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GRAPHENE and DERIVATIVES - SYNTHESIS TECHNIQUES, PROPERTIES AND THEIR ENERGY APPLICATIONS

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ABSTRACT

2D nanomaterials with exceptional electrical, mechanical and thermal properties are promising reinforcing materials for fabricating high-performance composite materials. Rapid developments in nanotechnology in recent years facilitates the development of advanced materials for functional devices and energy storage applications. The new material graphene has revolutionised the research in the electrical and electronic engineering with its exceptional properties. This review focuses on the recent development in the Synthesis of graphene-based materials and its derivatives. Properties reviewed and compared here include electrical, mechanical and thermal properties. This review is focussed on the application of graphene nanoparticle-based composites (GNP's) and graphene derivatives in the fields of energy storage and conversion.

Keywords: *Graphene oxide (GO), reduced graphene oxide (rGO), nanoparticles (NP) and graphene nanoparticles (GNP).*

1 INTRODUCTION

Graphene is a monolayer of carbon atoms that are arranged in a 2D honeycomb lattice with the C-C bond length of 0.142 nm. Graphene is considered as a wonder material due to its superior properties, such as high electron mobility of 250,000 cm^2/Vs [1], high thermal conductivity of 5000 W/m-K [2] and exceptional Young's modulus of 1TPa [3]. Due to these amazing properties, graphene is given a special attention by researchers and has opened a new path for materials research. Graphene can be used in gas detection, composites, energy storage devices [4-7] and transistors [8]. Figure 1 shows the industrial oriented applications of graphene, where energy-related applications and electronic applications occupies the highest percentages of 27% each, whereas composites represent 11% of application usages [9]. The importance of this field is evident from the increase in the number of graphene publications related to energy applications from energy journal, shown in Figure 2. There is no doubt that graphene possesses the potential to replace conventional materials in many practical applications. This review article provides a brief overview of the synthesis of graphene and its derivatives; their unique properties including electrical, mechanical and thermal; as well as their potential for energy storage and conversion applications. This review is followed by discussion and conclusions which summarise these activities and future potentials.

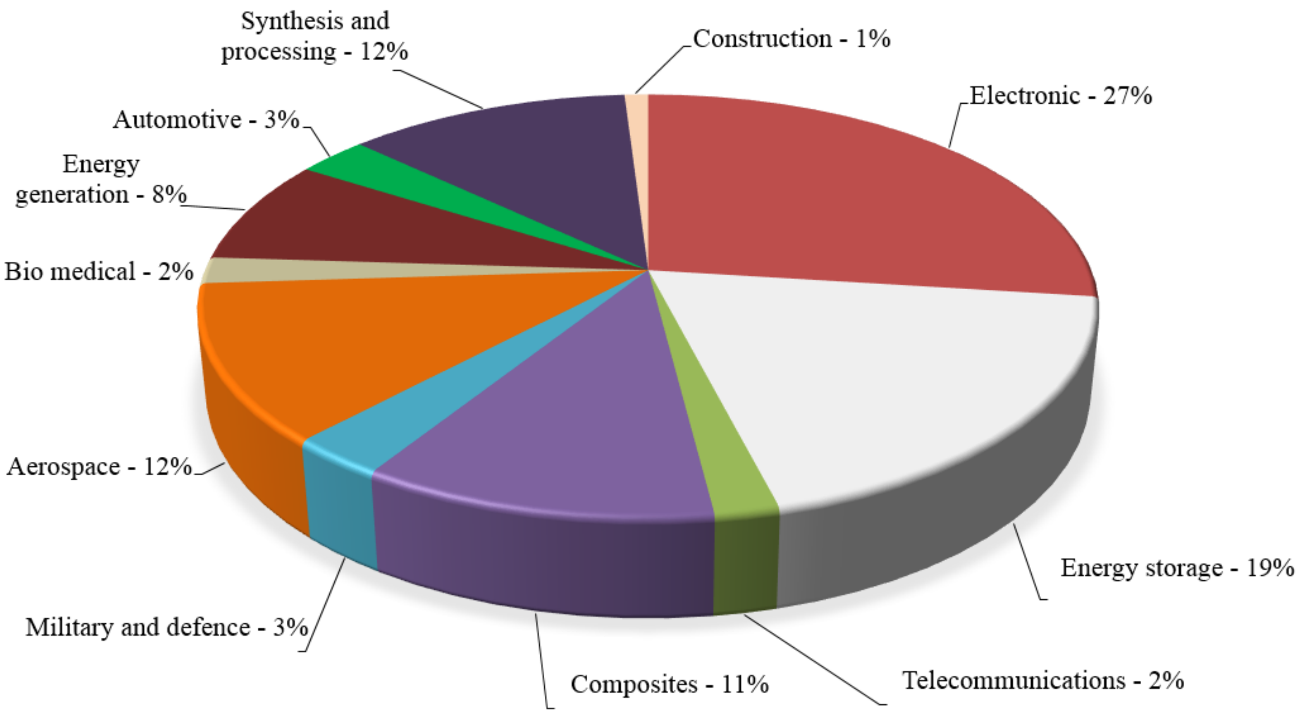

Figure 1: Industrial applications of graphene-based materials [9].

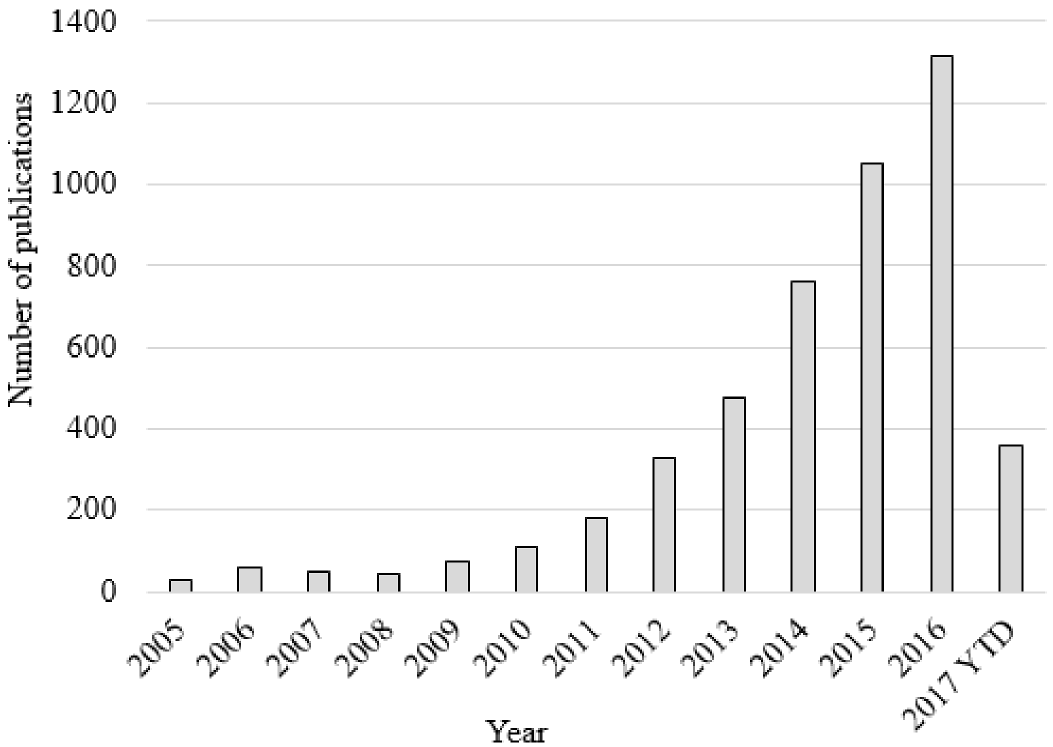

Figure 2: Number of graphene publications related to the field of energy research, Source: Web of Science.

2 SYNTHESIS OF GRAPHENE AND ITS DERIVATIVES

2.1 Graphene

2.1.1 Exfoliation of graphene and graphene nanosheets (GNS)

Mechanical exfoliation was the initial technique used to synthesise graphene, this method was first developed in the lab by noble prize winners Andre Giem and Konstantin Novoselov [10]. This method involves the peeling off of layers of highly oriented pyrolytic graphite sheet. Figure 3 shows a pictorial representation of the exfoliation of graphene sheets using the scotch tape method, where graphite is placed on a substrate and repeatedly peeled using adhesive tape until monolayer sheet is obtained. Even though this process facilitates the production of a large amount of graphite oxide monolayer, Raman spectroscopy data have shown the existence of structural defects [11], these defects can in turn negatively affect the electrical conductivity due to the disruption of the electronic structure. Becerril et al. [12] have reported X-ray photoelectron spectroscopy (XPS) results that demonstrated that it is impossible to restore the structure of graphene after the thermal reduction of graphite oxide layers obtained by exfoliation. It is also possible to obtain a defect-free monolayer graphene by exfoliating graphite in N-methyl-pyrrolidone however, this process is not recommended due to the high cost and high boiling point of the solvent [13].

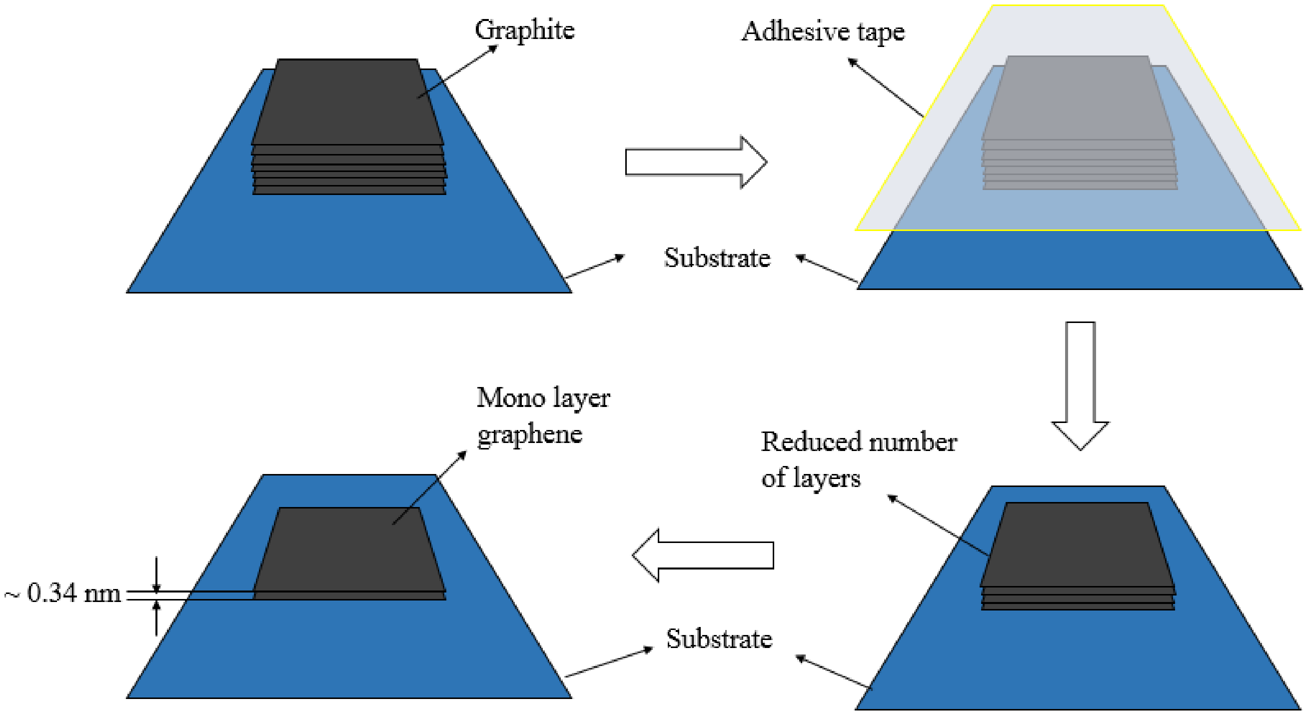

Figure 3: Schematic representation of sequential steps followed to exfoliate graphene layers using the scotch tape method.

Graphite intercalation compounds (GIC's) or expandable graphite (EG) are graphene layers that incorporate small molecules between its layers to reduce agglomeration but the conductivity is reduced due to the disruption of the sp^2 structure. The EG can be synthesised either by oxidation [14] or electrochemically in intercalating acid [15]. The parameters of ultrasonic solvent, ultrasonic time and ultrasonic power effects the volume of the expandable graphite. Due to the thermal expansion of the gases that are trapped in between the graphene sheets, EG can be easily expanded to 100 times in volume at high temperature [16]. Zhuang et al. [17] have reported the use of Fe as reducing agent to obtain GNS from exfoliated graphite. This method proved to be an eco-friendly route to produce GNS as this avoids the use of poisonous gases like hydrazine and hydroquinone. A new method to produce GNS of high quality was reported by Lei at al. [18], this includes a shear assisted supercritical CO_2 exfoliation which is accelerated by high temperature and the high rotation speed of the CO_2 fluid. The application of shear stress to the CO_2 fluid helps to expand the graphite powders to GNS.

2.1.2 Chemical vapour deposition of monolayer and multi-layer GNS

Chemical vapour deposition (CVD) is one of the most promising techniques to produce monolayers of graphene sheets on a large scale. Somani et al. [19] have successfully fabricated few layer graphene (FLG) through CVD, by using camphor as the precursor on Ni. This has opened a new path to researchers to address controlling the number of layers, and to control the thickness on various metal substrates [20-26]. Bae et al. [27] have reported the synthesis of 30-inch wide graphene films through CVD. Their process includes adhesion and etching followed by transfer of layers to the substrate. The schematic representation of the sequential steps followed during the process is shown in Figure 4 [27]. It is also noted that the produced graphene films have shown half-integer quantum Hall effect which indicates the high-quality graphene monolayers. A four-layer film with layer-by-layer doping has shown ~90% transparency. It can be noted that the graphene layers synthesised by this method possess a potential to replace commercially available transparent electrodes. The possibility of substitutional doping by the introduction of other gases eg: NH_3 during growth, is one of the interesting features of the CVD approach [24]. Qu et al. [28] have demonstrated the application of nitrogen doped graphene for the reduction of oxygen in fuel cells and it can be noted from the results that N-graphene electrode displayed catalytic current of ~3 times higher than that of the Pt/C electrode. It can also be noted that N-graphene electrode facilitates long-term stability and Poisson’s effect over the Pt/C electrode during oxygen reduction in alkaline electrolytic solutions. The potential application of N-graphene in lithium-ion batteries has also been reported, as this has a notable reverse discharge potential (~2 times of pristine graphene) due to surface defects induced by nitrogen doping [29].

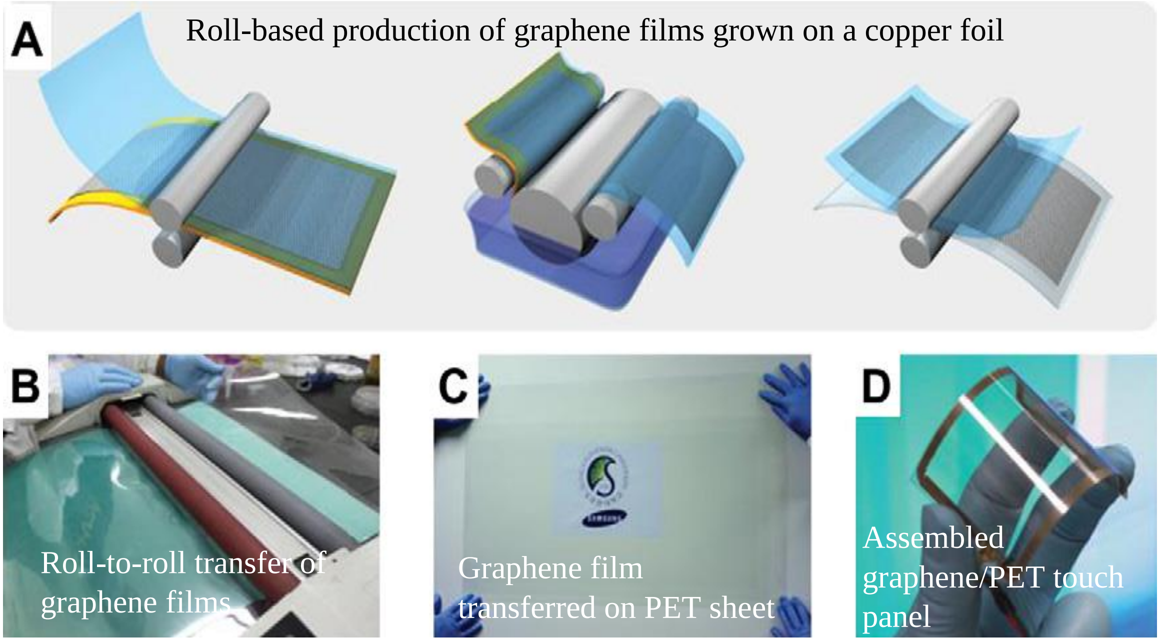

Figure 4: Sequential steps followed during film transfer of graphene films produced via the CVD approach [28].

Graphene can also be synthesised at low temperatures than the thermal CVD process of 1000˚C, by a technique known as plasma enhanced chemical vapour deposition (PECVD). This technique was first developed in 2004 using a gas mixture of 5-100% CH_4 in H_2 at the power of 900 W and the substrate temperature at 680˚C to produce mono and few-layer graphene sheets [30,31]. The major advantage of the PECVD technique is a lower deposition time of ~5 min and a lower growth temperature compared to the conventional CVD process. Researchers have reported a new method of producing graphene using ultra high vacuum (UHV) annealing of SiC which proved to be beneficial in the semiconductor industry due to the advantage of obtaining the products on the surface of SiC [32-34]. The mechanism of UHV annealing of SiC involves heating the SiC substrate under UHV, to sublimate the silicon atoms from the substrate, this leads to the re-arrangement of graphene layers with surface carbon atoms. The annealing time strongly influences the thickness of the obtained graphene layers. Tedesco et al. [35] and Emstev et al. [36] have reported the production of few-layer graphene (FLG) sheets with improved thickness and homogeneity at higher temperatures, ~400˚C above the UHV temperature. Even though the results obtained have in terms of homogeneity are promising, the challenging aspects of using this method for industrial applications is the control of the thickness of graphene layers and the epitaxial growth patterns of different SiC polar face. This method also lacks in addressing the issue of the existence of interface layer in between graphene, substrate and its effect on properties of the end product. A similar technique can be applied to grow graphene layers on metallic substrates. Porga et al. [37] and Sutler et al. [38] have reported the synthesis of epitaxial graphene sheets on ruthenium (Ru) crystals under UHV. A strong bonding of the first layer of graphene sheets with Ru substrate was reported. Whereas the second layer did not interact with the substrate and demonstrated a similar electronic structure as that of the free-standing graphene.

2.1.3 Organic synthesis of graphene nanoribbons (GNR)

Another method of producing the graphene is an organic synthesis that produces graphene-like poly acyclic hydrocarbons (PAHs). This method possesses the advantage of the versatility of synthesis, the capability to modify solubility. The major challenge during this process is preserving the dispersibility and plane geometry of the produced PAHs. A group of researchers have conducted a large quantity of research on PAHs [39] and reported the synthesis of 2D graphene ribbons with 12 nm length through the coupling of 1,4-diido-2,3,5,6-tetraphenylbenzene with 4-bromophenylboronic acid [40]. They have also reported the synthesis of GNR's on gold surface through bottom-up method, see Figure 5 [41].

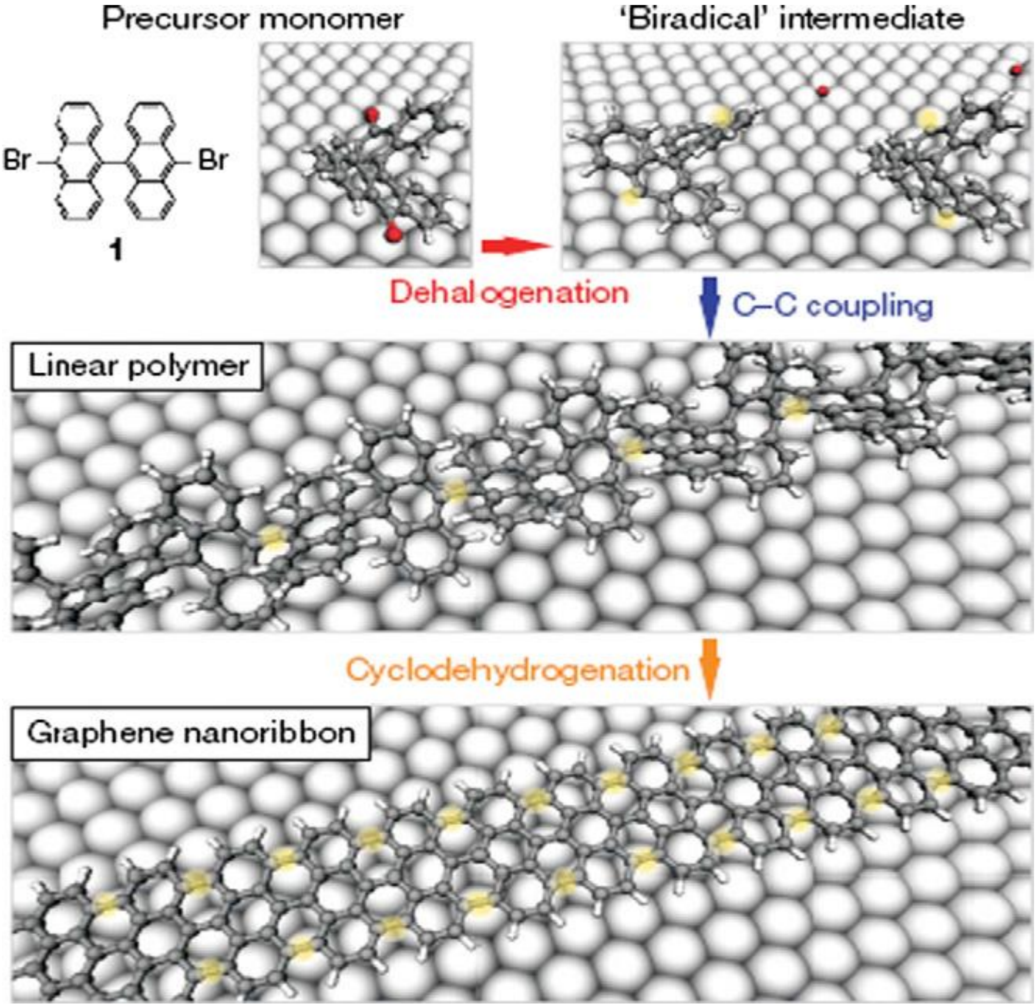

Figure 5: Sequential steps followed during the synthesis of GNR using bottom-up approach [41].

The synthesis includes dehalogenation in which halogens can be removed from the precursors using thermally deposited monomers on a gold surface. This facilitates the formation of surface-stabilized bi radical species that can diffuse across the surface to form the linear polymer chains during the first thermal activation. It can also be noted from the results that the bottom-up approach is one of the versatile techniques to produce GNR with better control over the structure and compositions resulting in superior electrical and mechanical properties.

2.1.4 Synthesis of graphene nanoribbons (GNR) by unzipping CNT's

In order to use graphene in semiconductor devices, the major aim is to incorporate an energy gap in graphene of this zero gap material. This can be achieved in two different approaches, controlled oxidation of FLG and synthesis of GNR. Researchers have predicted that the GNR with a width of 10 nm has band gaps for transistors at room temperature. GNRs possess smooth edges and provides high switching speed and carrier mobility for transistor operations [42-45]. Han et al. [46] have reported the synthesis of GNR of 20 nm width from graphene sheets through e-beam lithography. Even though the method reported to produce GNRs is straight forward, the produced GNR can have edge roughness. Jaio et al. [47] have reported an innovative method of producing GNR through unzipping CNTs by an Ar plasma etching method. This method includes the embedding of multi-walled CNTs (MWCNTs) in polymethyl methacrylate (PMMA) layer on a Si substrate. After baking, the PMMA/MWCNT is dipped in KOH solution and peeled off, this leads to exposing of the MWCNT to the Ar plasma treatment. The unzipped CNT/GNR can be obtained by etching the exposed MWCNT area, it can be noted that the exposed area can be etched faster than that are covered by PMMA. The diameter of CNT, the number of layers of MWCNT and etching time are the important factors that affect the formation of mono, bi- and multi-layer GNRs. By characterization of the GNRs obtained by unzipping the MWCNTs by Atomic force microscopy (AFM), it was noted that the produced GNRs have smooth edges. Raman spectroscopy data provide quantitative information about the D band and G bands, from this I_D/I_G was calculated and the values measured were 0.38, 0.3 and 0.28 for mono, bi- and multi-later respectively, which indicates the high quality of the graphene [47]. Recent work reported by Schimizu et al. [48] have demonstrated the synthesis of GNR through oxidation and unzipping MWCNT in concentrated H_2SO_4 and treating it with $KMnO_4$. The AFM and Raman spectroscopy results reported have shown the presence of surface defects due to the inefficient removal of oxidized groups, which in turn affect the electrical properties. Although the graphene synthesised through unzipping methods have shown superior electrical properties than the mechanically peeled graphene sheets [48-54] there is still a long way to go for the GNRs to be industrially applicable to produce transistors due to the lack of optimised parameters to produce defect free, highly oriented and high-quality graphene sheets.

2.2 Synthesis of graphene oxide (GO) and reduced graphene oxide (rGO)

Due to the high costs related to the synthesis of graphene, the chemical conversion of graphite into GO is a promising economical alternative to the graphene [55-57]. The molecular structure of GO and rGO are shown in Figure 7 [58]. From the molecular structure it can be noted that the GO is heavily oxygenated by hydroxyl and epoxy groups on sp^3 hybridized carbon and carbonyl, carboxyl groups on sp^2 hybridized carbon. This leads to the hydrophilic nature of GO and can be easily exfoliated in aqueous solution. GO is a monolayer material produced from exfoliation and have similar chemical properties as that of the graphite oxide. It can also be noted that the existence of hydroxyl and epoxy functional groups disrupts the electronic structure and GO behaves as an insulating material with irreversible defects and it has been suggested that chemical reduction could partially restore its conductivity [11,59,60]. The most popular method of synthesising GO through oxidizing graphite is the Hummers method [61]. This method involves oxidizing graphite using oxidants like H_2SO_4, HNO_3 and KM_nO_4. The GO films produced are thicker than the pristine graphene sheets of 0.34 nm thick due to the displacement of sp^3 hybridized atoms. The synthesis of GO has been completed by the Brodie [62], Staudenmaier [63] or Hummers methods [61]. The oxidizers used by Brodie and Staudenmaier to oxidize graphite includes a combination of $KClO_3$ with HNO_3. Yanwu et al. [64] have reported the use of graphite salts that were made by intercalating graphite with acids like H_2SO_4, HNO_3 or $KClO_4$ as precursors for the oxidation of GO.

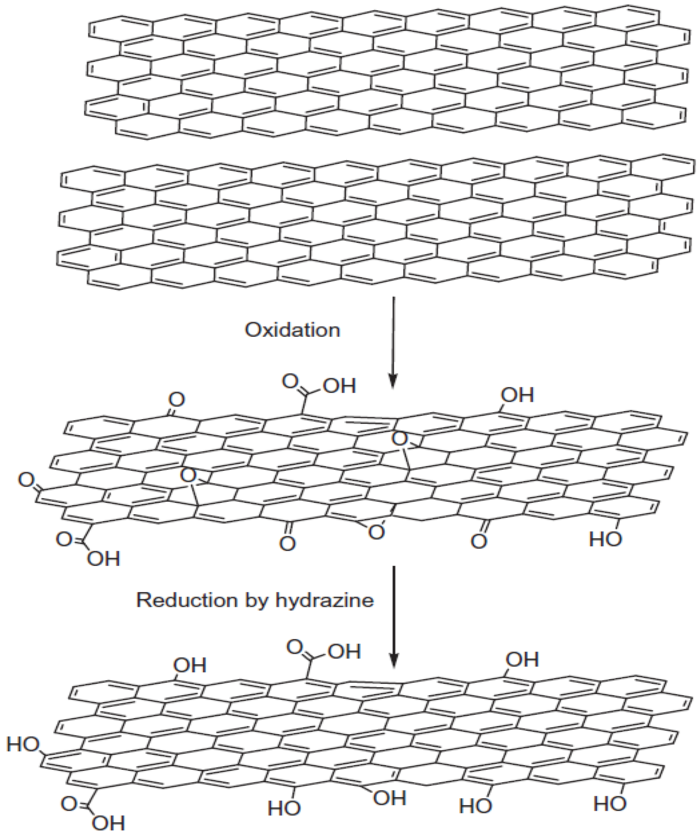

Figure 7: Oxidation of graphite to GO and reduction of GO to rGO [58].

The chemical reduction of GO sheets can be performed in the presence of different reducing agents, including hydrazine [12,57,65-67], sodium borohydride [60,68,69], hydroquinone [70] and ascorbic acid [71]. Out of all the reducing agents hydrazine hydride was referred as the best reducing agent to produce very thin graphene sheets, additionally, it does not react with water. During the reduction process, the oxygen atoms can be removed, which results in less hydrophilic nature of GO sheets

[11,59]. The molecular structures of GO during oxidation and reduction of GO using hydrazine are shown in Figure 7 [58]. It can also be noted that the rGO can tend to agglomerate due to the hydrophobic nature until and unless stabilized by the selected surfactants. NaB_4 is another reducing agent that effectively reduces the GO [60] and it is also reported that NaB_4 is more effective than hydrazine but the problem with NaB_4 is slow hydrolization by water. Athansios et al. [60] have reported the production of rGO using NaB_4 and the comparison of rGO obtained by two different reducing agents hydrazine and NaB_4 was also reported. It can be noted from their results that rGO obtained by using NaB_4 has a low sheet resistance of 59 kΩ/square compared to that of the rGO produced using hydrazine of 780 kΩ/square and high C:O ratio of 13.4:1 compared to that of the rGO produced using hydrazine of 6.2:1. Out of all the chemical reduction processes, reduction by hydrogen proved to be effective with C:O ratio of 10.8-14.9:1.

The thermal reduction is another way of reducing GO that involves the removal of oxide functional groups by heat treatment. Allister et al. [72] have reports the removal of oxide functional groups as CO_2 by heating GO to 1050°C. It was reported from the AFM study that the thermal reduction can reduce ~80% single layer rGO, whereas 30% of mass can be lost due to the removal of oxide functionalities which leaves vacancies and structural defects that may affect the mechanical and electrical properties of the produced rGO [56]. An approach that provides rGO at low temperatures is proposed by Dubin et al. [73]. This involves the production of rGO dispersion in organic solvents like N-methyl-2-pyrrolidinone (NMP) at 200°C.

It is important to control the exfoliation behaviour of GO and rGO which helps in widening their potential applications, which can be achieved using surface functionalization of GO. There are two mechanisms in surface functionalization, covalent functionalization and non-covalent functionalization. In order to change the surface functionality of GO, if the oxygen functional groups on GO surfaces that include carboxylic acid groups at the edge of the epoxy/hydroxyl groups on the basal plane are used then it is called covalent functionalization. The carboxylic acid groups should be activated in order to use them on GO to stabilize other molecules. This activation can be either thionyl chloride [74], 1-ethyl-3-carbodiimide [75], N, N- di cyclohexyl carbodiimide [76]. The weak π-π interactions between the GO and target molecules can be used to functionalize GO in non-covalent functionalization. The conjugated polymers and aromatic compounds can be used to stabilise the rGO resulted from reduction reaction and can be used in the production of composite materials. The conjugated and aromatic polymers used are sulfonated polyaniline [77], conjugated polyelectrolyte [78], porphyrin [79] and cellulose derivatives [80]. The summary of advantages and disadvantages of various synthesis techniques is given in Table 1.

Table 1: Summary of advantages and disadvantages of graphene synthesis techniques.

Manufacturing method	Advantages	Disadvantages	Nature of produced graphene	Cost effectiveness	Number of layers produced
Exfoliation	This is a relatively simple technique of peeling graphene sheets using adhesive tape.	Graphene sheets produced by this process will be of several sizes, irregular shapes and orientations. This will reduce the applicability of graphene in potential applications.	Pristine	Low- budget technique but this has less relevance to the commercial high-end applications.	Single & multiple
Chemical vapour deposition (CVD)	This technique provides the advantage of selection of host substrate independent of the growth surface. This process facilitates the large scale production of graphene by limiting the size of substrate to the size of reactor. Mono layer and bi-layer graphene sheets	The transfer process often effects the integrity and performance of the produced graphene. Moreover, the transfer process enhances the formation of wrinkles, impurities and structural defects.	Pristine	Less-costly process as the cost per unit area of graphene produced will be limited to the size of the substrate. The selection of substrate often effects the cost of the process.	Single & multiple

	can be obtained using this process.				
Organic synthesis	This approach has an advantage of versatility and PAH's produces by this method can be substituted with aliphatic chains to modify the solubility.	Size of the sheets produced from this process is limited due to the reduction of solubility and increase in unwanted side reactions. These reactions lead to difficulties in dispersion preservation.	Chemically modified	The cost incurred in characterising the products of chemical reactions is high.	Single & multiple
Chemical derivation of graphene (production of GO and rGO)	This is the most viable technique to obtain graphene from graphite. Nearly 80% of single layer rGO sheets can be obtained through this process. The electrical conductivity can be partly restored during reduction process but will still be less than pristine graphene	The formation functional groups during the oxidation process leads to the irreversible effects to the band structure and reduces the electrical conductivity.	Chemically modified	This is the most affordable technique to produce graphene.	Single & multiple

3 SYNTHESIS OF GRAPHENE-NANO PARTICLE (GNP) COMPOSITES

Graphene nanoparticles (NP) have been explored for many potential applications. After the discovery of graphene, interest grew to their incorporate in various metals, metal oxide and semiconductors, aiming at obtaining a composite with better properties. However, there are some issues related to the production of graphene NP composites that need to be addressed. This includes separation of graphene sheets, non-uniform dispersion of NP on to the graphene sheets, the interaction of NP and graphene and the effect of size and defects of graphene sheets. There are three main stages in the synthesis of GNP composites, pre-graphenization, post-graphenization and syn-graphenization. Pre-graphenization involves the mixing of rGO with pre-synthesized rGO to produce the composite material. However, this process is limited to the organic solvents due to the hydrophobic nature of rGO. Post-graphenization involves the preparation of composite at primary level and the reduction of GO can take place after the production of the composite. This technique is most applicable to deposit metal and metal oxide NPs and semiconducting NPs onto the GO followed by reduction to form the composite. Syn-graphenization involves the use of stabilizer (second component of composite) to improve composite properties. Several rGO/GNP composites were reported in the literature based on the above three methods, some of shown in Table 2.

Table 2: Overview of methods presented in the literature for the synthesis of GNP based composites.

Base material	Method of Graphenization	Synthesis and reduction agents used during synthesis	Reference
Au	Post	Au NPs formation by reduction of Au ions in a gold salt solution on the RGO films	[81]
Pt	Pre	N doped RGO + DMF + NaOH + ethylene glycol + H_2PtCl_6+6H_2O	[82]
Pd	Pre	H_{22} electrochemical plasma rGO + Na_2PdCl_4+ $LiClO_4$	[83]
SnO_2	Pre	RGO + SnO	[84]
TiO_2	Post	TiO_2+ GO + antanase hydrothermal treatment	[85]
Ag	Syn	Heating 75 CGO on 3-aminopropyltriethoxysilane + AgNPs	[86]
Fe_3O_4	Pre	Reaction of ferric triacetyl acetonate with GO in 1-methyl-2pyrrolidone	[87]
TiO_2	Syn	GO + $TiCl_3$+H_2O in SDS solution	[88]

Mn_3O_4	Post	Mn_3O_4 on GO, 2 step method (Ni(OH)+ GO, TiO_2+ GO) + $KMnO_4$	[89]
Fe_3O_4	Post	GO + Fe_3O functionalizing with TEOS and magnetic separation	[90]
Fe_3O_4	Post	GO + $Fe(DXR)_3O_4$ + doxorubicin hydrochloride	[91]

In-situ growing of GNP is one of the techniques that were derived from growing CNT's. This technique facilitates the direct contact between graphene sheets and NP and homogeneous distribution of NP's due to nucleation of NPs in situ. Wang et al. [92] have suggested the use of carboxylic, hydroxyl and epoxy groups as the nucleation sites on GO to facilitate the control of morphology and crystallinity of NPs. They have also demonstrated the growth mechanisms of $Ni(OH)_2$ on GO and rGO sheets. Solvothermal synthesis is another technique to produce rGO/NP composites without any addition of reducing agents. This can be simply referred as a syn-graphenization technique which involves the reduction process result of high temperature and pressure during the solvothermal reaction. This technique is beneficial in preventing the aggregation of graphene layers [93]. The electrical properties such as conductivity is slightly higher than the rGO obtained through reduction using hydrazine [94]. Even though this method facilitates the better properties this possesses the disadvantages of poor dispersion of GO in organic solvents and lack of control of functional groups on GO and rGO surfaces. Watcharotone et al. [95] have reported the use of sol-gel methods to synthesize graphene/silica composite thin films, this involves the hydrolysis of tetra methyl ortho silicate in GO suspension in water followed by the reduction using hydrazine. UV assisted reduction was another technique used to synthesis rGO/NP composites. This involves photocatalytic reduction of GO under UV in the presence of TiO_2 [96]. This method is relatively fast and avoids chemical reduction but has a limitation of applicability to only external light irradiation sensitive NP systems.

4 PROPERTIES OF GRAPHENE

In the past decade, the research on graphene has been increased tremendously due to its fascinating properties such as absorption of visible light of 2.3% [97], the highest theoretical surface area of 2600 m^2/g and minimum hall conductivity of $4e^2/h$ [10]. This section of the paper includes exploring the electrical, mechanical and thermal properties which provide the wide range of potential applications of graphene.

4.1 Electrical properties

Pristine graphene is a zero-gap semiconductor. The extraordinary nature of charge carriers is one of the most notable aspects about graphene. The charge carriers in graphene behave as Dirac fermions (massless relativistic particles) and these behave abnormally compared to electrons when subjected to magnetic field [98], this was even observed at room temperatures. The low defect density of graphene's crystal lattice leads to high quality of single layer graphene sheets which is the main reason behind the high electrical conductivity of monolayer graphene sheets. The electrons in graphene behave as particles of light that do not scatter, which makes graphene a good conductor of electricity. Interfacial phonons [99], substrate ripples [100] and surface charge traps [101] are the factors that affect the conductivity of graphene sheets. Bolotin et al. [102] have demonstrated the minimum scattering using monolayer graphene layer in a suspended condition and demonstrated the effect of impurities on the surface of graphene sheets. A bipolar electrical field effect is another important characteristic of monolayer graphene sheets, this means by applying a gate voltage the charge carriers can be tuned between electrons and holes [103]. The major hurdle for graphene in potential applications is its zero energy gap, for eg: Field effect transistor, which needs on/off switch. Recent research in the area of graphene have reported the modification of graphene band structure by constraining graphene in nanoribbons [42,46,110] and graphene in quantum dots [105] and by biasing bi-layer graphene [112,113]. Evaldsson et al. [108] have reported the variation of the width of ribbons and disorders in the edges of both zigzag and armchair nanoribbons, this observation was supported by both experimental results and theoretical explanation.

Due to the advantage of scalability to electronics, epitaxial graphene has gained a lot of interest in recent years. There was a mixed opinion among researchers about the bandgap opening in epitaxial graphene, zero band gap on graphene layers was reported by Pen et al. [109] whereas 0.26 eV was reported by Kim et al. [110]. An innovative method of growing epitaxial graphene on SiC substrate was developed by De heer et al. [111], it was reported that the mobility of graphene grown on Si-terminated face is less than that of the graphene grown on carbon-terminated face, this is due to the difference in structures and this can also be gated. They have also reported the reduction in energy gap with an increase in thickness and it can be zero if the number of layers exceeds four. This matches well with observations reported by Peng et al. [109], in which energy gap was 0.26 eV for mono layer graphene 0.14 eV for the triple layer. Reina et al. [112] have used CVD to synthesise graphene layers on Ni substrate and reported a huge variation in filed effect mobility of 100-2000 cm^2/Vs due to ineffective modulated resulted from the non-homogenous thickness of graphene films. Kim et al. [113] have synthesised graphene layers through CVD technique on Ni and transferred it to SiO$_2$ substrate and the charge mobility was measured as 3700 cm^2/Vs which confirm the existence of mono layer graphene. Even though Ni is the most used metallic substrate to grow graphene [20,22,118,119] of high quality, this suffers a drawback of solubility carbon-nickel and deposition of multi layers at grain boundaries. Copper was used as an alternative to Ni to overcome the difficulty of high solubility. It was reported that the graphene layer is grown on copper foil through CVD shown a mobility of 4050 cm^2/Vs [23] and a mobility of ~3000 cm^2/Vs [20] by depositing graphene film on a large wafer of the copper substrate. The existence of difficulties in the synthesis of mono layer graphene sheets leads to the research related to the production of bi-layer and FLG. Novoselov et al. [114] reported that bi-layer graphene is almost gapless and remains metallic at neutrality points and charge particles are similar to that of the massless Dirac fermions but possess a finite mass and are called as massive Dirac fermions. Castro et al. [115] have reported a possibility of using bi-layer graphene as a tunable energy band gap semiconductor for energy applications by tuning the band gap by applying a magnetic field and it can be tuned up to 0.2 eV.

Numerous efforts have been made so far to reduce GO effectively in order remove oxygenated functional groups which incorporate the high electrical resistance 4 MΩ/square. It can also be noted that the thermal and chemical reduction can partially restore the electrical conductivity but introduces the structural defects that degrade the electrical properties compared to graphene. Gomez et al. [116] have measured the mobility and conductivity of rGO as 2-200 cm^2/Vs and 0.05-2 S/cm respectively. Li et al. [117] have reported the production of graphene nano sheets (GNS) and 72 S/m of electrical conductivity at room temperature was noted from the observations, however the conductivity of the GNS obtained was not promising. The recent results published by researchers from Graphenea Spain, have reported that the electrical conductivity of rGO reached to a value of 666.7 S/m for a film of 20nm thickness [118]. Table 3 gives the overview of electrical properties of graphene and its derivatives from the most recent studies.

Table 3: Electrical properties of graphene and its derivatives.

Material	Electrical conductivity (S/m)	Electron charge mobility (cm^2/Vs)	Energy gap (eV)
Graphene(mono layer)	10^8	15,000 – 200,000	0.26
Reduced graphene oxide (rGO)	666.7	17 – 2000	Tunable gap of 0.35 – 0.78
Graphene nano sheets (GNS – bi- layer/ tri-layer/multi layers)	72	290 – 5	0.14

4.2 Mechanical properties

In any practical applications, an external application of stress and unwanted strain affect the performance and durability. The inter atomic distances of a crystalline material can be effected by the external stresses on the crystalline material this leads to the redistribution of local charge. This in turn, affects the electronic transport due to the development of band gap in the electronic structure. It was anticipated by researchers that graphene outperforms CNT's with high strength and stiffness. Lee et al. [7] have used AFM to measure the elastic properties of mono layer graphene and reported Young's modulus of 1±0.1 Tpa and intrinsic strength of 130±10 Gpa. Tsoukleri et al. [119] have used Raman spectroscopy to measure the strain by applying compression and tension loads to the graphene mono layer and reported a strain of 1.3% and 0.7% in tension and compression respectively. Lee et al. [120] have reported the use of AFM to measure Young's modulus and strength of graphene and reported Young's modulus of 1.02 Tpa, 1.04 Tpa and 0.98 Tpa and fracture strength of 130 Gpa, 126 Gpa and 101 Gpa respectively for mono layer, bi-layer and tri-layer graphene. It can be noted that the increase number of layers increases the sliding tendency hence reduces the properties. Raman spectroscopy can be used to measure the compressive and tensile strains in graphene sheets by measuring the change in G and 2D peaks with applied stress. Ni et al. [121] have mentioned that it is possible to tune the band gap by introducing a controlled strain, as the strain may change electric band structure. Cristina et al. [122] have reported that the successful production of chemically modified graphene by reducing graphene oxide with hydrogen plasma, Young's modulus of 0.25 Tpa was noted from the results. Peng et al. [123] have reported the fracture toughness of pristine graphene as 4 Mpa$\sqrt{m}$, it can be noted from the values that the graphene tends to form agglomerates and imperfections in graphene leads to the brittle nature. There is still more research need to be done in unfolding the mechanical and structural capabilities of graphene. Table 4 gives the overview of mechanical properties of graphene and its derivatives, it can be noted from the table that Increase number of graphene nano sheet layers leads to the detoriation in properties.

Table 4: Mechanical properties of graphene and its derivatives.

Material	Young's modulus (Mpa)	Tensile strength (Mpa)	Fracture toughness (Mpa$\sqrt{m}$)
Graphene (mono layer)	10^6	1.3×10^5	4 – 5
Reduced graphene oxide (rGO)	2.5×10^5	0.9×10^3	2.8 – 3
Graphene nano sheets (GNS – bi- layer/ tri-layer/multi layers)	$1.04\times10^6 – 0.98\times10^6$	$1.26\times10^5 – 1.01\times10^5$	4.7 – 3.8

4.3 Thermal properties

Graphene finds most of its applications in the field of electronics as it is the best conductor of electricity known so far, thermal management is one of the major issues that needs to be addressed while working with the electrical devices. During the operation of the devices considerable amount of heat can be generated and dissipated. It is well known that the allotropes of carbon, i.e. graphite, diamond and CNT's possess high thermal conductivity due to the strong C-C covalent bonding. Until the arrival of graphene, single walled CNT's (SWCNT) and multi-walled CNT's (MWCNT) were known for having the highest conductivities of 3500 W/mK and 3000 W/mK [130,131]. Blandin et al. [2] have reported that the thermal conductivity of monolayer graphene sheets as 5000 W/mK using confocal micro-Raman spectroscopy. Ghosh et al. [126] have reported the use of confocal Raman spectroscopy to measure the conductivity of suspended graphene flakes for thermal management applications and thermal conductivity of 4100-4800 W/mK at room temperature was noted. Seol et al. [127] have used thermal measurement method to measure the conductivities of single layer graphene sheets suspended and on SiO_2 support and reported conductivity of 3000-5000 W/mK and 600 W/mK for suspended and on SiO2 respectively. There was a speculation among the researchers that the thermal conductivity of graphene was overly estimates and lee et al. [128] have reported the conductivity as 1200-2700 W/mK and bi layer graphene as 600-500 W/mK [129]. It can be noted that the electrical conductivity of graphene is affected by defect edge scattering and isotropic doping. The thermal properties of graphene and its derivatives are summarised in Table 5.

Table 5: Thermal properties of graphene and its derivatives.

Material	Thermal conductivity (W/mK)
Graphene	1200 – 2700
Reduced graphene oxide (rGO)	30 – 250
Graphene nano sheets (GNS – bi- layer/ tri-layer/multi layers)	600 – 500

5 APPLICATION OF GRAPHENE AND GNP BASED COMPOSITES

The potential applications of graphene includes single molecule gas sensing, biomedical devices, transparent conducting electrodes, optoelectronic devices etc [58,136,137]. The main focus in this paper is given to energy storage and conservation. The exceptional properties of graphene i.e. high electrical conductivity and high surface area makes graphene a promising material for energy conversion and storage applications.

5.1 Energy storage

Lithium-ion batteries (LIB) are one of the best energy storage devices due to the advantages of longer cycle life, higher specific energy and its rechargeable characteristics. As mentioned earlier high chemical stability, high electrical conductivity and high surface to volume ratio makes it an ideal candidate for energy storage applications. The electrode materials that are being used in LIB at present include SnO_2, CO_3O_4, Fe_3O_4, TiO_2 and MnO_2. Even though these materials have high theoretical capacities they would not perform as well in practical applications due to their lower electrical conductivity. Another major issue with LIBs at present are the chemical stability of the active material and decrease in cyclic performance. Recent research has suggested the incorporation of conductive materials such as CNT's and carbon particles to increase specific capacity [138-141]. Yoo et al. [136] have reported the use of GNS in rechargeable LIB and it was also reported the increase in specific capacity of the electrode through the interaction of GNS with C60 and CNT. Pan et al. [137] have demonstrated the application of disordered graphene sheets in LIB. It can be noted from their results that defected graphene sheets provide additional reversible storage sites for Li-ions. The problem with LIB using conventional materials can be avoided by the addition of graphene-based material to metal oxide which can improve the specific capacity and electrochemical stability for longer periods. This improvement can further increase the conductivity, specific area, stability and flexibility which are the principle requirements for an efficient energy storage. Graphene-encapsulated – CO_3O_4 was used as an anode material to improve the performance of LIB. It was reported that the energy density of 1100 mAh/g and current density of 74 mA/g [138]. Wu et al. [139] have reported that the synthesis of graphene-anchored CO_3O_4 as the anode material in LIBs to improve the capacity and cyclic performance and the values were noted as 935 mAh/g of energy density and 50 mA/g of current density at 30 cycles. Wang et al. [89] have reported graphene-Mn_3O_4 as an anode material for LIB with current density of 400 mA/g and energy density of 780 mAh/g and approximately 50 cycles. The same research group have reported SnO_2-graphene material in energy storage application with energy density of 625 mAh/g compared to pure SnO_2 of 782 mAh/g [140] and current density of 10 mA/g. Zhou et al. [141] have reported graphene –wrapped Fe_3O_4 as anode material in LIB with improved capacity and chemical stability. It can also be noted that this material displays energy density of 1026 mAh/g and current density of 35 mA/g. Furthermore there are still some unanswered questions that need a more basic understanding of the chemical and thermal stability of the anodic material at various environments. Xiaojun et al. [142] have reported the use of $COsnO_3$/GN/CNT composite papers as the anodic material in LIB to enhance their performance. It was also reported the produced composite exhibits excellent cycle performance through filtration, transformation and heat treatment. Seung et al. [143] developed a new porous MnO_3 nanorod/rGO hybrid paper as anode material for LIB. It was noted from the results that PMn_3O_4NR/rGO paper exhibits high discharge capacity of 943 mAh/g than pristine graphene with 183 mAh/g, it quickly attains stability.

Supercapacitors are another energy storage device that has caught the attention of many researchers due to their high power density, fast charge/discharge ability without degradation. Supercapacitors are used to store passive and static electrical energy and are mostly used in electronic gadgets and hybrid electric automobiles. Out of all the material used for capacitors, carbon-based materials are most commonly used due to high electrical conductivity, chemical and mechanical stability. The material with high specific capacitance plays a key role in efficient energy storage as the storing energy involves adsorption of ions onto electrodes that have high accessible surface area. As the graphene possess a high specific area of 2675 m^2/g it can be reported as a potential candidate for supercapacitor applications. Xia et al. [144] have reported an intrinsic capacitance of 21 $\mu F/cm^2$ of graphene, which has set a new upper limit for capacitance. Researchers have produced graphene –hydrous RuO_2 in aqueous KOH electrolytic solution for the application in supercapacitors. It is noted that the material has displayed capacitance 135 F/g in KOH electrolyte and 99 F/g in organic solvents. Whereas, with the same electrolyte KOH, the microwave-assisted reduction of GO has resulted in increased capacitance of 191 F/g and reduced surface area of 463 m^2/g [145]. On the other hand, the hydrazine reduced GO have displayed a surface area of 320 m^2/g and specific capacitance of 205 F/g [130]. Aggregation and vanderwalls attraction between the graphene layers are the major problems related to the use of rGO to use it in supercapacitor applications. Wu et al. [146] have reported the use of graphene-hydrous RuO_2 in 1M H_2SO_4 electrolytic solution in super capacitors, it can be noted that the produced composite displayed high capacitance of 570 F/g, the high energy density of 20.1 W h/kg and power density of 10 KW/kg. The same group produced MnO_2 nano wire-graphene composite to improve the capacitance, it was reported that capacitance of the produced composite as 31 F/g and power density as 30.4 W h/kg [147]. Kai et al. [148] developed a nitrogen doped graphene for supercapacitor applications. The results have shown the NG exhibits an outstanding specific capacitance of 197 F/g at a current density of 0.5 A/g in KOH solution. In addition, it can be noted that the NGs displays the long term electrochemical stability. Manoj et al. [149] have developed an innovative electric double layer capacitor (EDLC) using plastic crystal based gel polymer electrode (GPE) and GNP as electrodes. It can be noted from the results that the EDLC showed a low specific energy of 8.2 Wh/kg and high power density of 4 kW/kg.

Yanping et al. [150] have demonstrated comparative study on thermal performance of PA-SA by adding GNP and EG. It was noted that at higher loads the thermal conductivity of the phase change material (PCM) was 2.7 times higher than GNP and 15.8 times higher than that of EG. The EG material can be seen then to possess the potential to evolve as an efficient thermal energy storage material.

Mehrali et al. [151] have synthesised highly conductive palmitic acid/GO composites, this material finds applications in thermal energy storage. It was reported that PA/GO composites have shown an excellent thermal reliability and chemical stability and three times increase in thermal conductivity was recorded.

5.2 Energy conversion

Fuel cells are one of the promising energy conversion devices that have the advantages of high conversion efficiency, low operating temperature and ease of handling. Previously CNTs have been extensively investigated for fuel cell applications due to their enhanced catalytic activities [158,159]. However, this has changed after the invention of highly conductive 2D graphene sheets [160-163]. Fuel cells mainly consist of 3 parts: anode, cathode and a separation membrane. The most commonly used cathodic materials are Pt, Au, Ru and their alloys which are highly expensive [164,165]. Out of all these materials, Pt is most widely used the cathodic material for fuel cells which is expensive and at the same time less abundant as well. The Pt-based catalyst still suffer from poor tolerance due to the CO poisoning. It is really challenging to develop a metal free oxygen reduction reaction (ORR) catalysts with high current density and durable material to replace or to reduce Pt. one of such effort is a synthesis of Pt/graphene hybrids. Yoo et al. [160] have developed PtNP/GNS composites with a current density of 0.12 mA/cm^2 which is four times higher than that of the commercially available Pt/C with 0.03 mA/cm^2. The CO absorption rate is 40 times smaller than that of the Pt/C, which shows that PtNP/GNS as the promising material for fuel cell applications. Choi et al. [161] have reported the potentiality of Pt deposited onto the surface of GNS using a surfactant as a cathode material for the fuel cell. It can be noted that the current density was increased to three times that of the Pt/c. Rong et al. [162] have reported the application of functionalized graphene sheets prepared by thermal expansion of GO and Pt/NP composite in a fuel cell. It was noted in their results that the ORR activity of Pt/FLG reached 49.8% whereas Pt/C was at 33.6%. Lee et al. [163] have developed Pt-BCN-Gr/CB hybrid catalyst of the polymer electrolyte fuel cell and demonstrated the effect of boron/nitrogen CO-doping into the graphene and intercalation of the produced hybrid catalyst. It can be noted from the results that B and N doping enhanced the cell performance about 28%. Yang et al. [164] have demonstrated the Pt-B doped graphene intercalated by carbon black as a cathodic catalyst in the proton exchange membrane fuel cell. Pt-B-Gr/CB was shown to have better durability compared to conventional catalysts and ECSA increased with CB content. ECSA increased to 33.6 m^2/g with 30 wt% of CB. Jing et al. [165] developed thermally rGO grown with CNT to use as a support for fuel cells. The results have shown that rGO/CNT have exhibited a high electrical conductivity of 144.4 S/cm and Pt/Gr-CNT have displayed a very high ECSA of 77.4 m^2/g.

5.3 Graphene-based conductors

Graphene is one of the best conductor known to us so far, which conducts electricity better than copper as the electrons and holes both act as charge carriers. Ivan et al. [131] have developed new graphene-based transparent conductors by intercalating FLG with $FeCl_3$. It can be noted from the observations that these conductors display a sheet resistance of 8.8 Ω/sq which is far less than the critical value of 30 Ω/sq for multi-layer [166] and 125 Ω/sq for chemically derived graphene [167]. Sajid et al. [168] have reported the application of graphene-based conductors (GBC) as transmission lines (TL) and the coupling characteristics were investigated. The wave propagation of GBC transmission lines is similar to microstrip transmission lines and is less than 300 dB to 7 GHz. In addition, the GBC TL possess the capability to be evolved as a material for planar antenna arrays. In a review article written by Wang et al. [169], they demonstrate the possibility of graphene-based conductors in the area of light emitting diodes. It was also expected by these researchers that it is possible to obtain low sheet resistance by growing graphene directly through the CVD approach with tunnel junction design. Lee et al. [170] have reported the promising routes of producing graphene-based conductive films which open a new path for future electronic applications. It is noted that a sheet resistance of 50 Ω/sq was observed with four layers of graphene.

6 FUTURE PERSPECTIVE

It is evident from the significant amount of increase in publications in last 5 years that graphene possess a capability to surpass the use of silicon in the field of electronics and the conventional materials used in energy storage and conversion devices. The extraordinary properties such as high electrical and thermal conductivities, strength makes graphene an ideal material for potential industrial applications. However these properties were observed in pristine graphene and chemically, thermally modified graphene displays the reduced properties than pristine but still better than most of the conventional materials. Graphene has opened a new path towards the micro and nano electronics with the tunable band gap using GNR and GNS that allows for the large scale production of field effect transistors (FET). Graphene is still a developing material and needs development in sophisticated characterization and synthesis techniques, CVD is one such technique that provides the growth of mono, bi-layer and few layer graphene sheets and the scalability of transferring the sheets for the fabrication of devices. The graphene sheets produces through the CVD process offers the exiting and potential in semiconductor applications. Extending CVD process further to a high quality and cleaner transfer process leads to the production of thermal management devices and transparent conductive electrodes. Controlling the formation of number of layers is one such issue that needs to be addressed and is a major focus of graphene research community. The major breakthrough occurred in the large scale production of graphene is by deriving graphene from chemically and thermally modifying GO in a highly economical way. However this process has the major disadvantage of reduction in thermal and electrical conductivities due to the lack of control of functionalization of groups. The band gap will be altered during this process which limits the applications of graphene. Hence the controlled modification of graphite into graphene is crucial in expanding the potential applications of graphene based materials. It can also be noted that majority of the researchers are still unware of the health issues that might be caused due to the handling of large scale graphene, this needs to be investigates together with the toxic effects of graphene based products on environment and their bio-degradability. Therefore it is advised to pursue the chemical and thermal modification of GO to rGO in controlled environments.

The potential applications of graphene based materials includes electronic devices, thermal management devices, mechanical parts, energy storage, transparent conductive electrodes and bio-sensors. The major hurdle in using graphene as a reinforcement material composites applicable in industrial applications is its bonding with the matrix material, non-homogeneous distribution along the matrix, orientation of layers and existence of number of layers that effects the properties of graphene and needs more insight investigation. It is worth noting that the research in the area related rGO needs polishing in terms of investigating defects from the atomic level, formation of wrinkles and agglomerates. Most of the nano electronic devices produced using graphene include tuning the energy band gap but it is still a challenging aspect to create the energy gap while depositing the graphene layers. It can be noted from literature that for FET devices the GNR’s are the correct choice and more insight of material properties and sophisticated characterisations are required. GO use in the production in FET’s triggered interest among the researchers due its large scale integrity but there isn’t sufficient amount of research evidence to support this, more atomic level analysis needs to be done to understand the existence of homogeneity at nano level. It can be suggested that GNR, GO can possess a capability to facilitate the tunable energy gap for the fabrication of nano electronic devices.

7 CONCLUSION

In this article, the various production techniques of graphene were discussed along with GO, rGO and GNP. The potential applications of graphene and graphene-based composites were reviewed. The CVD method of synthesising graphene possess the exceptional potential to be used in industrial production of graphene with the development of an efficient transfer process. It is necessary to control the level of defects and the number of layers of graphene formed such that the performance of graphene-based devices can be controlled, which is a main challenge for the material community. More research is needed to understand the formation of these layers and their performance in various applications. The synthesis of reduced graphene can evolve as a cost effective alternative for graphene in the industry with more of an understanding and control of reduction reactions. This post-graphitization method, along with these other exciting developments, opens up new paths towards energy-related applications including supercapacitors, photodetectors, electrochemical sensors, solar cells and transparent electrodes. To conclude even though the new materials development and commercialization consumes more 20 years, graphene research is pursuing with a wonderful track record towards its commercialization opening new path to research and unfolding interesting properties.

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