

Novel Synthesis and Promising Applications of Graphene Nanostructures

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Abstract- The transition from semi-metallic to semiconducting states in graphene has ushered in nanostructured materials with novel and enhanced electrical, mechanical, physiochemical and optical properties. The scope of graphene and its potential for novel applications could be substantially impacted by this transition. This article reviews the properties, recent synthesis methodologies and emerging applications of this wonder nanomaterial. The differentiations among the merits and challenges of current techniques are made, aiming to offer evidences to develop scalable and novel synthesis methodologies. The emphasis is on the synthesis, and the possible emerging promising applications arising from these conversion methods, and their overwhelming implications on our current knowledge of graphene and graphene nanostructures.

Indexed Terms- Graphene, graphene nanostructures, chemical functionalization, substitutional doping

I. INTRODUCTION

Graphene has attracted a lot of attention due to its electrical, mechanical, optical and physiochemical properties [1-2]. Graphene is a single-layer, sp^2 -hybridized allotrope of carbon arranged in a two-dimensional (2D) honeycomb lattice [3]. Each carbon atom contains one s-orbital and three p-orbitals. Hybridization between one s-orbital and two p-orbitals in the honeycomb structure results in the formation of C-C covalent bond. The remaining p-orbital overlaps the contiguous carbon atom to form an empty π^* -orbital or conduction band and a filled π -orbital or valence band. Graphene exhibits high electrical conductivity, good theoretical surface area, high intrinsic mobility and superior thermal properties due to its structural and chiral geometry [4]. Graphene is emerging as a strong alternative to semiconducting silicon in post-silicon electronic applications due to its high carrier mobility which is several orders higher than that of silicon [5].

In spite of its impressive and excellent properties, graphene offers limited semiconducting applications due to the absence of a bandgap in its electronic structure. Graphene is basically a zero bandgap semiconductor or a semi-metal [6-7]. The absence of bandgap in graphene significantly affects several applications, particularly semiconducting applications where considerable bandgap is requisite. As has been established, the zero bandgap of graphene makes it more metallic than conventional metals. However, this is only possible when the dimensions of graphene layers enter the microns or nanometer scale range [8]. This problem can be circumvented by breaking the adjacent, in-plane lattice symmetry, and this constitutes a significant step towards opening up the bandgap engineering of graphene. The breaking of adjacent, in-plane symmetry of a carbon leads to the creation of a gap (bandgap) between the π and π^* bands, although realizing a well-tuned substantial bandgap in graphene has remained a major challenge.

The surface engineering of graphene can be tuned via structural alteration including chemical functionalization, chemical doping and controlled reduction, which hold enormous prospects for the synthesis of graphene-based semiconducting nanostructures with enhanced electronic properties. These nanostructures hold potentials for several promising applications, including but not limited to, transparent electrodes, conductive films, photonic and optoelectronic devices, organic and dye-sensitized solar cells, embedded resistors, organic light emitting diodes, biomedicine, stretchable

supercapacitors, field effect transistors, electrochemical biosensor and energy conversion applications [9-12].

There are several techniques to incorporate novel application properties into graphene, such as patterning in the form of graphene nanoribbon, quantum dots, graphene/nanoparticle hybrids and nanomesh. These techniques have shown tremendous promise, and have been investigated from both experimental and theoretical perspectives [13-14]. These techniques particularly focus on transforming metallic graphene into semiconducting modes via chemical functionalization, controlled reduction and doping. Although these novel techniques have attracted massive research attention, they have not been integrated into a unified, single document. Hence, a comprehensive and integrated literature documenting these novel synthesis methodologies and the resulting prospective potentials have become important. This review provides an overall structure and context on the latest synthesis advancements and possible emerging applications of graphene and graphene-based nanostructures.

These synthesis methods can be categorized into three broad areas. They are chemical functionalization of graphene, controlled reduction of graphene oxide (GO), doping of graphene by surface transfer and substitution methods. Functionalization involves the grafting of different functionalities onto graphene surface via covalent or noncovalent techniques. The doping of graphene with non-native atoms creates electronic and structural distortions inside the carbon sheet resulting in changes in the graphene bandgap. The reduction of graphene oxide is executed chemically, photochemically or thermally. However, the reduction of graphene oxide in the absence of a stabilizer triggers fast and irreversible cascading of graphene sheets, leading to the precipitation of graphene particles. Therefore, the surface functionalization of graphene oxide is paramount prior to the reduction process, and this can be executed covalently or noncovalently, followed by reduction [15]. While graphene can be synthesized via any of mechanical exfoliation, charge vapour deposition (CVD), reduction-oxidation (redox), thermal decomposition and exfoliation processes [16], more recent and novel methodologies are being considered for robust and large-scale production of graphene. These methods are discussed in the next section.

II. SYNTHESIS METHODOLOGY

2.1 Controlled reduction of graphene oxide

Controlled reduction of graphene oxide constitutes one of the latest procedures to engineer the surface of graphene to attain substantial bandgap opening [17]. This confers tunable electrical and optical properties on graphene nanostructures, making them useful for device applications. The presence of sp^3 hybridized carbon atoms covalently bonded to oxygen makes graphene oxide electrically insulating. The reorientation of sp^2 and sp^3 carbon atoms in graphene nanostructures tunes its bandgap to assume semiconducting properties different from its usual insulating properties in pristine mode. The reduction of graphene oxide creates lattice defects which significantly affects the carrier transport properties, and ultimately redesigns its bandgap engineering. The bandgap engineering of graphene oxide has elicited enormous attention owing to its critical roles in both fundamental research and device applications. Various novel reduction techniques have been proposed for this purpose. The chemical and thermal reduction methodologies are prominent in this aspect [18].

2.1.1 Chemical reduction

Chemical reduction has been demonstrated as a reasonable and simple solution-processing technique that can be implemented at low temperature and may employ a wide-range of reductants [19-21]. Substantial bandgap opening in graphene can be obtained from a controlled chemical reduction procedure. This causes graphene to transit from insulator to semiconductor and then to semi-metallic mode. Consequently, the differential in the transportation gap transits from insulating to semiconducting

mode, and progresses to zero with substantial reduction [22]. Therefore, adequate control in the reduction process is paramount for tuning the semiconducting properties in graphene oxide.

Velasco-Soto et al. [23] demonstrate the controlled elimination of chemical functional groups from the surface of graphene oxide via chemical reduction. The study employed a gas-based hydrazine technique at room temperature to attain a progressive tuning of graphene oxide optical gap from 3.5 eV down to 1 eV. Figure 1 shows a controlled hydrazine-based chemical reduction of graphene oxide with the associated functional groups [24]. Further investigation indicated that carbonyl groups were the most reactive to hydrazine vapour, attaining full reduction in about 8 hours of action. These were followed by phenolic groups which attained full reduction in 16 hours. The epoxy groups were reduced at 21.5 hours, with the carboxylic groups taking the longest hours (108 hours) to be reduced. These results present a new perspective in the application of graphene and its nanostructures as acceptors in the field of solar cells. Moreover, the match of energy levels of graphene-polymer derivatives is key to determining efficiency, and this can be achieved via appropriate functionalization through oxidation and reduction processes from pristine graphite. Graphene and its derivatives are believed to hold great promise in power conversion efficiency (PCE). Furthermore, the information on the control of bandgap at different phases of reduction presents a seamless platform and opportunity to alternate chemical alignment of graphene and its oxide, and tuning their optical and electrical properties for assortment of novel applications [25-27].

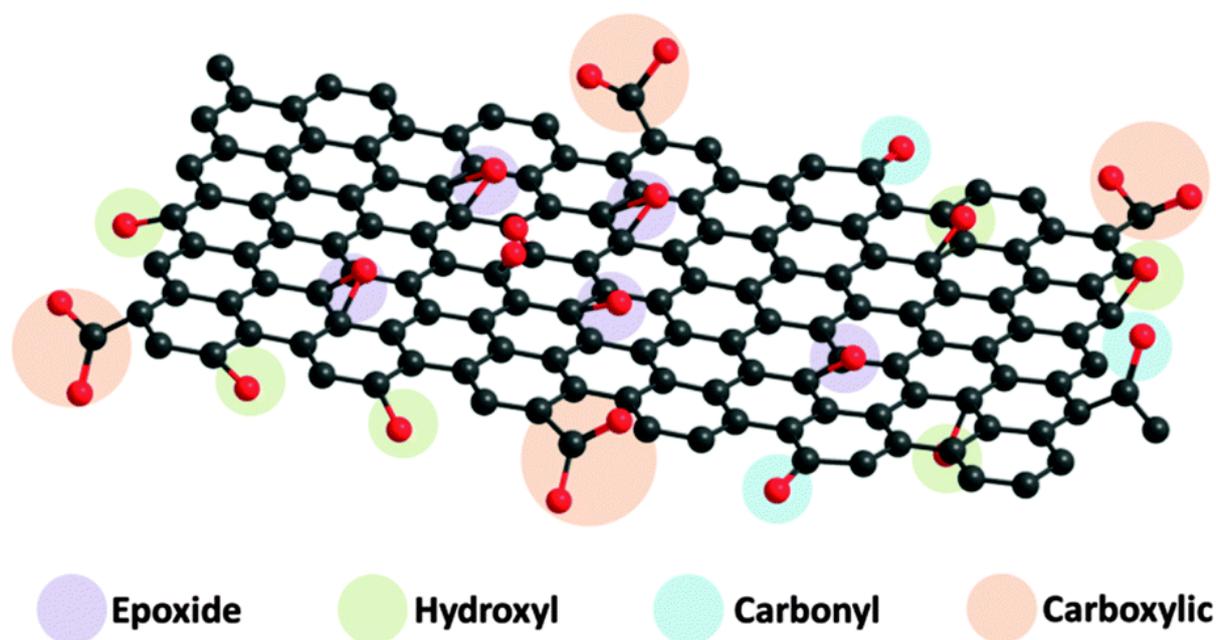


Figure 1: Structural model of controlled reduction of graphene oxide with associated functional groups [24].

2.1.2 Thermal reduction

Thermal reduction can be achieved via heating graphene oxide in the presence of unreactive atmospheric gas at high temperature [28-30]. Adequate control in the reduction technique is paramount for tuning the semiconducting properties in graphene oxide as substantial reduction may shrink the bandgap of the resulting structure to zero. Jung et al. [31] report the eventual transition of graphene oxide from insulating to semiconducting, and further to semi-metallic mode during thermal reduction process. They observed a correlation between the chemical formation of graphene oxide and its electrical properties. In another study, Eda et al. [22] investigate the correlation between the extent of

reduction and carrier transport properties of graphene oxide. Their findings indicated a strong dependence of carrier transport on temperature as a function of various levels of reduction. A carrier gap was observed for moderately reduced graphene oxide at low temperature. The energy gap was found to depend on the extent of reduction. The carrier gap appear to range from 10 to 50 meV and progresses towards zero with increasing reduction process. Adequately controlled reduction of graphene oxide could yield substantial bandgap that is able to induce semiconducting behaviour [22], opening up opportunities for highly diversified applications.

Hu et al. [32] demonstrate a reducing agent-free fabrication of 3D graphene network architectures on conductive surfaces via spontaneous reduction of graphene oxide. This method has been shown to be effective in fabricating a variety of unique graphene architectures. A major challenge in constructing 3D architectures via thermal reduction is the collapse of unsupported pore structure, which must be subsequently eliminated. However, attaining seamless elimination of the support material is equally challenging as the residual would naturally influence the electrical and thermal properties of the reduced graphene oxide. This can be overcome by incorporating an energetic support material such as nanocomposite (NC). Graphene oxide can seamlessly form a composite structure with NC with easy dispersion. Moreover, NC can easily be decomposed via thermal degradation of the composite, thus providing a methodical platform for reducing graphene oxide without the need for any material support.

2.2 Doping of graphene

The literature is replete with several attempts to redesign graphene and its electronic structure towards attaining substantial bandgap [33-35]. Doping, which accelerates the tuning of graphene bandgap stands out in this aspect. The nature and concentration of the charge carriers can be tuned by doping. The band engineering of graphene can be doped primarily by two fundamental methods – substitutional doping and surface transfer doping. Substitutional doping deals with the substitution of the carbon atoms within the graphene lattice. The agitation of the atoms within pristine graphene triggers structural and electronic distortions in the carbon sheet, leaving the bandgap engineering of graphene transformed. In surface transfer doping, atoms are adsorbed into graphene lattice structure. The inclusion of atoms could adjust the voltage point of graphene at Dirac point from negative through zero to positive gate voltages as a consequence of n-type or p-type graphene. In this section, a comprehensive overview of the recent theoretical and experimental investigations on the doping of graphene, and the resulting semiconducting behaviour are presented.

2.2.1 Substitutional doping

Substitutional doping can be attained by the replacement or substitution of carbon atoms in graphene lattice by a non-native atom. This doping mechanism has ignited tremendous interest due to its ability to infuse charge carriers into the electronic structure of graphene. In this process, carbon atoms are replaced with other atoms contiguous to single or multiple openings. In this aspect, metal atoms or heteroatoms are usually preferred. The lattice gap defects are created by bombardment of ions or by beaming electrons using scanning transmission electron microscopy (STEM) [36].

The unpaired charge carriers in pristine graphene are passivated and attached to the delocalized π structure which makes it chemically inert, and consequently obstructs its reactivity and absorption power [33]. The incorporation of heteroatoms can bequeath graphene with superior and robust active sites. Furthermore, the incorporation of heteroatoms with dissimilar electronegativity to carbon atoms has the effect of severing the electroneutrality of graphene, which could trigger unstable charged zones in graphene, which otherwise could function as active sites. These sites could also exist as structural imperfections that may arise from the strained lattice owing to the differentials in the atomic size relative to the dopants [37]. These sites have the potentials to enrich graphene with expanded bandgap and superior interaction, making it assume semiconducting properties for varied applications. The

substitutional doping of graphene using heteroatoms has been attained through various techniques, including solid-phase synthesis, direct synthesis and liquid-phase synthesis.

The charge vapour deposition (CVD) and the segregation-growth synthesis mechanisms are at the core of the direct synthesis technique. CVD has proved effective in doping different heteroatoms, with catalytic growth mechanism yielding graphene films. In this process, heteroatoms are directly incorporated into the graphitic carbon lattices, with a metal catalyst acting as a substrate. This is followed by melding a carbon source with any of solid, liquid or gas-accommodating heteroatoms in a furnace at high temperature as shown in figure 2.

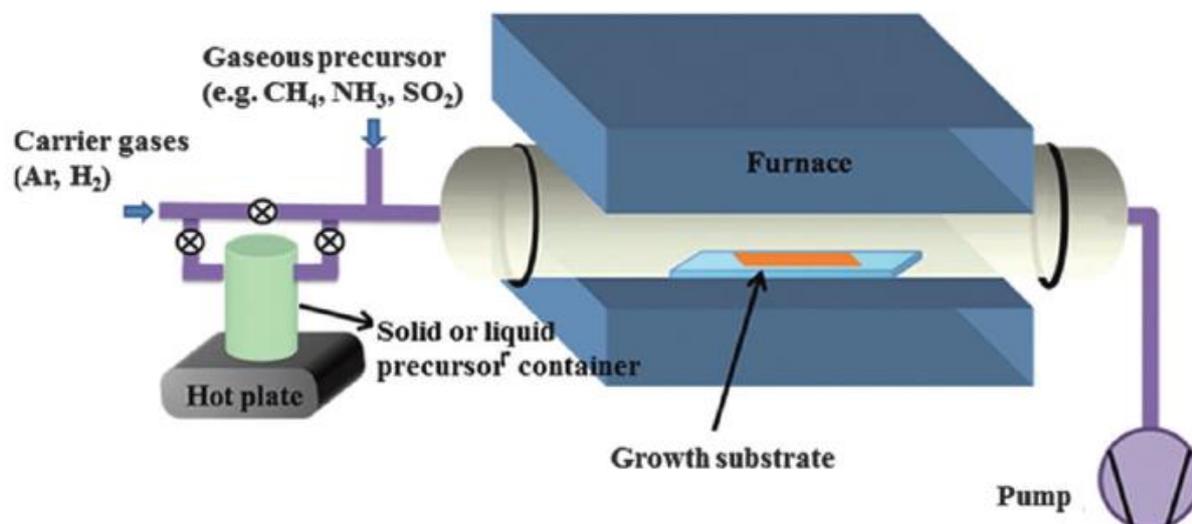


Figure 2: Schematic assembly for a CVD-based graphene doping [38]

These precursors tend to disintegrate and recombine on the surface of the catalyst through precipitation into the graphene-heteroatom complex [39]. CVD has been widely employed to prepare nitrogen-doped graphene. This sort of substitutional doping of nitrogen is predicted to hold promise in transforming graphene into an n-type semiconductor, along with remarkable adjustment in electronic transport and carrier mobility [40-42]. Doping of graphene with nitrogen results in an evolution from metal to semiconductor, with enhanced bandgap, increasing the potential for massive application of graphene in electronic and optoelectronic devices [43]. The CVD technique enables simultaneous doping and growth conditions, and thus allows tunable doping. This is a convoluted procedure which requires high operating temperature. Other by-products of this process are hazardous materials and waste gases. Moreover, this method is characterized by high cost and low yield [44].

The solid-phase synthesis can be attained at high temperature, along with arc-discharge and thermal annealing procedures [45-46]. The thermal annealing of graphene oxide or reduced graphene oxide can be exploited in doping with heteroatoms only in the presence of suitable precursors. During thermal annealing, heteroatom-doped graphene is produced at high temperature. For instance, Yang et al. [47] employ porous silica to confine graphene oxide sheets for N- or S-doping in order to attain free gas transport and circumvent aggregation problem. N-doping was found to be more effective compared to S-doping, with S-doped structure yielding thiophene-like formation at the intersection of the defect sites, as shown in figure 3. One significant advantage of thermal annealing is the provision of a wider range of precursors, and ensuring adequate control of the doping process. However, the application of high temperature in this reaction does not preclude the need to recover the sp² carbon network [48]. Doped graphene can also be synthesized via arc discharge method [49]. This procedure employs

heteroatom reactive radicals to initialize the doping mechanism. Arc discharge method can also be used to synthesize doped graphene by evaporating the carbon source at high operating temperature. This method has been extensively employed to synthesize nitrogen-doped graphene. Rao et al. [50] demonstrate the synthesis of nitrogen-doped graphene using arc discharge in the presence of pyridine vapour or ammonia (NH_3). Similarly, multi-layered nitrogen-doped graphene sheets have been synthesized via arc discharge in the presence of NH_3 buffer which acts as N precursor [51]. This procedure has also been exploited to synthesize boron-doped graphene [52]. A similar method has been employed to produce boron-doped graphene in the presence of H_2 and B_2H_6 , with boron-filled graphite acting as an electrode. This method is known to be scalable, although high operating voltage and low doping level present a huge challenge, making it only suitable for multi-layer graphene [51, 53].

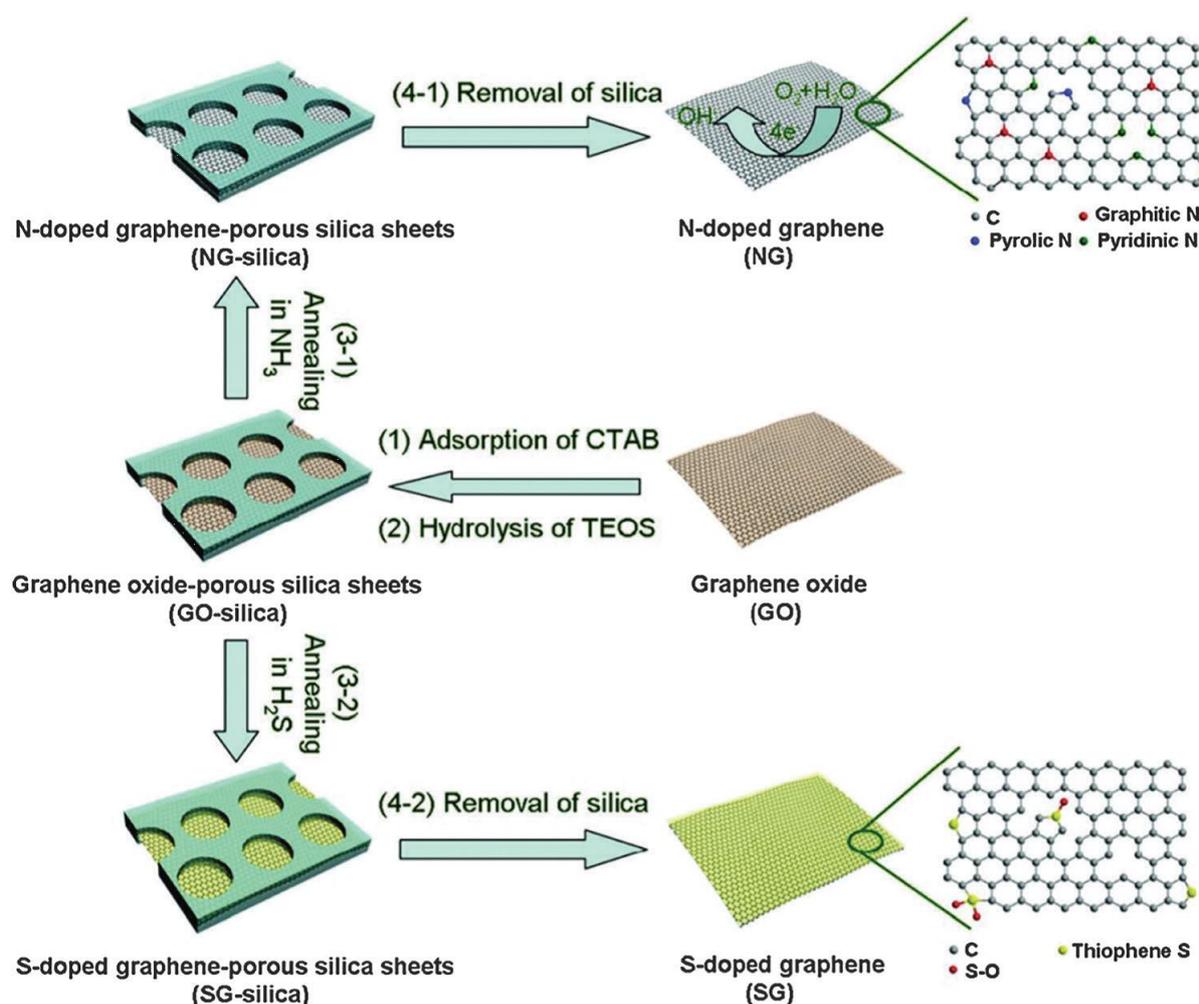


Figure 3: Schematic of N- or S-doping on porous silica confined to graphene oxide sheets via thermal annealing [38].

The liquid-phase production of graphene involves solvothermal and hydrothermal treatments [54]. This method was first used to synthesize gram-scale graphene [55]. The gram-scale synthesis of nitrogen-doped graphene can be attained at a temperature of about 300°C using solvothermal means. Nitrogen-doped graphene with varying amounts of nitrogen can be synthesized by blending either of cyanuric chloride with lithium nitride or lithium nitride with tetrachloromethane, and

tetrachloromethane [56]. A similar procedure for the synthesis of nitrogen-doped graphene under moderate condition reaction of lithium nitride and tetrachloromethane was demonstrated by Deng et al. [56]. Sulphur doped graphene can also be synthesized via solvothermal process. To this end, sulphur doped graphene with pristine thiophene S-bonding via a rapid microwave-assisted solvothermal procedure using benzyl disulphide and graphene oxide has been demonstrated [57]. A doping threshold of 2.3 percent within a 6-minute duration was attained during the solvothermal procedure. Doped graphene synthesized via this method enjoys superior chemical properties [57].

2.1.2 Surface transfer doping

The surface transfer doping is achieved via the exchange of charge carriers between graphene and graphene-surface absorbed-dopants. This sort of doping, otherwise called adsorbate-induced doping, is a nondestructive and reversible procedure [58]. For surface transfer doping of graphene, a substantial hole-doping in the graphene could be achieved via the adsorption of atoms with extreme affinity for electrons. These atoms, which include antimony (Sb), gold (Au) and bismuth (Bi) could be absorbed on graphene surface and may adjust the electronic properties of graphene [59]. Benayad et al. [59] investigate the consequence of Au-ion treatment on the electronic structure and work function of reduced graphene oxide. Their findings showed a gradual decrease in the relative percentage of carbon, and a sharp increase in the relative percentage of Au with corresponding increase in the doping concentration. This could be attributed to the charge transfer from the sp^2 electrons to Au-ion solution. In addition, the carbon oxide species with functional groups C=O and O=C=O are suspected to donate electrons to Au-ions, which triggers spontaneous transformation of the Au-ions into Au owing to the charge transfer from the reduced graphene oxide to the Au-ions (see figure 4). As the minimum conductivity falls at the Dirac point of graphene, the resulting voltage is expected to oscillate in the direction of negative gate voltage due to n-type doping or positive gate voltage due to p-type doping. The adsorbed Sb and Bi atoms automatically withdraw electrons from graphene, causing the Dirac point to oscillate in the direction of Fermi level without overlapping it. However, the element with the highest electron affinity (in this case, Au) shifts the Dirac point to the vacant states, inducing p-type doping in graphene.

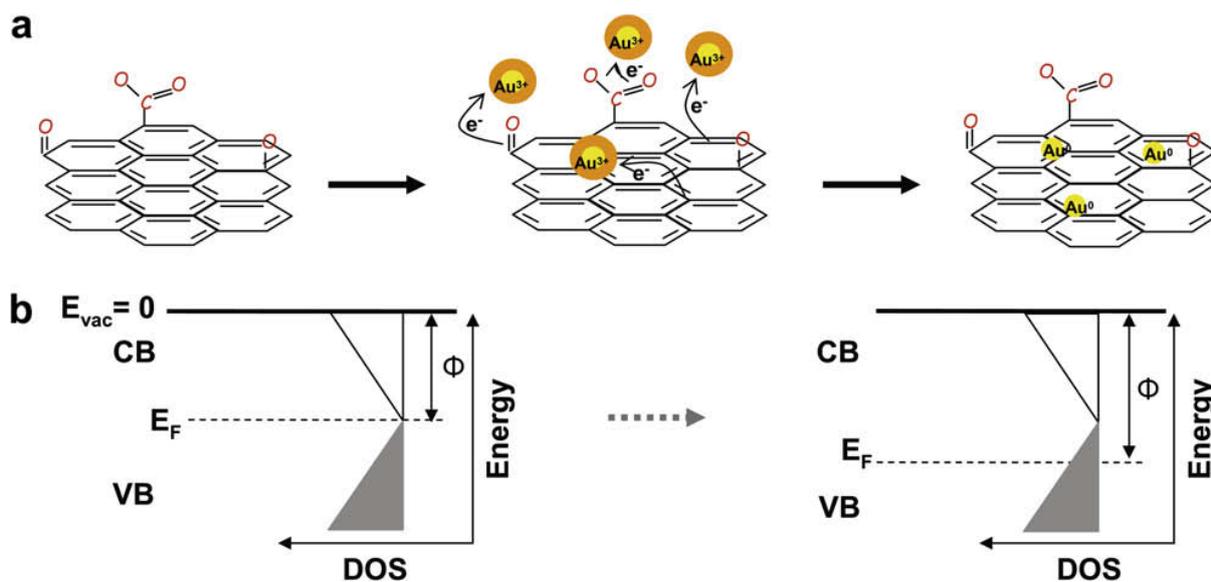


Figure 4: a) Schematic of surface transfer doping in graphene b) illustration of the band diagram of graphene oxide before and after treatment. CB, VB, E_F, E_v and ϕ denote conduction, valence band, Fermi level, vacuum level and work function respectively [59].

The charge transfer is believed to be triggered by the difference in the interactions of metal components with graphene and the work function, consistent with the existing literature [60]. Graphene is doped with holes when its work function is less than the work function of the participating metal. This is in contrast to doping with electrons where the work function of graphene is larger than that of the participating metal. Alkaline metals are able to donate electrons due to their strong ionic bonding properties, which facilitates the ejection of lone-paired electrons in the conduction band, raising the quantum of charge carriers in graphene [61].

2.3 Functionalization of graphene

The chemical functionalization of graphene represents an alternative methodology to govern its electronic properties. In this procedure, the sp^2 matrix is converted into the sp^3 equivalence, leaving the transformed graphene electrically insulating. Therefore, graphene can be modified from metallic state to semiconducting state using appropriate surface functionalization method [62-67]. Additionally, the massive surface exposure could be realized through the appendage of other functional species on graphene or graphene derivatives [68]. Graphene can be functionalized mainly by covalent and noncovalent methods, although other functionalization approaches exist. Figure 5 shows the molecular models of functionalization of sp^2 hybridized graphene. The presence of functional species facilitates the expansion of the application landscape of graphene through the formation of donor-acceptor complex, which results in tunable electrical, optical and photovoltaic properties [31, 69]. Functionalizing a sheet of pristine graphene is challenging, and often times unachievable due to the poor solubility. However, a promising starting point is the use of graphene oxide sheets with reactive functional groups, such as epoxy, hydroxyl, carboxylic acid groups on its edges and basal planes.

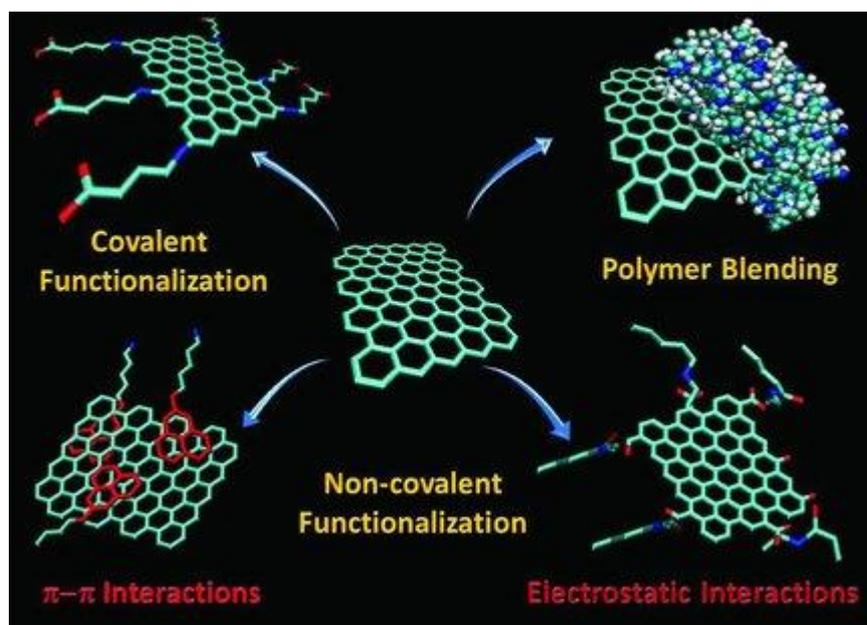


Figure 5: Schematic of molecular models of sp^2 graphene interactions with various polymer matrices; covalent, non-covalent functionalization and polymer blending. [70].

2.3.1 Covalent functionalization

Covalent functionalization involves the formation of covalent bonds at the intersection of graphene edges or at its basal planes. Graphene or graphene-derivatives that are covalently bonded are assembled through appendage of atoms to sp^2 carbons or molecular groups. This transformation preserves the graphene 2D lattice architecture, although some vital characteristics are sacrificed owing to the loss of the π -electron cloud present in the upper and lower ends of graphene. Functionalization of graphene can be attained via the interaction of unsaturated π -bonds, organic functional moieties and oxygen atoms on graphene oxide [71-72]. These interactions reconstruct the sp^2 atoms into sp^3 hybridization, precipitating semiconducting and unconducting regions in graphene layers. Most of the reported investigations focus on the covalent-linkages in various functional species and oxygen moieties in graphene oxide [73].

The covalent modification of graphene with organic moieties has been exploited in realizing the semiconducting applications of graphene. Yu et al. [74] demonstrate a novel variety of charge transport materials in polymer solar cells (PSCs). In particular, CH_2OH -terminated region regular poly(3-hexylthiophene) has been chemically grafted onto carboxylic species of graphene oxide via esterification reaction as shown in figure 6 [75]. The bilayer photovoltaic application realized from this functionalized platform showed increased power efficiency when compared with the P3HT/ C_{60} structure. The remarkable advancement in the performance of this architecture is attributed to the robust electronic interaction and excellent matching in the bandgap between graphene and P3HT to augment charge transport. These results demonstrate the role of graphene derivatives as effective hole transporting platforms in the active band of PSCs. The functionalization of graphene sheets with fullerene exploiting covalent fisher esterification reaction has been demonstrated [76]. The covalent hybridization of 2D graphene with 0D fullerene is predicted to furnish graphene-hybrid with novel characteristics with potential for highly diversified applications.

2.3.2 Noncovalent functionalization

The noncovalent functionalization of graphene is frequently exploited to redesign graphene surface towards various applications. In contrast to the covalent functionalization, noncovalent functionalization does not interject the sp^2 structure of graphene, thereby preserving its electrical conductivity. The noncovalent functionalization between graphene and other functional species involves electrostatic forces, hydrogen bonding, π - π stacking and Van der Waals interaction [77-78]. Recently, Zhang et al. demonstrated the noncovalent functionalization of graphene with semiconducting fullerene using π - π interaction, and incorporating same into conjugated polymer [79] and epoxy composites [80], leading to enhanced thermoelectric performance of the polymer composites. Similarly, Zhang et al. [81] demonstrate an improvement in the thermoelectric characteristics of $rGO_x/F-C_{60}_y$ nanohybrids synthesized via noncovalent lithiation technique, as shown in figure 7. Meanwhile, figure 8 illustrates the modulating effect of $F-C_{60}$ on the band structure of reduced graphene oxide. Through this interaction with semiconducting nanostructures, the bandgap of graphene increases up to 2.9 eV, demonstrating the potentials of p-type modulation.



Figure 6: Schematic illustration of synthesis mechanism for chemical grafting of graphene with CH₂OH-terminated P3HT matrix [75].

Noncovalent functionalization of graphene can be demonstrated by employing varied species of organic modifiers. Table 1 shows varying noncovalent functionalization of graphene oxide using varying modifying agents, along with the transformations in their electrical conductivity.

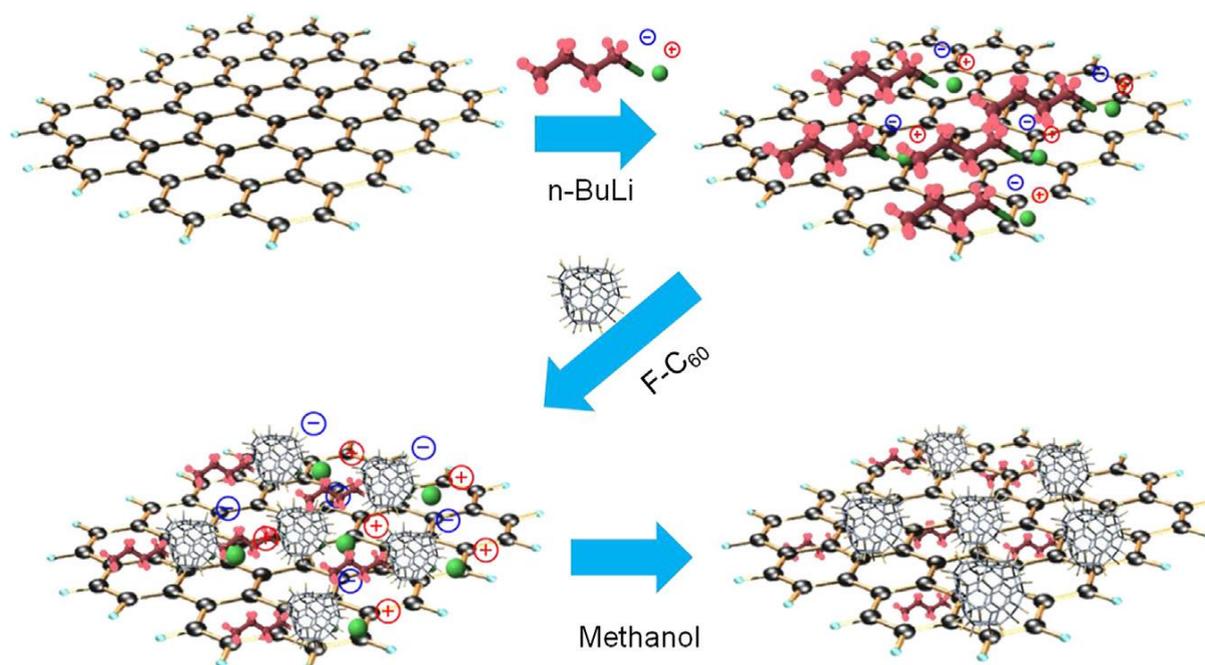


Figure 7: Schematic of noncovalent attachment of F-C₆₀ on rGO via lithiation reaction [81]

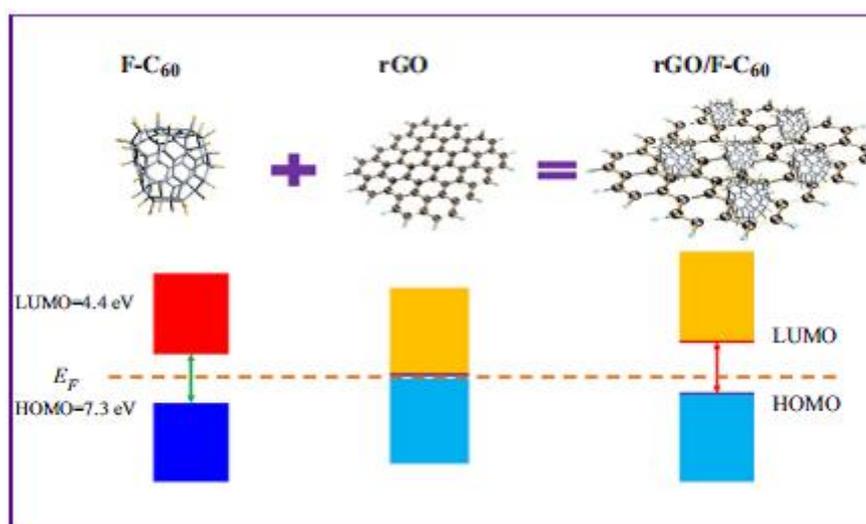


Figure 8: Illustration of modulation of band structure of rGO using F-C₆₀ [81]

Table 1 Electrical conductivity of noncovalent modified graphene oxide with varying modifying agents

Modifying Agent	Conductivity (S m ⁻¹)	Reference
Amine terminated polymer	1500	[82]
PANNI	10.6	[83]
PANI/GO	23.12	[83]
PANI/graphene	168.7	[83]
PDMS	1000	[83]
SPANI	30	[84]
PIL	3600	[85]
PBA	200	[86]

III. APPLICATIONS OF GRAPHENE-BASED NANOSTRUCTURES

3.1 Biosensing

Biosensing particularly involves the detection of biologically copious analytes such as small biomolecules, proteins, amino acids, deoxyribonucleic acid (DNA), ions and ribonucleic acid (RNA). In this aspect, electrochemical and Forster resonance energy transfer (FRET)-based detections are predominant. This is because these methodologies are very sensitive and efficient. However, methodologies like surface enhanced Raman scattering (SERS), surface plasmon resonance (SPR) and fluorescence spectroscopy have demonstrated promising results in biosensors. The target species under investigation in biosensing are particularly critical ingredients that can be exploited to monitor the transformations within a biological ecosystem. Since its isolation in 2004 [87], graphene has been widely investigated for various sensing applications [88-90], including applications in which graphene is hybridized with other nanoparticles such as carbon nanotubes [91].

Graphene as a promising matrix for electrochemical biosensors has elicited considerable interest. Exploiting graphene in biosensor modification mechanism amplifies the surface area of the biosensor resulting in the immobilization of substantial quantum of enzymes, cells and antibodies. This results in the amplification of the electrochemical detection response [92]. However, the poor solubility of graphene in water and other organic solvents, coupled with lack of surface functionalization limits its practical applications in biosensors. For instance, graphene has been employed for various glucose

sensing schemes [93]. In addition, graphene or electrochemically oxidized graphene has been suggested to be a promising candidate for highly sensitive electrochemical sensing owing to the presence of controllable quantum of defects [94].

Bioanalysis plays significant role in disease diagnostics and management; thus sensitive and selective detection of bacteria, DNA and proteins are paramount for disease diagnosis and therapeutics. For example, Alzheimer and various cancers are closely associated with DNA mutation [95]. Therefore, suitable biosensors are needed for targeted early detection of diseases as well as disease evolution. Graphene-based nanostructures have been employed to construct varying species of biosensors based on varied sensing mechanisms, including electrochemical and optical (fluorescence) sensors [96]. Depending on the particular sensing mechanism, biosensors either exploit their unique structures (surface-to-volume ratio and atomic layer geometry), electrochemical properties (charge transfer rates) or electrical properties (charge carrier mobility) for biomolecule detection [97-98]. Figure 9 shows the schematic assembly of graphene-based electrochemical sensor used in biomedical application.

These advantages position graphene nanostructures as ideal materials for construction of biological sensors with extreme sensitivity, low detection limit and ultra-selectivity. The microscopic biological information can be transformed through the fast electron transfer kinetics of graphene, leading to the production of a highly sensitive sensor. In addition, graphene can easily conjugate with biomolecules to detect cancer cells and proteins with low limit of detection owing to its large surface-to-volume ratio [90]. In general, biosensors comprise of two essential components: a transducer and a receptor. The receptor can be any device that can interact with the target species (analytes). The transducer converts biological information into electrical information, and is usually connected to the biological sensing element. The transducer also maintains a connection to a measuring device which ultimately converts the electrical signal into a measurable quantity [99]. In a graphene-based biosensor, graphene is exploited as a transducer element which transforms its electrical properties upon interaction with the attached sensing element.

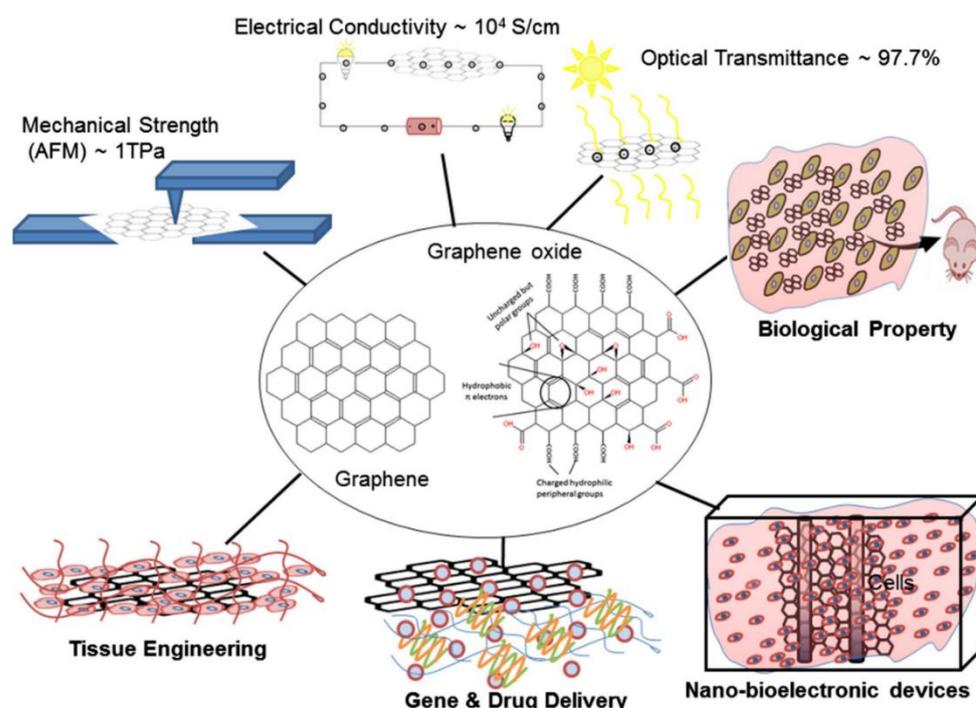


Figure 9: Schematic of graphene-based electrochemical sensors in cancer cell, DNA and protein detection, reflecting the electrical, mechanical and optical characteristics of graphene [100].

3.2 Lithium-Ion batteries

Lithium ion batteries are energy storage devices with low energy delivery capacity and high energy storage capacity. Charge carriers (ions) are transported from the cathode to the anode during charging of a lithium ion battery. The nanostructures of pristine graphene possess high energy barrier for the infiltration of ions through graphene layer and moderate binding energy towards lithium ions, making them limited in lithium ion energy applications [101-102]. This limitation can be compensated by employing functionalized graphene in lithium ion batteries [103]. Moreover, the existence of edge-like defect sites in graphene enables the penetration of lithium ions, and circumvents aggregation of lithium due to the unyielding contact between the edge-like defect sites and lithium.

Heteroatom doping has been demonstrated to conserve optimal balance between the diffusion for electrodes and lithium storage [104-105]. Experimental and theoretical investigation indicated that lithium atom is an effective electron donor. Consequently, the storage capacity is amplified when graphene is doped with an electron-deficit atom, boron for instance [106]. This limits the delithiation phenomenon while increasing the binding energy between boron-doped graphene and lithium, and ultimately enhances the battery capacity. While exhibiting diminished storage capacity, nitrogen-doped graphene displays superior delithiation which may be attributed to the electrostatic repulsion and diminished binding energy between nitrogen and lithium. Therefore, these materials can enhance the charge/discharge rate performance of the battery [102]. Chemically modified graphene and functionalized graphene electrodes are also employed in Li-ion batteries for enhanced performance. In this arrangement, efficient conduits for charge transfer kinetics are provided in the batteries towards enhanced rate capability and improved capacity.

Electrons and lithium ions are reserved at relatively towering potential in the functional species on the surface of graphene in the modified graphene cathode, while in the reduced graphene oxide anode mode. Similarly, electrons and lithium ions are reserved at relatively lower potential on the surface of graphene. Kim et al. [107] demonstrate all-graphene-battery constructed by melding a functionalized graphene cathode in lithiated mode with a reduced graphene oxide. This battery exhibited improved electrochemical properties, with specific capacity of about 170 mAhg^{-1} , depending on the mass of the cathode, which particularly suited the implementation of this cathode.

3.3 Tissue engineering

Tissue engineering is yet another biological field that holds great promise as biomedical substitutes to maintain, scaffold and restore tissues or cells of an organ [108]. The scaffold is expected to mimic the structure and properties of the organ it aims to surrogate and essentially functions as an artificial extracellular platform to support cell growth and survival. Tissue engineering is a rapidly emerging field in biomedical engineering, revealing great potential for assembly of bioengineered tissues to restore lost function owing to damaged organs and tissues [109]. Owing to the superior mechanical and electrochemical properties, graphene can be integrated with appropriate biomolecules to yield tissue surfaces with desirable characteristics. Consequently, graphene can be exploited as a biocompatible films, reinforcement materials in hydrogels and other tissue engineering scaffolds. A graphene nanostructure-based nanocomposite exploiting chitosan-polyvinyl alcohol (CS-PVA) scaffolds for wound healing has been demonstrated, revealing excellent healing effect on damaged tissues and organs [110-111]. A similar study indicated a faster healing process for graphene-based CS-PVA reflecting the potential of graphene-based devices in tissue rehabilitation and healing.

Fan et al. [112] demonstrate graphene-based nanosheet (GNS) blended with hydroxyapatite (HA), which is a considerable constituent of natural bone tissue, aiming to exploit the scaffold to modulate the morphology of HA as well as enhance rigidity of HA. Characterization of GNS/HA showed 55 nm and 13 nm as average length and diameter respectively. The as-synthesized GNS/HA complex containing 40 wt% of HA was found to exhibit excellent bone cellular proliferation induction, high osseointegration capacity with adjoining tissues and superior biocompatibility than individual pristine

GNS and HA. These findings highlight the potentials of GNS/HA composites as bio-engineered materials for bone replacement, regeneration and tissue engineering applications.

3.4 Supercapacitors

Supercapacitors have attracted significant interest as energy storage devices owing to their high power density and long lifecycle. Supercapacitors exploits long life cycle, high energy storage and high power delivery for large scale applications. Recently, graphene-based nanomaterials have been employed in supercapacitors due to their inherent electric double-layer capacitance (EDLC) [113]. However, the lack of electrochemical capacitance coupled with the chemical inertness of pristine graphene makes its application in supercapacitors challenging. Doped or functionalized graphene is shown to be attractive in this aspect [114].

Another possibility is the controlled introduction of defects into the structure of graphene via doping to enhance its supercapacitor applications. Heteroatom-doped graphene is shown to offer improved chemical reactivity, high conductivity and increased stability relative to pristine graphene. These materials are promising for supercapacitor applications due their superior conductivity, miniscule charge transfer resistance and enhanced electrochemical activity compared to pristine graphene [115-116]. Supercapacitors based on nitrogen-doped graphene have been demonstrated to exhibit superior capacitance compared with their pristine counterparts [117-118]. Furthermore, these materials have been shown to diminish charge transfer resistance of the electrode and accelerate electron transfer kinetics, thus improving device capacitance [117].

The effect of co-doping of graphene nanostructures with two or more atoms has also been reported. For instance, electrodes based on boron and nitrogen co-doped graphene have been found to exhibit higher capacitance than those of individual atoms or pristine graphene. This can be attributed to the synergistic influence of the two co-dopants. Supercapacitors constructed from these electrodes tend to achieve amplified energy and power density [119]. Controlled oxidized graphene can also be applied in semiconducting applications. The inter-dependency of the degree of oxidation and the resulting capacitance was highlighted by Deyoung et al. [120], revealing the modulating effect of oxidation on the ion accessibility towards the surface of electrodes. This technique demonstrates the potential of graphene to catalyse electrode optimizations, although computational restrictions of the parameterized variables remained.

3.5 Transparent and flexible Electronics

Recently, researchers have intensified investigations into the various routes to construct transparent and flexible electronic devices for varying species of applications, including solar cells, smart windows, light emitting diodes (LEDs), liquid crystal diodes (LCDs) and integrated circuit (IC) cards [121]. Graphene is considered an attractive candidate, integrating array of superior properties including electrical conductivity, optical transparency and mechanical flexibility. Several groups have reported the melding of graphene composite electrodes, including CNT-graphene hybrid, graphene/pentacene into flexible and transparent electronic devices [122-124].

Organic FETs-devices based on pentacene have been incorporated into a flexible substrate via either transfer and patterning (T-P) or patterning and transfer (P-T) procedures that are underpinning the graphene electrodes [121]. This procedure employs a PEDOT/PSS-based plastic substrate as a gate electrode and poly-4-vinylphenon (PVP) as a cross-linker. A carrier mobility of 0.01 and 0.12 cm²/Vs were estimated for (T-P) and (P-T) respectively [121]. Moreover, the universal electronic properties of the organic FETs connected with the (P-T) procedure was found to be superior to that connected with (T-P) [121]. In addition, the electrical variation of resistance as a function of the quantum of graphene layers points to more windows to enhance the electronic properties, particularly the carrier mobility, making it amenable for large scale applications [121].

3.6 Space Applications

Space technology is an emerging field with tremendous opportunities and prospects for profits. The devices and materials employed in space applications should integrate nanoscale size with high functionality to optimize cost effectiveness. The greater cost of launching a satellite into orbit concerns its weight, therefore reducing the weight to nanoscale can significantly diminish the overall cost. Size savings can be attained by replacing heavy components with lighter, low-density nanoscale materials such as carbon nanotubes and graphene. Another concern is joule heating from conventional metallic components which increases the overall cost. However, the melding of exceptional electronic and thermal properties of graphene has the potential to revolutionize the creation of light-weight electronic devices to be employed in space applications. In this aspect, graphene is a promising alternative due to its ballisticity which limits joule heating.

Graphene can also be employed as nanofiller to construct robust and light weight nanocomposites for space applications. Zhang et al. [125] propose two methodologies to launch a rocket into space, exploiting the radiation pressure acting on the sail morphology and a laser to superheat the rocket propellant, although the inability to obtain intrinsic properties of single-layer in bulk mode limits these applications. To overcome this limitation, a rotation of bulk sponge with nanoscale dimension and direct light-initiated macroscopic propulsion are implemented [125].

IV. CONCLUSION

As noted in the forgoing, the superior electrical, mechanical, optical and physiochemical properties of graphene make them attractive devices for assorted species of applications. Although faced with numerous challenges, owing mainly to the presence of zero bandgap, varying techniques have been invented to incorporate a tunable bandgap, and thus compensate for the limitations. This article has reviewed three fundamental methodologies to actualize this – functionalization, doping and controlled reduction of graphene. The enormous prospects of graphene-based nanostructures in highly diversified applications have also been discussed.

In spite of the progress made in the field of graphene engineering, many challenges associated with synthesis still remain. The transfer doping of graphene lacks long-time stability. This is due to the desorption of the absorbed species from the surface of graphene, which causes it to interact with reactive molecules. In this aspect, the substitutional doped graphene is a promising alternative, as the atoms are bonded to the carbon linkage of graphene. The substitutional doped graphene enjoys appreciable amount of stability, although challenges associated with mechanisms, controllability and large-scale production remain. For one, high temperature and raucous doping conditions impact negatively on large-scale production. The controlled and green synthesis mechanisms are preferred in this aspect. Moreso, the innovative applications and constant evolution of novel materials have made the reaction mechanisms particularly challenging. Additional investigations in doped graphene nanostructures will ultimately advance newer technological applications. The controlled reduction methodology is particularly promising for large scale production of graphene, although the problems associated with the control of the reduction mechanism and the removal of oxygen-containing species present significant limitations. Moreover, as this procedure is bound to impose defect limitations, further advancement is desired to yield high-quality graphene. The use of graphene in some applications such as energy systems also experiences some challenges. For instance, although functionalized or doped graphene has proved to be promising in supercapacitor applications apparently due to the presence of high EDLC and pseudocapacitance, the absence of a strong mechanical stability presents a significant challenge. In lithium-ion applications, the built-up of solid electrolyte interface (SEI) and high irreversible capacity in the battery electrodes are notable disadvantages. In spite of the challenges, graphene nanostructures are considered promising candidates for energy systems applications. The future of this wonder materials is bright as more and newer applications are expected.

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