2.1 Review of Literature on Fabrication and Characterization of Graphene-based Conducting Polymer Nanocomposites

Andre Geim and Konstantin Novoselov, from University of Manchester, UK, received 2010 Nobel Prize, due to their research investigation entitled "for groundbreaking experiments regarding the two-dimensional material graphene." Geim, Novoselov and their co-workers extracted graphene from graphite by micromechanical cleavage method in 2004 (Novoselov et al. 2004), and since then, the discovery has drawn interest from different communities across the world. In this section, a general review of the history of the rise of graphene is described along with its' general properties and synthesis methods. Further, in this chapter we have discussed about graphene and graphene-based nanocomposites and their applications as conducting materials and for energy storage devices like supercapacitors.

2.2 History and Development of Graphene

As described before, in graphene, a single layer of carbon atoms is structured as a honeycomb in a two-dimensional hexagonal lattice arrangement. The material is considered as the basic building block for different graphitic materials with different dimensions (Neto et al. 2006) such as graphene, graphite, carbon nanotube and fullerene.

Graphene structure was pictorially represented on the top left of Fig. 2.1, as a 2D hexagonal arrangement of highly ordered carbon atoms, each electron found covalently bonded to three others, with the remaining valence electron unbounded. This unbounded electron is responsible for electrical conduction. The charge carriers in graphene have zero rest mass and are called massless Dirac fermions (Novoselov, et al. 2005); (Heersche, et al., 2007). Since its’ discovery in 2004 (Novoselov et al. 2004), numerous investigations on the unique physical, chemical, and mechanical properties of graphene has been conducted and reported (Novoselov et al. 2005; Zhang et al. 2005; Altland et al. 2006; Meyer et al. 2007; Schedin et al. 2007). With the discovery of graphene, a newer regime of research for material science and condensed matter physics has begun contributing to diverse applications of graphene-based materials.
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2.3 Synthesis of Graphene

Graphene has attracted the attention of researchers for its’ potential for different applications, and therefore synthesis of high-quality graphene tuned to targeted applications have become crucial, for both fundamental research and for device applications point of view (Geim et al. 2007).

In 1975, graphene was reported to be synthesized by thermal decomposition (Lang et al. 1975). After two and a half decades, in 2001, graphite was cleaved to graphene and was well reported (Shioyama et al. 2001). However, the credit of first approach and discovery of reproducible graphene with newer synthesis routes, particularly for graphene nanosheets, in 2004, goes to Geim and Novoselov.

2.3.1 Exfoliation and Cleavage

As reported by Novoselov et al. 2004, for graphene synthesis, a mesh (of 5 μm deep and 0.4 to 4 mm² area) was made by dry etching of sheets of Highly Oriented Pyrolytic Graphite (HOPG) in an oxygen plasma. Subsequently, with a scotch tape, thin flakes of layers were peeled off from graphite sheets. Then, they were transferred to silicone substrates. The thin flakes thus obtained were subsequently identified as graphene sheets of single to a few layers. The process was quite simple and proved reliable also. The process was improved further with precise controls on exfoliation parameters with the optimized quality of graphene obtained. By this synthesis route, under controlled exfoliation, few-to-single layered graphene flakes were obtained, that were also large

Fig. 2.1 Graphene, graphite, carbon nanotube and fullerene (C60), arranged in order from top left to right.
and flat (Huc et al. 2008). Further synthesis has been made from borosilicate glasses by exfoliating graphite leading to few-layered graphene sheets of a large area with mm order size (Shukla et al. 2009), thus making insulating substrates as potential candidates for obtaining graphene. In addition to solid phases, exfoliation approaches in liquid phase were also successful with materials, such as hydrazine hydrate (Stankovich et al. 2006; Stankovich et al. 2007), N-methyl-2-pyrrolidone (Hernandez et al. 2008) and sodium dodecyl benzene sulfonate (Lotya et al. 2009).

2.3.2 Chemical Method

The above process of micromechanical cleavage of bulk graphite had two significant limitations: a) the process was able to produce a limited quantity of graphene flakes; b) the entire process was hard to control. To address the above, growth of ultrathin epitaxial graphene was attempted on single-crystal silicon carbide using vacuum graphitization techniques. The later process was suitable for fabrication of a patterned graphene structure, facilitating electronic applications, as reported by Charrier et al. 2002; Berger et al. 2004; and Berger et al. 2006. Recently, polystyrene-graphene based composite materials have demonstrated electrical conductivity at room temperature, leading to a new class of composite materials with enhanced properties and functionalities (Stankovich et al. 2006). Graphene oxide papers exhibit high mechanical stiffness and strength, resulting from a novel interlocked arrangement of nanosized graphene oxide sheets (Dikin et al. 2007). Therefore, graphene has great potential to be massively used as an engineering material with the demand exceeding one million tons annually (Wang et al. 2008). Micromechanical cleavage and ultrahigh vacuum graphitization certainly cannot meet such high demands in future. Thus, with a soft chemical synthesis route, high-quality graphene nanosheets with large-sized graphene nanoplatelets can be prepared (Wang et al. 2009). In a typical synthesis process, various steps involved are as follows:

a. Graphite in powder form was sourced naturally and then oxidized to graphite oxide. The method was described in Hummers et al. 1958.

b. One gram graphite powder was mixed with 0.5 gm of sodium nitrate (NaNO₃). The mixture was poured into 70 ml of concentrated H₂SO₄ under an ice bath. Subsequently, 3 gm potassium permanganate (KMnO₄) was gradually added to it.
c. Then mixture was stirred for about two hours. De ionized (DI) water was added to the mixture along with 5% H₂O₂ for dilution. Colour of the mixture was observed to be changed to brilliant yellow.
d. The as obtained graphite oxide was treated with de ionized water. Subsequently, it was subjected to ultrasonication for further exfoliation. Graphene oxide nanosheets were obtained.
e. The obtained graphene oxide nanosheets were poured into a round bottomed flask with hydrazine monohydrate added as a reducing agent.
f. To obtain dispersed graphene nanosheets, the mixed solution was refluxed at 100 °C for two hours. The color of the solution constantly shifted to dark black.
g. Dispersed graphene nanosheets were centrifuged for about 15 mins at 3000 rpm speed to remove remaining small amount of precipitates.
h. The supernatants were directly dried in a vacuum oven to extract graphene nanosheet powder samples.

2.3.3 Electrolytic Exfoliation
Graphene nanosheets can be electrolytically exfoliated from graphite and this method had already been reported (Wang et al. 2009). The method also reported for large scale production of graphene nanosheets. The products were found to be stable after being treated with aqueous solutions. Thus, synthesis of graphene in bulk was helpful for their applications in different areas.

The electrolytic exfoliation process can be described in the following steps:
About 6mm size and 100% pure graphite rods were used as electrodes along with a compound Poly Sodium-4-Styrenesulfonate (PSS), dissolved in DI water. The solution forms the electrolyte.
5V DC was then applied to the two electrodes for about 20 mins, and the mixture was exfoliated. A black product was observed to gradually appear at the anode. After such continuous exfoliation for four hours, the dispersed product was removed.
The obtained product was centrifuged at 1000 rpm speed. By this, to large agglomerates were removed and subsequently, the top portion was decanted. The suspension is called graphene – PSS suspension.
The suspension was observed for as long as six months. As no precipitation was observed even after this, the product was considered to be very stable.
The dispersion was further washed with de ionized water and ethanol, dried in a vacuum oven at 80 °C to obtain dry graphene powder.
The dried graphene powder and the dried sediment were weighed and about 15 wt% yield of graphene was reported.

### 2.3.4 Other Methods

Various other methods have also been developed for production of graphene. Through chemical vapor deposition (CVD) growth of graphene on nickel layers, graphene nanosheets were prepared. The sheets exhibited a sheet resistance and 80% optical transparency, (Kim et al. 2009). By another substrate-free method, liquid ethanol droplets were passed into a microwave plasma reactor (Dato et al. 2008). A solvothermal synthesis combined with pyrolysis has also been proposed to synthesize gram-scaled fused arrays of graphene nanosheets by mild sonication with common reagents of ethanol and sodium (Choucair et al. 2009).

### 2.4 Polymer/Graphene Nanocomposites

Hybrid materials resulting from dispersion of graphene in nano level in the polymer matrix show considerable improvement in different properties compared to conventional composites or virgin polymers. These properties can be tailored according to the ability of dispersion of the nanofillers and low filler loadings in the polymer matrix. Such methods were widely reported by Lindley 2010; Stoller et al. 2008; Wang et al. 2011; Wang et al. 2012; Li et al. 2011; Zhang et al. 2011; Bruce et al. 2008; Balaya et al. 2006; Meethong et al. 2007; van Schalkwijk et al 2002.

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2.5 Synthesis Methods of Polymer-Graphene Nanocomposites

Interactions in polymer-graphene nanocomposites occur as pressure drops in a nano range. Further, the miscibility between polymer and graphene results in the formation of nanocomposite graphene. Such nanocomposite formation can be influenced by factors in the polymer and the solvent, such as polarity, molecular weight, hydrophobicity, reactive groups, etc. (Guo et al. 2009).

Generally, polymers can be embedded into the host materials in three different ways:

In in-situ interactive polymerization method, graphene or modified graphene is taken. It was then swollen within a liquid monomer. Subsequently, it was diffused with a suitable initiator. Then, either by heat or radiation, polymers comprised obtained (Wang et al. 2008; Chang et al. 2002). Preparation of polymer nanocomposites using this method had been widely reported, i.e. polystyrene (PS)/graphene (Li et al 2008; wang et al 2008; Chang et al 2002), poly (methyl methacrylate) PMMA)/EG (expanded graphite) (Ma et al 2010), polystyrene sulfonate (PSS)/LDH (layered double hydroxides) (Aifantis et al 2011), polyimide (PI)/LDH (Aifantis et al 2012), poly (ethylene terephthalate) (PET)/LDH (Cheon et al 2004) etc.

In a second approach, called solution intercalation method, the polymer was solubilized in a solvent. In the solution, graphene, as well as modified graphene layers, begin to swell (Lindley et al. 2010). The graphene/modified graphene layers are bound by weak forces, and therefore different solvents, like water, acetone, chloroform, toluene etc. can be used to disperse the above. The polymer then adsorbs onto the delaminated sheets. Subsequently, the solvent evaporates, and then, the sheets reassembles with the polymer forming nanocomposites (Park et al. 2007). This process
is widely adopted for synthesizing epoxy-based nanocomposites with a critical solvent removal difficulty (Stankovich et al. 2006).

The polymer intercalation from solutions results from the entropy gained by desorption of solvent molecules, compensating for the decrease in conformational entropy of the intercalated polymer chains. Hence, a relatively large number of solvent molecules need to be desorbed from the filler to accommodate the incoming polymer chains (Tarascon et al. 2009). This method is preferred by low polarity polymers for the synthesis of intercalated nanocomposites.

The third method for obtaining polymer nanocomposites is based on polyethylene grafted maleic anhydrides. (PE-g-MA)/graphite (Wang et al 2005), epoxy/LDH (Wang et al 2011; Li et al 2010), PS (Lindley et al 2010; Wang et al 2002), polypropylene (PP) (Wu et al 2009), poly(vinyl alcohol) (PVA)/graphene (Subramanian et al 2005), poly(vinyl chloride) (PVC)/CNT(carbon nanotubes) (Park et al 2007), ethylene vinyl acetate (EVA)/LDH (Lian et al 2011), etc., have been prepared using this method.

2.6 Graphene Based Nano Materials for Energy Storage Applications

We have presented earlier that, graphene nanosheets have very promising electronic properties, and, therefore graphene has found applications covering a broad range of areas. Graphene has been used to detect step-like changes in resistance when a gas molecule attaches to or detaches from its surface, as graphene is an exceptionally low-noise material electronically (Schedin et al. 2007). A major contribution of quantum confinement could be made for electron transport in quantum dot devices carved entirely from graphene, especially for quantum dots smaller than 100 nm (Ponomarenko et al. 2008). It might be possible to explore graphene field-effect transistors with shorter channel lengths and higher speeds to avoid the adverse short-channel effects, which restrict the performance of existing devices (Schwierz 2010). Nano-graphene oxide has been used for live cell imaging and loading doxorubicin, a widely used cancer drug, with antibody for selective killing of cancer cells in vitro (Sun et al. 2008). Moreover, graphene has been the preferred material worldwide for energy storage and energy conversion related applications. Applications in super capacitors, (Wang et al. 2011) lithium-ion batteries, (Wang et al. 2009) lithium-sulfur batteries, (Wang et al. 2011; wang et al. 2012) and the latest developed lithium-air batteries, (Li et al. 2011; Sun et al. 2012) have also been intensively investigated.

However, graphene produced from chemical methods are often stacked to multiple layers in the dry state and form irreversible precipitate agglomerates. This will result in
almost no difference in the electrochemical behavior compared to bulk graphite platelets, as the compressed graphene nanosheets have very low surface area. Hence, the major challenge is a synthesis of graphene with the ultrahigh surface area, for different electronic applications. This can be achieved by minimizing the stack degree of graphene nanosheets or ideally preventing the stack when graphene is in the dry state by inserting spacer materials between graphene nanosheets (Si et al. 2008).

The spacers could be any nanosized materials to separate graphene nanosheets so that both sides of the nanosheets are available for use. However, considering the routes to introduce nanomaterials to the interlayers of graphene and the specific electronic applications, highly electrochemical active embedded nanomaterials are preferred. In fact, graphene can also be considered as conductive and buffer matrix to improve the performance of the electrochemically active materials. Therefore, this thesis focuses on investigating electrochemically active materials for decorating graphene nanosheets to enhance the overall electrochemical performance of the nanocomposite materials.

In the following sections, conducting polymers as well as graphene and graphene based materials for super capacitor applications have been reviewed individually. Related electrode materials, including graphene and graphene-based nanocomposites have been introduced for many reviews of the current development of graphene-based nanocomposites.

2.6.1 Conducting Polymers

For super capacitor applications, use of polyaniline, polypyrrole, polythiophene and their derivatives as typical electrode materials, have been widely reported (Rudge et al. 1994; Naoi et al. 2000; Laforgue et al. 2001). Using polyaniline, super capacitors with a specific capacitance of 150 F g\(^{-1}\) was reported with energy and power densities as 5 Wh kg\(^{-1}\) and 1200 W kg\(^{-1}\), respectively (Fusabta et al. 2001). With polypyrrole as electrode materials, a very high specific capacitance of 480±50 F g\(^{-1}\) in 1 M KCl was observed, with a very stable cycle life. Polypyrrole's excellent performance was credited to it’s highly porous nanostructure (Fan et al. 2006)[80]. Despite these, the drawback with conducting polymer electrodes is their poor cycling stability, reducing the initial electrode performance (Kotz et al. 2000). Most of the current research on conducting polymers have been found on hybrid super capacitors where the resulting materials have been doped with metal oxides and other carbon materials to increase its electrochemical performances.
2.6.2 Graphene and Graphene-based Materials

Graphene is one of the carbon based materials with high Specific Surface Area (SSA) to deliver double layer capacitance. The unique 2D sp² carbon arrangement makes graphene nanosheets accessible by active ions on both sides and also leads to the possibility of further modification on the vacancy sites to maintain a well exposed surface area for the electric charge storage.

The first report on chemically modified graphene was in 2008 where the surface functionalities to yield specific capacitances of 135 F g⁻¹ and 99 F g⁻¹ in aqueous and organic electrolytes, respectively was presented (Stoller et al. 2008). The synthesis of graphene with adopting hydrazine reduction method was maintained and well separated graphene nanosheets were obtained with a maximum specific capacitance of 205 F g⁻¹ (Wang et al. 2009). Later, preparation of graphene nanosheets with mesopores to achieve a stable specific capacitance of 150 F g⁻¹ for 500 cycles (Du et al. 2010). Morphology-controlled graphene nanosheets have also been obtained with a single curved layer and mesopores (Liu et al. 2010). This graphene based supercapacitor achieved an ultrahigh energy density. The latest breakthrough is the successful synthesis of chemically activated graphene nanosheets, having a specific surface area of 3100 m² g⁻¹ and delivered a specific capacitance of 166 F g⁻¹ at various current rates in an organic electrolyte (Zhu et al. 2011). Recently high performance supercapacitors have been obtained with the help of nitrogen doped graphene (Jeong et al. 2011). The electrochemical properties of graphene considerably improved because of the intervention of all of the above.

Graphene based supercapacitors can also be prepared by inserting nanocrystals between graphene layers forming composite materials. Such nanocomposites have also been widely reported. Some of them are, with Ni(OH)₂ nanoplates (Wang et al 2010), with Co(OH)₂ (Chen et al 2010), with RuO₂ (Wu et al 2010), with SnO₂ (Li et al 2009), with Co₃O₄ (Yan et al 2010) and various MnO₂ nanostructures (Chen et al 2010; Yan et al 2010; Chen et al 2011; Fan et al 2011; Huang et al 2011; Lee et al 2011; Yu et al 2011; Zhang et al 2011).

2.6.3 Graphene based Nanocomposite

Maximum specific lithium insertion capacity for graphite is 372 mAh g⁻¹, that corresponds to the formation of lithium insertion capacity (LiC₆). LiC₆ is a first stage graphite intercalation compound (GIC). During the intercalation process, lithium
transfers its' 2s electrons to the carbon host and is positioned between the carbon sheets. There can be three possibilities: (i) lithium can be inserted into the cavities in carbon (Sato et al. 1994) (ii) lithium can get absorbed on both sides of the carbon sheet (Dahn et al. 1995) and (iii) lithium can be bonded to the covalent sites (Zheng et al 1996).

Graphene is highly conductive and has a high surface-to-volume ratio. Therefore, a high lithium storage capacity in lithium-ion batteries is possible. Based on first principle calculations, lithium can be stored on both sides of graphene nanosheets, inducing a theoretical capacity of 744 mAh g$^{-1}$, two times that of graphite (Wang et al. 2009).

In reports of the employment of graphene as an anode material, graphene has been shown to be capable of delivering large reversible lithium storage (540 mAh g$^{-1}$ in the first cycle) with a retained capacity of 460 mAh g$^{-1}$ at the 100th cycle; a much better performance than a graphite anode. As discussed earlier, graphene nanosheets always naturally stack into multiple layers and these results in limited accessibility of the sheets to lithium, causing the real capacity to be much lower than the theoretical value. Graphene-based nanocomposites with jammed nanocrystals are therefore synthesized so that re-stacking of graphene nanosheets are prevented.

The metal oxide/graphene nanocomposites such as SnO$_2$/GNS have been prepared by reassembling graphene monolayers in the presence of SnO$_2$ nanoparticles (Paek et al. 2009) and by in-situ chemical reduction (Yao et al. 2009). The SnO$_2$/GNS nanocomposites from both methods have been shown to have better lithium storage capacities than bare graphene nanosheets and excellent cycling stability. A super-paramagnetic composite such as Fe$_3$O$_4$/GNS was produced via a chemical deposition. This product was shown to have promising applications for lithium-ion batteries (Li et al. 2011). In the case of CuO/GNS, the material was prepared from CuO and graphene upon reduction using hydrazine vapor (Xu et al. 2009).The formation of TiO$_2$/GNS composite was reported to have been facilitated by SO$_4^{2-}$ surfactants, which acted as the stabilizer of the graphene monolayers in situ (Wang et al. 2009).The prepared TiO$_2$/GNS composite exhibited more than double the specific capacity of pure TiO$_2$ phase at high charge rate.

2.7 Earlier works and the lead points for taking the Present Work

Preparation, characterization, and properties of different Graphene filled polymer based nanocomposites for some polymers had been studied and discussed widely. Most properties of such nanocomposites were found to be superior compared to the base polymer matrix as well as other carbon filler (CNT, CNF(carbon nanofibers), and
graphite) based composites. Further, these properties were obtained with a very low graphene content (≤ 2 wt. %). Though in some cases, higher graphene loading (~15 wt.%) was required, it was comparable to other conventional fillers. Some of the enhanced properties of polymer/graphene nanocomposites are discussed below:

I. Nanocomposites prepared from graphene-based polymer exhibit better mechanical properties compared to the neat polymer or conventional graphite based composites. Mechanical properties of the nanocomposites show significant improvement when made by the solution mixing process rather by melt mixing method. The data reveals the storage modulus property of graphene was > 100% while that for FG (functionalised graphene) was < 42% because of a high aspected ratio of the graphene filler.

II. Graphene is an attractive choice as a nanofiller for fabrication of thermally stable nanocomposites because of its remarkably high thermal stability. Thus, Graphene filled polymer nanocomposites in some cases showed 100 % improvement in thermal stability compared to the neat polymer. It is noted that five at % GO filled epoxy composites was four times higher than that of the neat epoxy resin.

III. Graphene-based polymer nanocomposites show a remarkable increase in electrical conductivity due to the formation of a conducting network by graphene sheets in the polymer matrix. However, the maximum value was obtained using a very low graphene loading in different polymer matrices compared to other carbon fillers.

IV. It is a matter of interest to record that the mechanical, thermal and electrical properties of graphene-filled polymer nanocomposites and the properties of host polymer matrices will improve due to the presence of graphene alone. The degree of improvement in the properties varies for different nanocomposites, and the method of processing also contribute significantly towards tunability of these properties.

V. The homogeneously dispersed graphene nanocomposite in the polymer matrix also exhibits excellent barrier properties. The addition of functionalized graphene to these nanocomposites suppressed the permeation rate of N\textsubscript{2} and He. It is due to the formation of a ‘tortuous path’ in the presence of graphene in the nanocomposites.
VI. It is observed that the electrochemical stability of the PANI/graphene nanocomposites is much higher than the pure PANI or PANI/ITO (Indium-Tin-Oxide) composite electrode.

VII. Graphene-based polymer nanocomposites exhibit good electromagnetic (EMI) shielding efficiency. The EMI shielding efficiency of 15 at.% graphene-filled epoxy composites was 21 dB, which was rather higher than the target value (20 dB) for commercial applications.

2.8 Scope of the Study

Graphene and graphene-based materials offer lots of superior properties in materials science and are considered to meet all the critical requirements for a practical electrode material due to their unique 2D nanostructure. Therefore, in work reported here, a few graphene-based nanocomposites have been systematically studied.

2.9 Conclusion

An overview of graphene from its history, properties, and preparation of its application is briefly stated in this chapter. The synthesis of high-quality graphene nanosheets with high yield percent has become feasible with possible applications of graphene nanosheets in energy storage devices, especially super capacitors. Graphene represents a promising low-cost carbon material for a broad range of practical applications and its potential in electronics industry shall be further developed shortly.