively [13].

5.3 RAMAN ANALYSIS

Raman analyses are performed on the pristine GO and sulphur doped graphene to obtain D peak (1362 cm^{-1}) and G peak (1586 cm^{-1}) for the plot between intensity and Raman shift [4]. The D band is associated with the structural defects whereas the G band is linked to the in-plane bond stretching of carbon atoms. The D/G ratio gives the information about the defect density in graphene. Sulphur doped graphene has a high D/G ratio as compared to GO because of the differences in bond length and angles [4, 5]. Table 5.3 shows the comparison of the I_D/I_G ratio for GO and sulphur doped graphene for sodium sulphide and thioacetamide.

Na_2S: When sulphur doped graphene is prepared by using GO to Na_2S ratio as 1:0.1 results in sulphur doped graphene sheet with 2.22 at% sulphur doping shows D peak and G peak at 1350cm^{-1} and 1595cm^{-1} respectively [4]. After the incorporation of sulphur atom into the graphene sheet results in broadening of the D band and G band which provide evidence for structural defects [7]. The D peak and G peak shifted to 1354cm^{-1} and 1587 cm^{-1} respectively when the sample is prepared by using GO to Na_2S ratio as 1:1.6 [6]. When the same sample is prepared by using GO to Na_2S ratio as 1:1 results in shifting of D peak at 1335cm^{-1} and G peak at 1590cm^{-1} [5].

Thioacetamide: From the Raman analysis, it is observed that I_D/I_G ratio rises from GO to sulphur doped graphene which indicates that sulphur doped graphene is more defective because of the doping of thioacetamide as sulphur source with high temperature. Sulphur doped graphene possessed two broad D peak and G peak around $1342cm^{-1}$ and $1592cm^{-1}$ respectively when sample consists of GO to C_2H_5NS ratio as 1:0.25 [11]. Raman spectra of sulphur doped graphene exhibit D peak and G peak at $1353cm^{-1}$ and $1603cm^{-1}$respectively and I_D/I_G ratio increases from 0.83 for GO to 1.16 for sulphur doped graphene when sample is prepared by using GO to C_2H_5NS ratio as 1:1 and $FeSe_2$ as additive [13].

Table 5.3: Comparison of I_D/I_G ratio for GO and S-GO

S. No	References	Precursor Used	S (at%)	I_D/I_G ratio for GO	I_D/I_G ratio for S-GO
1.	**Tian, Zhengshan, et al.[4]**	Na_2S	2.22	0.86	1.10
2.	**Chen, Yi, et al.[5]**	Na_2S	4.19	1.18	2.66
3.	**Vulcu, A, et al.[6]**	Na_2S	1.72	-	1.43
4.	**Siddiqui, Ayesha Saleem, et al.[7]**	Na_2S	-	0.88	1.01
5.	**Wang, Yiting, et al.[11]**	C_2H_5NS	2.1	1.09	1.21
6.	**Liu, Yanxia, et al.[12]**	C_2H_5NS	3.74	0.79	1.31
7.	**Zhang, Zhian, et al.[13]**	C_2H_5NS	2.4	0.83	1.16

5.4 CONCLUSIONS

- During the hydrothermal reaction process, Na_2S acts as sulphur dopant as well as a high-efficient reducing agent which improves the electrical conductivity of sulphur doped graphene. Sulphur doped graphene prepared using Na_2S as a precursor has high sulphur content.
- Sulphur may or may not be incorporate when doped in graphene during hydrothermal method using sulphur powder as a precursor. Increasing the sulphur content results in the better electrocatalytic activity of the samples.

- The synthesis of sulphur doped graphene using thioacetamide as a precursor results in the existence of a C-S bond at the edge sites. It provides active sites which are beneficial for electrochemical energy storage applications.

5.5 EXPERIMENTS UNDERTAKEN

The work was planned to compare all the three precursors, viz, Na_2S, S and C_2H_5NS under similar conditions and also understand the role of changing precursor concentration on the sulphur doping in the synthesized product. The GO prepared using modified Hummer's method and the precursor in the prescribed amount were dispersed in de-ionized water by ultrasonication. It was followed by the hydrothermal treatment at 180 °C for 12 hrs in a Teflon lined steel autoclave. Table 5.4 gives the details of the synthesized samples. The synthesized samples could not be characterised due to the Covid pandemic.

Table 5.4: Preparation of samples by hydrothermal method in 20ml of DI water and 28.6 mg of graphene oxide.

S. No	Sample	Precursor	Weight (mg)
1.	GN1	Na_2S	58.4
2.	GN2	Na_2S	102.2
3.	GN3	Na_2S	146.2
4.	GN4	Na_2S	219.3
5.	GS1	S-Powder	23.6
6.	GS2	S-Powder	41.4
7.	GS3	S-Powder	59.2
8.	GS4	S-Powder	88.8
9.	GTA1	C_2H_5NS	55.6
10.	GTA2	C_2H_5NS	97.3
11.	GTA3	C_2H_5NS	139
12.	GTA4	C_2H_5NS	208.5

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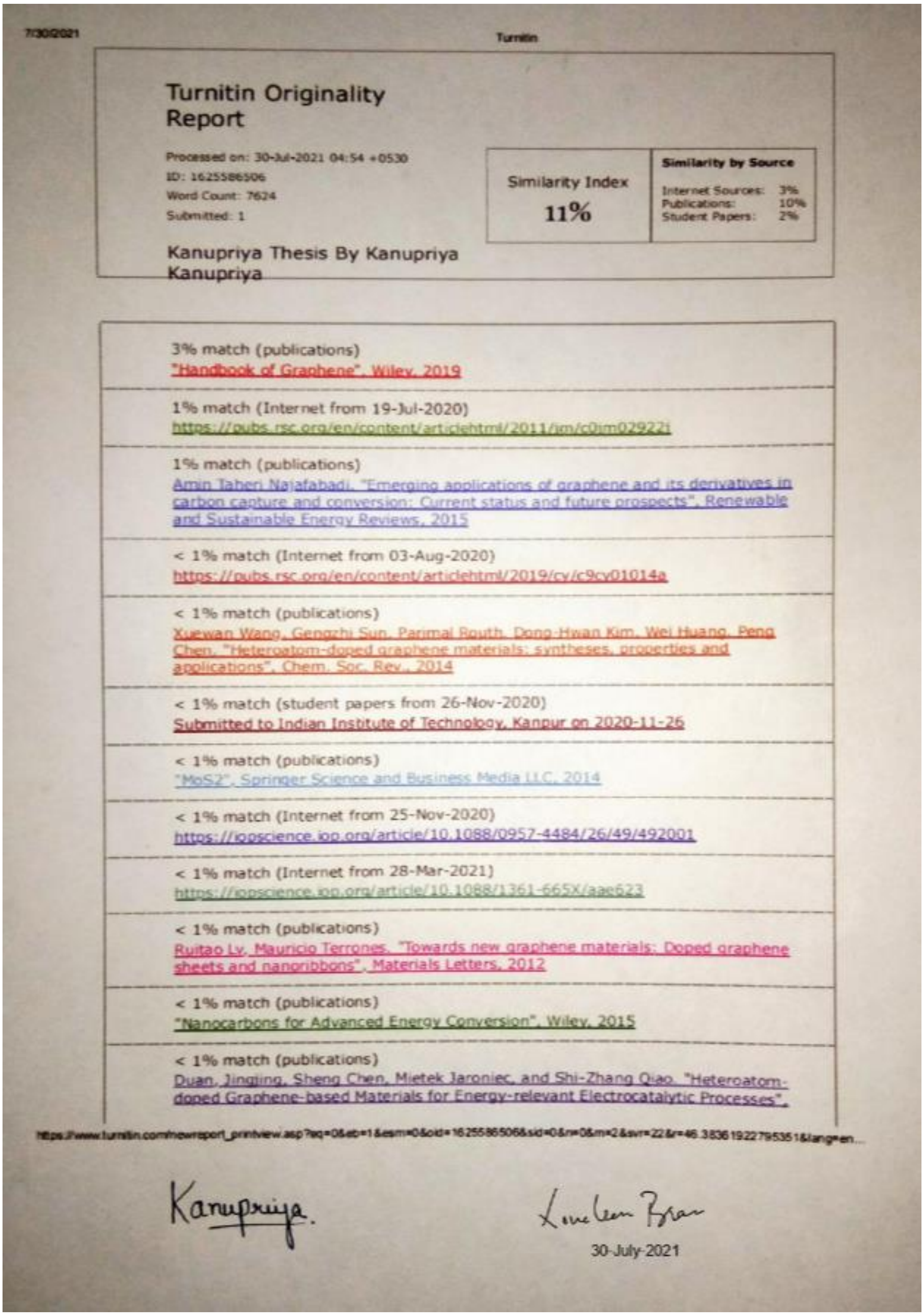
CHAPTER 6

SUMMARY

A single layer of sp^2 bonded carbon atoms makes up graphene, a two-dimensional material. It has attracted considerable interest due to its remarkable properties and diverse applications. The weak van der waals interaction between the graphene sheets results in the reduction of specific surface area due to the stacking of individual sheets. Also, zero band gap of graphene is not suitable for switching applications. Doping is a good approach to change the electric and magnetic properties of materials. Doping of heteroatoms into the graphene sheet causes structural and electronic distortions leading to change in properties such as thermal stability, band gap, fermi level, optical and magnetic properties. Among the different heteroatoms, sulphur is an attractive dopant for graphene because resulting material is expected to have a distorted structure due to large size of sulphur and a wide band gap due to its electron-withdrawing character. The addition of sulphur atoms into the graphene sheets enhances the activation regions on the surface which improves its catalytic ability and opens the band gap giving its numerous applications in batteries, super-capacitors, biosensors and other technologies. Sulphur doped graphene based super-capacitors have a large specific capacitance of 343 Fg^{-1} in comparison to pure graphene. C-S bonds present at the edges enhances the charge storage capacity and electro-catalytic activity of the sulphur doped graphene. Oxidized rich-S doped graphene has relatively low conductivity, while thiophene rich-S doped has better conductivity and charge transfer ability. Sulphur doped graphene can be prepared by using a various methods like chemical vapour deposition, thermal annealing, electrochemical deposition and hydrothermal method. Chemical vapour deposition and thermal annealing, are both carried out at high temperatures and require specific instruments. These are the two most common methods for synthesising heteroatom doped graphene. Because of the low cost and low processing temperature, the hydrothermal method is often preferred in order to synthesise sulphur doped graphene. In hydrothermal method, sulphur doping in graphene can be done by using different precursors such as Na_2S, sulphur powder and thioacetamide. Na_2S not only acts as sulphur dopant but also a highly efficient reducing agent. Sulphur may or may not be incorporated into the synthesis of sulphur doped graphene when it is employed as a precursor in hydrothermal conditions. Both Na_2S and thioacetamide emerged good precursors for the hydrothermal production of sulphur doped graphene from literature study. A systematic study is needed to compare the three precursors.



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