Synthesis of Graphene based nanocomposites and their application – A Review

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Abstract—There are two categories in the graphene preparations which are top-down and bottom-up methods. Top-down methods consist of mechanical exfoliation, chemical exfoliation and chemical synthesis reduction. Meanwhile, chemical vapor deposition (CVD), pyrolysis and epitaxial growth synthesis under bottom-up methods. Graphene has its own limitation and unsuitable for certain applications. Thus, functionalizing the graphene with selected molecules and nanomaterials may result in graphene functionalized nanomaterials that improve the feature of the graphene. Many methods can be done to synthesize graphene based on nanocomposites and can be divided into two types which are in-situ methods and ex-situ methods. Hydrothermal methods, electrochemical deposition methods and reduction methods are categorized in in-situ methods, while covalent interaction and non-covalent interaction are categorized in ex-situ methods. Application of graphene based nanocomposite on biosensor and supercapacitor is discussed in this review paper.

Keywords—graphene; nanocomposite; supercapacitor; biosensor

I. INTRODUCTION

There are various existing allotropes with different dimension, which is zero-dimensional (fullerenes), one-dimensional (carbon nanotubes), two-dimensional (Graphene) and three-dimensional (Graphite) [1, 2]. In carbon materials, graphene can be considered the basic building block, which can produce many other new materials. Graphene can be rounded into fullerenes by the heating process, rolled up into cylindrical carbon molecules to form carbon nanotubes (CNTs) and layered 2-Dimensional (2D) structure to graphite [1, 3, 4]. Graphene is the thinnest material in the universe in the form of a single-layer sheet of sp2 hybridized carbon of atoms [5-7]. The carbon atoms in graphene are in a honeycomb crystal lattice structure that is bounded by a weak van der Waals force [3, 8].

In 2004, graphene was discovered, where scientists found a thin graphene flake on the Scotch tape method. This founding was done by rapidly sticking and peering off a layer of graphite
using tape until the thinnest layer was found. In 2010, Nobel Prize in Physics was given to Andre Geim and Konstantin Novoselov for their discovery of “for groundbreaking experiments regarding the two-dimensional material graphene” [4, 6, 9]. These Nobel Prize award has attracted researcher attention to graphene and in addition to the uniqueness of graphene properties that are useful for improvement in a certain application. Graphene has very high stiffness with young’s modulus of 1TPa, large theoretical specific surface area around 2630 m2g-1 and high intrinsic mobility which is 200000 cm2v-1s-1. It has the highest electrical conductivity at room temperature with thermal conductivity of approximately 5000 Wm-1K-1. All these properties are useful for various graphene applications [3-5, 10].

Despite its excellent properties, graphene also has its limitation where it was resulting in the limit on certain applications. Thus, to increase the exposure of graphene in real applications, graphene is of immense interest in nanocomposite materials. There are many methods that can be done to prepare the functionalized graphene nanocomposites, such as chemical vapor deposition, hydrothermal and solvothermal growth [11]. This review is intended to discuss the method to synthesis graphene that based on nanocomposites as well as its applications.

II. SYNTHESIS OF GRAPHENE

To use graphene in a certain application, synthesis of graphene is needed, where it is a process of fabrication and extracting graphene. The first trial of graphene synthesis was by B. Lang et al. in early 1975, where the thermal decomposition of graphene is used to form mono- and multilayered graphene [12]. Two types of synthesis that can be used are top-down and bottom-up methods. The top-down method is referred to as the destruction method approach, while the bottom-up method is known as the construction method approach [5]. Figure 1 shows the graphene synthesis techniques.

![Graphene synthesis techniques](image)

Mechanical exfoliation, chemical exfoliation and chemical synthesis reduction are categorized in a top-down method. Mechanical exfoliation is a repeated peeling process which is also used by Andre Geim and Konstantin Novoselov [13]. This process used scotch tape to extract thin layers of graphene by repeating peeling off the tape to separate the graphene from a graphite crystal [5, 14, 15]. Chemical exfoliation process consists of dispersion in an appropriate solvent, exfoliation and purification [5]. The process was first prepared by Broglie in 1859 where the graphite will react with the potassium chloride in fuming nitric acid [16, 17]. After several years, Staudenmaier then improved the synthesis by mixing nitric acid and sulfuric acid and then potassium chloride was added to the mixture reaction [18]. Nowadays, Hummers’ method is the most common method used in preparing GO. Three important chemical (KMnO₄, NaNO₃, H₂SO₄) are used in this method [19, 20]. Figure 2 shows the comparison of GO preparation by using Hummers’ method where HGO is Hummers’ method, IGO is Improved Hummers’ method and HGO+ is Modified Hummers’ method respectively. In Hummers’ method, the amount of chemical used for KMnO₄: H₂SO₄: NaNO₃ are 3 : 1 : 0.5. In Improved Hummers’ method, NaNO₃ is excluded from the reaction and replace with phosphoric acid (H₃PO₄), increasing the amount of KMnO₄ and performing the reaction in a 9:1 mixture of H₂SO₄/ H₃PO₄. Meanwhile, for Modified Hummers’ method, the amount of KMnO₄ is increase. Among these three method, modified Hummers’ method produce high yield than other method. Meanwhile, chemical vapor deposition (CVD), pyrolysis and epitaxial growth synthesis are categorized in a bottom-up method [5, 21]. CVD is a chemical process that uses a carbon source as a precursor and will decompose on the surface of the substrate at high-temperature conditions [5, 14, 22].

III. SYNTHESIS OF GRAPHENE BASED NANOCOMPOSITE

There is a certain limitation of the graphene to a certain application. Thus, functionalizing the graphene with certain molecules and nanomaterials may result in graphene functionalized nano-materials that improve the feature of the graphene [23]. The combination of graphene and its derivative with nanocomposites gives open eyes to the researcher of its potential for enormous applications [24, 25]. Many methods can be done to prepare graphene nanocomposites. These methods are divided into two types which are in-situ methods
and ex-situ methods. Hydrothermal methods, electrochemical deposition methods and reduction methods are categorized in In situ methods, while covalent interaction and non-covalent interaction are categorized in ex-situ methods [2, 11, 22].

A. In-Situ Method

1) Polymerization method: In-situ polymerization technique consists of mixing the liquid monomer with graphene, and the mixture is then dispersed with a suitable initiator by either heater or radiation [13, 25-27]. For example, this method is used to prepare GO-Contained Polyimide nanocomposites where GO was dispersed in N, N-Dimethylacetamide (DMAc). Then, before adding the diamine (ODA), the suspension was ultrasonicated for an hour to obtain the GO suspension in DMAc. After the ultrasonic steps, the suspension is then transferred into the three neck round bottom flask and stirred for about 10 minutes before adding the dianhydride (PMDA) [28]. The same methods are also used to prepare PEDOT:PSS/graphene nanocomposites. The first steps required graphene aqueous dispersion to be prepared using chemical exfoliation. Then, EDOT and the graphene aqueous dispersion were used to produce PEDOT:PSS/graphene nanocomposites using in-situ polymerization [29].

2) Hydrothermal Method: Hydrothermal method is categorized as one of the in-situ methods. This method is classified as in-situ method because the water is used as a solvent [30]. Heating and stirring are included throughout the process. After the heating and stirring process, the mixture is sealed into the Teflon-lined stainless steel autoclave before being cooled at room temperature. Basically, the chemical and thermodynamic parameters will affect the final formation of the particle in the process [31]. Fig. 5 shows the schematic diagram of Graphene-MnO₂ preparation by using hydrothermal methods. In the process, MnCl₂, GO powder, and NaOH were dissolved in deionized water, and then stirred continuously. Then sealed the mixture in a Teflon-lined stainless steel autoclave for hydrothermal process [32, 33].

W.chen et al. synthesized the graphene/MnO₂/PANI nanocomposites using hydrothermal methods [34]. Graphene was mixed with aniline, MnSO₄ and hydrochloric acid (HCl). The mixture is then will go through an ultrasonicated process before transferred into the Teflon-lined stainless steel autoclave. Then, as an initiator, a fresh solution ammonium persulfate in HCl and KMnO₄ in deionized water were transferred to Teflon-line stainless steel autoclave. The Teflon will then be sealed and heated for about 10 h. After the heating process, the mixture is then filtered and dry in the vacuum before containing the Graphene/MnO₂/PANI nanocomposites. Besides, graphene/Bi₂WO₆ composites is prepared by hydrothermal method where it used ethanol as a reducing agent [35].

3) Electrochemical deposition: The other type of synthesis for graphene nanocomposites is the electrochemical deposition method, which can be called electrodeposition. In this method, a certain substrate will be selected and used as an electrode, while the mixed solution of catalyst precursors is used as the electrolyte of electrolytic cells. By controlling the current, potential and deposition time throughout this process, a uniform distribution of nanoparticles layer can be obtained [33]. Au-graphene nanocomposites electrode was prepared by H.Shu et al. through electrodeposition methods [36]. In the process, DC regulated power supply with a Pt plate was used as a positive electrode while GCE was the negative electrode. Before going through electrodeposition, the precursor solution was synthesized to obtain a complete mixture of HAuCl₄ in GO suspension. The CGE was then immersed in the suspension, and DC-regulated power supply was conducted during the electrodeposition process. Figure 3 shows the steps of formation of Au-graphene nanocomposites. Y.Mai et al. produced a composite coating of RGO/Cu using a pulse current electrodeposition process where H₃PO₄ was used as a substrate, and alumina powders were polished onto the surface of the substrate [37]. To remove the oil contamination, it is then sonicated in acetone as well as ethanol. Pure copper was used as a counter electrode in order to maintain the copper ion concentration in the plating solution. After the electrodeposition process, the deposits were then rinsed in deionized water before being dried in the air.
4) Reduction methods: Reduction methods is another type of in-situ methods that commonly used to synthesize metal nanoparticle/GO and metal nanoparticle/rGO hybrids. It is a reduction of metallic salts that using reducing agents such as sodium citrate, ethylene glycol and sodium borohydride [2, 38]. The steps of reduction process is when the mixture of metal precursor and GO sheets are mixed into the aqueous solution and reduced concurrently. To be more specific related to the mechanism of the reduction process is when the existence of negatively charged functional group on the surface of GO such as hydroxyl (C-OH), carbonyl and carboxyl (COOH) allow the nucleation process of positively charged metallic salts [39]. Besides, the addition of reducing agent in the process exhibit the reduction of metal ions which results in growth of metal nanoparticles on the GO and rGO surface [38].

P. Marques et al synthesized silver/graphene nanocomposite by using in situ reduction methods [20]. By simultaneous reduction of Ag⁺ and GO in the presence of reducing agent, hydrazine hydrate (N₂H₄.H₂O ), silver nanoparticles were synthesized on the surface of GO sheets where Ag⁺ was nucleated onto graphene and both Ag⁺ and GO were reduced. Besides, RGO/Cu₂O nanocomposites was prepared by I. Roy et al [40] using the same methods. GO dispersion is formed by using ultrasonic method. Then, an aqueous solution of CuSO₄ was added to the dispersion to produce a suspension. NaOH solution was added in order to control the pH. The formation of RGO/Cu₂O nanocomposites can be produced by adding an aqueous solution of lactulose into the mixture and sonicated in the conical flask [40]. Figure 4 shows the flow of RGO/Cu₂O nanocomposites preparations.

B. Ex-Situ Methods

In this ex-situ method, the surface of graphene sheets will be attached to the nanoparticles that have been synthesized, where this attachment can be either in covalent interaction or non-covalent interaction. This method includes π-π stacking, Van der Waals forces, hydrogen bonding or electrostatic interaction [2]. For non-covalent interactions, the process is carried out by absorption of molecules, which does not include any chemical reactions. It is slightly different from covalent interactions, where in covalent interaction, functionalization can be achieved by chemical reaction [2, 41].

IV. APPLICATION OF GRAPHENE BASED NANOCOMPOSITES

A. Supercapacitors

A supercapacitor is electrochemical energy storage that has both characteristics of capacitors and batteries. Superconductors have a properties of long cycle life, high-power density and environmental protection compared to batteries and capacitors [42]. Besides, the structure of 2D nanocrystalline sheets contribute to a high performance of energy storage because of short ion diffusion path, large specific area as well as high electron conductivity. Micro-ultracapacitors (MSC) by using MXene/rGO (EGMX) hybrid film is prepared in order to examine the effectiveness of the 2D nanocrystalline sheets in the field of supercapacitor [43]. It shows excellent results in a capacitance area and volume which exceeds most advanced graphene-based MCSs and also shows an excellent performance in an electrochemical field. Besides, the combination of graphene and various polymer also
resulting a high performance of supercapacitor. In this combination, a polymers with a great electrical conductivity and a high pseudo-capacitance are used such as PANI and PPy. Graphene/PANI nanocomposites is produced by in situ anodic electrochemical polymerization of aniline monomers into a PANI film on a graphene paper [41, 44].

B. Glucose Biosensor

Biosensors are capable of producing electroanalytical data using biological recognition system. Graphene has become the most promising material for producing a sensor with high sensitivity, lower detection limit, selectivity as well as good stability due to its unique properties and structures [45]. The irst electrochemical biosensor was developed by Clark and Lyons in 1962 [23]. These electrochemical sensors are used for monitoring blood glucose levels using enzymes as electrode materials. There are three steps of development in electrochemical glucose sensors. The first is when the measurement has first relied on oxygen consumption of enzyme-catalyzed reaction where the glucose levels can be identified by measuring the amount of enzymatic reaction that generates H₂O₂. The second step is when the mediated electron transfer (MET) -based glucose sensor are used which through this electron transfer process between the flavin adenine dinucleotide (FAD) site of GOx and also the electrode’s surface [22].

To produce a glucose sensor [46], AuNPs is attached on the surface of the GO nanosheet by using benzene (Ph). Then, 4-aminophenyl modified from a glassy carbon electrode (GCE) is then attached to the GO-Ph-AuNPs nanocomposites. After that, the GCE/GO-Ph-AuNPs nanocomposites were synthesized with 4-carboxyphenyl (CP), and GOx was covalently combined to form GCE/GO-Ph-AuNPs—CP/GOx base glucose sensor. Besides, the sensitivity of biosensor increased by accelerating the direct electron transfer (DET) properties. This can be achieved due to high conductivity, high intrinsic mobility of electrons and holes as well as high specific surface area of graphene [47]. To modify glassy carbon electrodes (GCE) that have a high loading of glucose oxidase (GOD), which is 1.12×10⁻⁹ mol/cm², RGO-CHI nanocomposites were used by Kang et al.[48] in which the linear detection range obtained was (0.08 – 12 mM). Besides, polyethyleneamine-functionalized ionic liquid (PFIL) was introduced to design a polyn vinylpyrrolidone (PVP) – protected RGO/GOD/PFIL-modified GCE, which can disperse the RGO as well as can immobilize the negatively charged GOD. The linear range detection of this was 2 – 14 mM, which also provides good reproducibility [47].

V. CONCLUSIONS

In summary, this paper presents a review of graphite nanocomposites preparations based on in-situ methods such as polymerization method, hydrothermal, electrochemical and reduction method. Besides, ex situ methods also have been discussed, which include covalent interaction and non-covalent interaction. The methods of functionalizing graphene and nanocomposites are widely used in certain applications to improve their effectiveness and sensitivity performance.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interest regarding the publication of this paper.

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