A REVIEW OF GRAPHENE BASED MATERIAL: PRESENT AND FUTURE APPLICATION ON ELECTRONIC PACKAGING

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ABSTRACT

Graphene is a two-dimensional material which composed of carbon atoms that arranged in a honeycomb-structure. Due to its excellent and unique properties, it has drawn an enormous interest among scientists nearly in every field of engineering and science. The aim of this review article is to provide a significant scientific progress of graphene up until now and to evaluate the prospect of its future application. Several key aspects have been reviewed which include the synthesis, functionalization, characterization, properties and its future application. Their thermal, electrical transport, mechanical properties, chemically derived graphene and other aspect also are discussed along with their future potential application. The article concludes with a brief discussion on the environmental impact of this graphene and the future prospects of this promising material.

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1. INTRODUCTION

Recently, graphene has attracted a great deal of scientific and engineering interests due to its superior mechanical, electrical and thermal properties originating from its two-dimensional sp2 carbon atoms' honeycomb structure [1-7]. Therefore, it can produce a dramatic improvement in many properties at very low filler content in composite materials [8-10]. Electrons in graphene behave like massless relativistic particles contributing to very peculiar properties such as the absence of localization and an anomalous quantum Hall effect [4-5]. In addition, graphene has demonstrated a variety of intriguing properties which include high electron mobility at room temperature (250,000 cm^2/Vs) [7, 11] and exceptional thermal conductivity (5000W/mK) [6] as well as superior mechanical properties with Young's modulus of 1 TPa [12]. Having a Young's modulus of almost 1 TPa and intrinsic strength of 130 GPa approximately, graphene is the strongest material ever measured, also having a low weight [13-18]. It was found that graphene shows promise as reinforcement in high-performance nanocomposites [19]. Its high levels of stiffness and strength can lead to the production of nanocomposites with outstanding mechanical properties [20-21]. Its potential applications include transparent conducting electrodes, single molecule gas detection, composites and energy storage devices such as supercapacitors and lithium ion batteries [22-34]. Apart from that, a distinct band gap can be generated as the dimension of graphene is reduced into narrow ribbons with a width of 1-2 nm which produce semi-conductive graphene with potential applications in transistors [22-24].

Graphene-based materials are commonly classified into two categories which are large-area graphene films produced by chemical vapor deposition (CVD) and small graphene-based platelets, produced by chemical treatment of graphite by solution processes. The latter can be easily applied to prepare homogeneous colloidal suspensions of graphene-based platelets [29]. Therefore, it can be used in many practical applications such as energy storage materials [35], energy conversion systems [32], polymer composites [33] and paper-like materials [36]. It has also been targeted for supercapacitor electrodes due to its high electrical conductivity that

improves performance over a wide range of voltage scan rates [35].

2. BACKGROUND OF STUDY

2.1. Chemical Vapor Deposition

2.1.1. Thermal CVD

Chemical vapor deposition is a process widely used to deposit or grow thin films, crystalline or amorphous, from solid, liquid or gaseous precursors of many materials. CVD technique is the most suitable technique for large scale production of mono- or few-layer graphene films. The major productions of graphene for electronic devices rely on catalytic CVD [37]. Recently, high-quality graphene has been achieved by CVD using metal foils as catalytic substrates such as Cu [38-39], Ni [40-41], Pt [42-44] and Ru [45], etc. A typical CVD process uses nickel as a substrate where carbon is dissolves in the nickel substrates and then continues by a precipitation of carbon on the substrate by cooling the nickel. Then, followed by placing the nickel substrate in a CVD chamber at a vacuum of 10^{-3} Torr and temperature below 1000ºC with a dilute hydrocarbon gas [46]. This method is suitable for large scale production of graphene films as it can produce a large domain of graphene. It only consumes a low cost and has the potential to enable several large area applications of graphene in the future. However, the cons of CVD technique include the difficulty to control the process, thickness and quality of graphene may be affected due to the different cooling rates and also the graphene growth is self-limiting [47]. CVD process will damage the electrical conductivity of grapheme, due to the disruption of the network of sp^2 carbon-carbon bonds in the graphene sheets [48].

Cu or Ni are the most widely used catalyst due to their low cost, etchability and large grain size [49-51]. Even though, it is significance noting that other metals can be successfully used for catalyzing CVD graphene growth, e.g. Pt [52], Co [53], Ir [54] or Ru [55]. This review highlight almost entirely on Cu and Ni, as they are currently the most promising candidates for upscale graphene production with direct links to applications in electronic or optics.

Generally, during the CVD of graphene, the precursor in a gas phase is injected into a reaction chamber where it reacts with a catalyst at elevated temperature and graphene is formed on the

catalyst's surface. The growth temperatures range from several hundred degrees Celsius up to the melting point of the catalyst metal. Depending on the catalyst, two fundamental mechanisms of graphene growth are proposed. For polycrystalline Ni, the precursor is decomposed at the surface and carbon is dissolved in the metal. When the substrate is cooled, the solubility of C in Ni decreases and graphene first segregates and then grows on the Ni surface. Hence, it is very important to control the cooling conditions to reach a monolayer graphene (1LG) [56].

2.1.2. Plasma Enhanced CVD

Plasma Enhanced Chemical Vapor Deposition (PECVD) is alternatively used to promote graphene growth rate at relatively lower temperature and have been widely used in the synthesis or functionalization of carbon nanomaterial such as graphene [57]. During the fabrication of "nanostructured graphite-like carbon" using a dc discharge PECVD, thick graphite structured is obtained. For PECVD, besides of using a furnace to provide the heat energy for substrate annealing, an RF frequency AC current is passed through the substrate. This spark ionizes the gases in the chamber, enhancing the deposition onto the substrate [58]. A very short deposition time (< 5 min) and a lower growth temperature of 650°C compared to a thermal CVD method that approach 1000°C are among the advantages of this PECVD [46]. However, PECVD produces lower quality graphene films compared to thermal CVD [59].

2.2. Chemically Derived Graphene

2.2.1. Synthesis of Graphene Oxide and the Reduction

Low cost graphene can be produced in bulk through a chemical oxidation and reduction process using graphite as a raw material and the product obtained is known as reduced graphene oxide (RGO) [60]. Graphine oxide (GO) has received much attention because it is more available and easily scalable than other 2-dimensional carbon materials. In addition, it has tunable electrical and optical properties that are tuned through chemical and thermal routes [61]. The use of GO which is exfoliated from layered GO is the most promising method for the generation of colloidal suspensions because of the presence of a wide range of hydrophilic oxygen-containing functional groups and the high tolerance of such reactive functionalities for further chemical modification. The GO is commonly synthesized through

the oxidation of graphite using oxidants including concentrated sulphuric acid, nitric acid and potassium permanganate based on Hummers method [46]. In [47] proposed a method of oxidation of graphite to improve and enhance the oxidation of graphite. In their study, they used a water free mixture of concentrated sulphuric acid, sodium nitrate and potassium permanganate. The final suspension with hydrogen peroxide (H_2O_2) was treated to remove impurities due to permanganate and manganese dioxide [62]. This oxidative treatment of graphite was first introduced by [63] in 1909. The Hummers method was accomplished within two hours instead of several days and weeks and the whole process was carried out at temperature below 45ºC. Therefore, Hummers method is the most efficient method for oxidation of graphite and gives a brownish graphite oxide. Quick oxidation in Hummers method was easily achieved because of the formation of dimanganese heptoxide. This is due to the use of $KMnO_4$ which has strong ability to oxidize carbon atoms in graphite [64]. Oxidation of graphite via this method can be done from various commercially available sources, but graphite flakes are the most commonly used. However, this mechanism is very challenging to ascertain, owing to the complexity of flake graphite and the inherent defects that may occur. As for reduction, the chemical reduction of graphene oxide sheets has been performed by several reducing agents including hydrazine [61]. Unlike other strong reductants, hydrazine hydrate does not react with water and was found to be the greatest one in producing very thin and fine graphite-like sheets. However, it requires great care because it is highly toxic and potentially explosive. A number of several techniques have been explored as an alternative ways. For example, the use of Sodium borohydride ($NaBH_4$), hydroquinone, gaseous hydrogen, vitamin C and strong alkaline solution as a reductant. As an alternative chemical method, a research using this method such as electrochemical reduction, photocatalytic reduction and reduction using photocatalytic flash has been done [61].

2.2.2. Surface Functionalization of Graphene Oxide (SFGO)

In general, there are two major categories of functionalization which are chemical and nonchemical. Both can induce some property changes for graphene, but the chemical routes are more effective. Chemical functionalization is recognized through the formation of new covalent bonds between the atoms native to RGO/GO and the guest functional groups. In

contrast, nonchemical functionalization is mainly based on π interaction between guest molecules and RGO/GO which are mainly a physical interaction. Chemical functionalization of graphene can be used to tailor the electronic properties of graphene via doping and bandgap engineering effects, produced by chemical modification or adsorption of molecules onto the graphene surface [14-15]. The research also demonstrates that the size of the graphene (particularly the thickness of the ribbons) is strongly affects the reactivity of graphene and the application of the functionalized graphene [65]. The thinner the ribbons, the more reactive they are. Moreover, it is also confirmed that carbon atoms on the ribbon edge are more reactive than those in the middle of the ribbon [65].

2.3. Graphene Characterization

The transparency of graphene that has indeed grown on a metallic foil is difficult to verify with the naked eye. Thus, the Raman spectroscopy can be used to observe the presence of graphene. In this method, a laser is pointed at the material and the re-emitted light is measured. The incoming laser light excites the characteristic of molecular vibrations in the sample, which emit photons at characteristic frequencies. Therefore, there is graphene on the copper sample if the frequencies associated with carbon-carbon bonds are observed [66]. The Raman spectra of all carbon materials showed a couple of bands in the range of 1000 to 3000 cm-1 region. By analyzing their shape, intensity and positions it was possible to distinguish amorphous carbon, graphite, carbon nanotube and graphene [67].

2.4. Graphene Properties

2.4.1. Electrical Transport Property

One of the most interesting aspects of the graphene is its highly unusual nature of charge carriers, which behave as massless relativistic particles or Dirac fermions. Dirac fermions behavior is abnormal compared to electrons when subjected to magnetic fields; for example, the anomalous integer Quantum Hall Effect (QHE). This effect was observed at room temperature [1-2]. The graphene has distinctive nature of its charge carriers that imitate relativistic particles, considered as electrons those have lost their rest mass which can be described by (2 + 1) dimensional Dirac equation [4-5]. Various factors have been proposed on the effect of the conductivity such as interaction with the under laying substrate while

measurement, surface charge traps [68].

2.4.2. Optical Properties

Several reports confirmed that single layer graphene absorbs 2.3% of incident light over a broad wavelength range in spite of being just a monolayer [27]. Graphene transmittance can be well described in terms of fine structure constants [69]. The exceptional electrical transport properties in conjunction with optical properties have fueled a lot of interests in novel photonic devices. It has also been suggested that the zero band gap, large area monolayer and few layer graphene FET can be used as ultrafast photo detectors [70]. The absorption of light on the surface generates electron-hole pairs in grapheme, which would recombine quickly (picoseconds) depending upon the temperature as well as electrons and holes density [71]. When an external field is applied, these holes and electrons can be separated and photo current is generated. Similar behavior occurred in the presence of internal field. This field has formed near the electrode and graphene interface [70]. Another property of graphene is photo luminescence (PL), where it is possible to make graphene luminescent by inducing a suitable band gap. Two routes have been proposed, the first method involves cutting graphene in nanoribbons and quantum dots. The second one is the physical or chemical treatment with different gases to reduce the connectivity of the p electron network [29].

2.4.3. Mechanical Properties

After carbon nanotubes, graphene has been reported to have the highest elastic modulus and strength. The strongest bond in nature, the C-C bond covalently locks these atoms in place giving them remarkable mechanical properties [72]. The mechanical properties of the single, bilayer and multiples layer of graphene are summarized in Table 1. A single defect free graphene layer is predicted to show the highest intrinsic tensile strength with stiffness similar to graphite. One method to determine the intrinsic mechanical properties is to probe the variation of the phonon frequencies upon the application of tensile and compressive stress [49]. The Raman spectroscopy is one of the techniques which can monitor the phonons frequency under uniaxial tensile and hydrostatic stress.

Table 1. Mechanical properties of graphene

Method	Material	Mechanical Properties	References
AFM	Mono layer graphene	E = 1 ± 0.1 TPa	[13]
		rint = 130 ± 10 GPa at eint = 0.25	
Raman	Graphene	Strain _1.3% in tension	[73]
		Strain _0.7% in compression	
AFM	Mono layer	E = 1.02 TPa; r = 130 GPa	[14]
	Bilayer	E = 1.04 TPa; r = 126 GPa	
	Tri-layer	E = 0.98 TPa; r = 101 GPa	

2.4.4. Thermal Properties

Most of the thermal properties of graphene are derived from those of graphite and bear the imprint of the highly anisotropic nature of this graphite. Heat removal has become a fundamental issue for continuing progress in the electronics industry due to increased levels of dissipated power. Carbon allotropes such as diamond, graphite and carbon nanotubes have shown higher thermal conductivity due to strong CAC covalent bonds and phonon scattering. Previously, carbon nanotubes are recognized for the highest thermal conductivity with room temperature value 3000 W/mK for MWCNT [50] and 3500 W/mK for single wall CNT. Nevertheless, a large thermal contact resistance is the key issue with CNTs based semiconductor. Recently, the highest room temperature with thermal conductivity up to 5000 W/mK for the single layer graphene (pure defect free graphene) has been reported [74] whereas for supported graphene conductivity is 600 W/mK [74]. Fig. 1 shows a new approach of determining thermal conductivity of a thin atomic layer of graphene [75]. By using this method, a suspended graphene layer is heated by laser light (488 nm) and the heat propagated laterally towards the sinks on side of the corner of the flakes. The temperature change was determined by measuring the shift in the graphene G peak using confocal micro-Raman spectroscopy which acts as a thermometer. The defects edge scattering [76] and isotopic doping was found as the factors that affected the thermal conductivity [77].
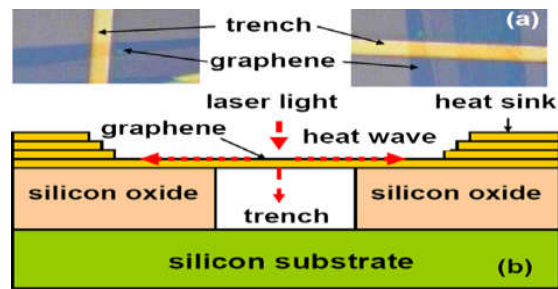
Fig.1. (a) High-resolution scanning electron microscopy image of the suspended graphene flakes (b) Schematic of the experimental setup for measuring the thermal conductivity of graphene

2.5. Chemically Derived Graphene: Properties and Applications of RGO

2.5.1. Application of RGO for Photodetector

Photoconductivity of bulk RGO thin film has been studied by previous scholars using various intensities of light, external field and photon energies. Their studies showed higher photocurrent under same photon energy with the increasing of incident light intensity and external electric field. RGO film generates more charge carriers upon increasing of external field and light intensity. Thus, RGO films generate more charge carriers per unit volume upon irradiation of higher photon energy. Moreover, RGO film shows high photocurrent generation efficiency compared to single walled nanotube (SWNT). Therefore, since RGO thin films have a lot of defects, it will also help in dissociation of excitons into free-carriers and causes a hole-electron separation at the interface that will result in positive photo-voltage.

2.5.2. RGO for Electrochemical Sensors and Biosensors

RGO possess better properties for electrochemical and biological sensors that arise from their different functionalities on the edge and very sensitive to the change in chemical and biological environment. The responses have been analyzed by the changes in term of conductivities, capacitance and doping effects. It also has been used as biosensors as well. The fabrication and functioning of a novel RGO-based is being reported recently. RGO increases both the conductivity and the mobility when incorporate with DNA due to the interaction between charged amine group and the RGO.

2.6. Challenges and Future Applications

2.6.1. Challenges of Using Graphene

Every new technologies and products have their own challenges in this modern world. The

biggest challenging problem to be mass production is the cost of production of graphene are still very expensive. Many major companies in the world charge high price for their service to produce graphene and the top equipment facilities required. Besides that, another significant challenge is the properties of graphene such a good conductor cannot be switched off so it cannot be adopted into electrical systems. However, researcher has been studies about to solve this problem and make graphene are applicable for electrical systems.

2.6.2. Future Applications of Graphene

2.6.2.1. Medicine

Medicine is the most potential field that can be applied including development of bioelectric sensors and bio imaging devices, drug and gene delivery, more effective powerful disinfectants and DNA sequencing. Besides that, the artificial implants are also being explored, the neural system can be connected directly by harnessing graphene's conductive properties. Graphene could also be used to produce more effective spinal surgical equipment.

2.6.2.2. Computer Components

A lot components in computer can be upgraded and improve by using graphene as main material. Graphene can be used to improve the computer processing power of computer chips. Many researchers study and try to develop new brand of computer and it will likely bring the trend computers with graphene-based CPUs that are more powerful than our current devices and that consume less energy.

3. CONCLUSION

1. Graphene and polymers based nanocomposites show promising growth in technology and applications. Nevertheless, some raising challenges need to be addressed and resolved regarding synthesis methods, applications and costs in order to realize the potential of this graphene.

2. Graphene have shown the lowest percolation threshold for electrical conductivity and improved mechanical, thermal and gas barrier properties. Yet, the main issues such as the homogeneous distribution of individual graphene platelets, connectivity, orientation and interface bonding with matrix still require more study.

3. The chemical exfoliations of graphite into GO, followed by thermal and chemical reduction has led to a cost effective production route of reduced graphene oxide on a large scale.

4. There are few possible applications of graphene-based material which include transparent flexible electrodes, energy storage, graphene/polymer composites for mechanical parts, sensors and organic electronics.

5. Large surface of low density GO and RGO in mass production may cause handling difficulty, which can initiate a health risk due to inhaling and handling toxic reducing chemicals. Thus, the health risk associated with graphene and their derivatives needs to be thoroughly evaluated.

6. As the visibility of monolayer graphene under an optical microscope requires the suitable substrate to create contrast between different layers due to interference, more research is required to develop a simple detection method of pristine graphene [78] that is independent of support material.

4. ACKNOWLEDGEMENTS

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