Graphene from waste and bioprecursors synthesis method and its application: A review

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INTRODUCTION

Nowadays, carbonaceous materials like porous carbon, carbon nanotubes and graphene have gathered great interest owing to their high surface area and pore size, ease of functionalization and chemically stable structure (İlbay et al., 2017). Generally, graphene has remarkable electronic, mechanical, and thermal properties (Somers, 2015). In addition, graphene also has large theoretical specific surface area (2630 m^2 g^-1), high intrinsic mobility (200,000 cm^2 V^-1 s^-1), high Young’s modulus (~1.0 TPa) and thermal conductivity (~5000 W m^-1 K^-1), high optical transmittance (~97.7%) and good electrical conductivity (Bhuyan et al., 2016). Thus, it is applied in many applications which include polymer composites, energy-related materials, sensors, paper-like materials, field-effect transistors (FET) and biomedical applications (Gao, 2015). The structure of graphene is consisted of two equivalent sub-lattices of carbon that bonded together with σ bonds. Meanwhile, each carbon atom in the lattice has a π orbital that contributes to a delocalized network of electrons (Zhu et al., 2010).

Conventionally, graphene is formed from a technique called micromechanical cleavage in year 2004 which obtained by extracting monolayer sheets from the three-dimensional graphite. However, a lot of methods nowadays that can be applied to synthesize graphene without the formation of graphene oxide (GO) such as epitaxial growth by ultrahigh vacuum graphitization, chemical vapor deposition (CVD), solvothermal synthesis with pyrolysis and electrochemical methods (Antolini, 2012; Zhang et al., 2009). Nevertheless, the chemical process of the production of graphene from exfoliation of graphite oxide involves hazardous and toxic reagents even it shows a route for scalable synthesis (Purkait et al., 2017). Generally, preparation of synthetic graphene can be divided into two categories (i) top-down and (ii) bottom-up.

For top-down approach, graphene is exfoliated into graphene layers via overcoming van der Waals forces between the layers using oxidation or other treatments (Yi and Shen, 2015). However, during the sheet separation, graphene tends to possess surface defects which can cause re-agglomeration and low yields (Das et al., 2017). In addition, chemically produced, reduced graphene oxide is not acceptable for energy storage device as it suffers from poor electrical conductivity (Purkait et al., 2017). On the other hand, graphene needs to be prepared from scratch in bottom-up method. It starts with simple carbon molecules like methane and ethanol (Chua and Pumera, 2014). Bottom-up methods include chemical vapor deposition (CVD) and epitaxial growth on silicon carbide (SiC) (Bhuyan et al., 2016).

Conventional method of preparing graphene

The most common conventional method to produce graphene is via mechanical exfoliation method which also known as "scotch-tape method". By using a scotch-tape, high purity graphite will be separated into few layers of graphene (Martinez et al., 2011). However, it is very challenging to overcome the van der Waals attraction between adjacent graphene flakes when preparing graphene from this method (Yi and Shen, 2015). In addition, the monolayer that will be formed is difficult to control (Chang et al., 2010).
CVD is comparatively an easier method to produce graphene with desired features. This method involves the decomposition of a carbon feedstock either polymers or hydrocarbons (Seah et al., 2014). To synthesize a good quality of graphene via CVD, few ranges of transitions metals can be used which include platinum (Pt), cobalt (Co), nickel (Ni) and copper (Cu) (Seah et al., 2014; Lee et al., 2016). By applying this technique, the number of graphene layers can be controlled by the type and thickness of the catalyst chosen. On the other hand, the size of catalyst will affect the graphene size (Seah et al., 2014).

Besides that, GO can be prepared via several methods which are modified Hummers, Brodie and Staudenmaier (Seah et al., 2014). Meanwhile, graphene is commonly produced by reduction of GO (Park et al., 2011) through the removal of the oxygen containing groups with the recovery of a conjugated structure (Pei and Cheng, 2012). GO can be reduced via chemical or thermal reduction (Sun and Shi, 2013). Chemical reduction of GO is commonly used due to several advantages such as the product can be produced in bulk and graphene with processability and functionality can be obtained (Yuan et al., 2015). In addition, this method is very suitable to be carried out under mild conditions (Yin et al., 2015) and cheaper (Pei and Cheng, 2012). The common reductant used to reduce GO includes hydrazine, sodium borohydride (NaBH₄) and hydrobromic acid (HBr) (Fernández-Merino et al., 2012). On the other hand, thermal reduction usually need high-temperature treatment (1000 – 1100 °C) (Yin et al., 2015) and this will prevent the rGO to be redispersed in solutions (Sun and Shi, 2013). Unfortunately, the reduction process can cause structural defects into the produced graphene (Seah et al., 2014).

Table 1 summarizes the conventional method used to produce graphene.

| Method                          | Advantages                             | Disadvantages                                      | References |
|---------------------------------|----------------------------------------|----------------------------------------------------|------------|
| Mechanical exfoliation (scotch-tape) | Able to produce a single layer of defect-free graphene. | Difficult to overcome the van der Waals attraction. | (Singh et al., 2011; Lee et al., 2013; Yi and Shen, 2015) |
| CVD                             | Simple method.                         | Not suitable for large-scale production.           | (Zhu et al., 2010; Seah et al., 2014; Yin et al., 2015) |
| Reduction of GO                 | Easier to control the number of graphene layer. | Not suitable for large-scale production.           | (Dubin et al., 2010; Sun and Shi, 2013) |
|                                 | Large surface area of graphene.        |                                                   |            |
|                                 | High quality of graphene with minimal defects. |                                                   |            |
|                                 | Graphene produced is suitable for energy applications. | Produced graphene with many defects. |            |
|                                 |                                       | Environmental issues (hazardous reductant is used in most of the reduction processes). |            |

The present review is mainly focused on graphene preparation using different precursors instead of aforementioned conventional precursors. The waste generation and accumulation become inevitable, so wise use of any waste is a commendable approach. Further converting the waste into advance material-like graphene is an appreciable act. Bio-precursor such as chitosan, glucose, and alginate, also supports the preparation of graphene. Even coal has been used to prepare graphene quantum dots. The entire review deals with the study on preparation of graphene via different unusual precursors, which will be discussed in later section with reference to literature. Every approach has its own merit and demerit, and nevertheless, each approach is admirable and novel. If graphene is successfully and economically produced using biomass or other waste, it can be used for several applications from energy to environment.

**Importance to prepare graphene from different precursors**

Graphene, which is prepared from conventional method may not compatible for polymer composites because it cannot produce graphene in a large amount (Kim et al., 2010). Currently, bio-waste materials have been a great source for production of carbon. In addition, bio-waste materials are abundant and need for recycling. Furthermore, the management of waste biomass is challenging especially in well-developed countries. Thus, it is suggested to convert the material into carbonaceous materials which can be used in enormous applications (Purkait et al., 2017). Hence, researchers have put a lot of effort to synthesize graphene sheets using eco-friendly biomass precursors such as waste corn shell, egg shell and gelatin (Chen et al., 2016).

**Graphene derived from bioprecursors and waste material**

**Glucose-based graphene**

Glucose or also known as sugar molecule (C₆H₁₂O₆) is abundant and renewable carbon source. Recently, researchers have started to use glucose as a starting material to prepare graphene (Priyanka and Saravanakumar, 2017). Zhang and coworkers reported that graphene sheet is obtained via carbonization and calcination of a glucose and activating agent mixture (Fig. 1) (Zhang et al., 2014). FeCl₃ is necessary to obtain high-quality graphene material. From the Raman spectrum, there are three typical bands found which are the D-band, G-band and 2D-band (Zhang et al., 2014; Wu et al., 2016). G-band indicates the existence of sp²-hybridized carbon atom. Meanwhile, the defects like disorders, edges and boundaries of the graphene are shown by the D-band and the 2D-band provides the number of layers of the graphene material. Without the addition of activating agent, the quality of the graphite material is disappointing due to the amorphous carbon structure. This is proven by the weakening 2D-band while the intensity of the D-band is increased. Upon the addition of activating agent, the properties of graphene are getting better (Zhang et al., 2014). For instance, the electrical conductivity is found to be at 768 S/cm, which is similar to the graphene that is formed via CVD method (Chen et al., 2011). In addition, the peak of the amorphous carbon is decreased and the graphite carbon is increased (20 = 26°) when being analyzed with X-ray Diffraction (XRD). Hence, with the addition of FeCl₃ it can be concluded that a high quality of graphene is obtained. (Zhang et al., 2014).

**Fig. 1 Illustration of preparation of graphene via carbonization and calcination (Zhang et al., 2014).**
Besides that, graphene quantum dots (GQDs) are also derived from glucose. GQDs which are luminescent carbon nanomaterials, have received massive attention in various areas of analytical chemistry. This is because GQDs have higher surface area, larger diameters and better surface grafting properties (Li et al., 2013). Hallaj and coworkers reported that the GQDs are prepared via simple pyrolysis of glucose for chemiluminescence (CL). XRD spectrum of GQDs shows a broad peak around $2\theta = 20^\circ$, which indicated that graphite structure is obtained (Hallaj et al., 2014). Two peaks around 1370 and 1705 cm$^{-1}$ are found in the Raman spectrum which corresponded to the D and G band of graphene, respectively (Tang et al., 2013). It is reported that GQDs shows a small intensity ($I_D/I_G$) which is about 0.5-0.6. This indicates that the produced material is made up of high quality crystalline of graphitic system (Hallaj et al., 2014; Shehab et al., 2017).

**Rice-husks derived graphene**

Approximately, 120 million tons of rice husks are produced annually in the world. Due to the massive production of rice husk, it receive abundant of attention as a starting material to generate high value-added materials such as silica and porous carbon. To prepare graphene from rice husk, typically potassium hydroxide (KOH) is used to activate the agricultural waste. This is because, KOH can greatly helps in the formation of pores in carbon materials including carbon nanotubes, graphene, and carbon fibers, thus enhancing their electrochemical performance (Muramatsu et al., 2014). On top of that, KOH also assists in the formation of high purity graphene material containing stable and clean edges (Priyanka and Saravanakumar, 2017).

Singh and coworkers reported that graphene is synthesized by activating rice husk with KOH and annealing at 900 °C (Fig. 2). The results show that the produced graphene has few layers of graphene with agglomeration of silica particles when it is observed using TEM (Fig. 3(a)) (Singh et al., 2017). Using the same method, Muramatsu and colleague claimed that they have produced graphene with high crystallinity and corrugated containing pores and active edges (Muramatsu et al., 2014). Meanwhile, the $I_D/I_G$ ratio (0.55) on Raman spectrum confirms that the synthesized sample consists of few layers of graphene (Singh et al., 2017). The growth of crystalline graphene is confirmed using XRD. Silica peak around 23° on RHA is disappeared after chemical activation with KOH. On the other hand, weak peaks around (002) and (100) are observed in the graphene sample, which indicated the absence of regularly stacked graphitic structure (Fig. 3(b)) (Muramatsu et al., 2014).

**Chitosan-based Graphene**

After cellulose, chitosan is found to be the second most abundant biopolymer in nature and it has been used in a broad range of applications such as biomedical, pharmaceutical and industrial applications because of its good biocompatibility, biodegradability, and multiple functional groups of amino (NH$_2$) at C-2 and hydroxyl (OH) at C-3 (Kumar and Koh, 2014; Anandhavelu and Thambidurai, 2013). Interestingly, chitosan can adhere to negatively-charged surface or adsorb negatively-charged materials when it is dissolved and carried with the positive charge of –NH$_3^+$ groups. Thus, chitosan has been used widely to disperse nanomaterials and immobilize enzymes for constructing biosensors (Yin et al., 2010). In addition, chitosan is a natural nitrogen containing biopolymer which able to produce graphene that is suitable for electrocatalyst. The presence of nitrogen atoms inside the graphene sheet will greatly enhance their electronic bands and become semiconductor (Lavorato et al., 2014).

Cobos and teamwork reported a novel study on the effect of nano filler (graphene and plasticizer (glycerol)) on chitosan (CS) matrix. Based on the FT-IR spectrum analysis, plasticized CS-graphene has showed that NH$_2$ band is shifted from 1552 cm$^{-1}$ to 1539 cm$^{-1}$ as compared to pristine plasticized CS. This is because, when graphene is introduced into the matrix, there is an electrostatic interaction between negatively-charged surface of graphene with positively-charged chitosan (Cobos et al., 2018). The crystallinity of plasticized CS-graphene is observed under XRD analysis. It shows that plasticized CS-graphene has only a single peak at 20 = 23° which indicated that the incorporation of graphene has resulted in the decrease of the crystallinity of CS (Ogawa et al., 1984). Besides that, the SEM image confirms the existence of graphene as it shows a rough fractured surface and wave-like morphology without any aggregation which indicated that the graphene sheets are dispersed homogeneously in the CS matrix (Figure 4) (Han et al., 2011).
indicated to the chemical binding that associated with amine and amide groups (Akar et al., 2016). Raman spectrum illustrates that there are G-band at 1582 cm\(^{-1}\) and 2D-band at ~ 2700 cm\(^{-1}\). The 2D-band suggests that the graphene is formed in few layers. On the other hand, the \(I_D/I_G\) and \(I_G/I_D\) shows that graphene sheets are defected lesser and thinner in this study (Yang et al., 2010). Around 23\(^\circ\) on RHA is disappeared after chemical activation with KOH. On the other hand, weak peaks around (002) and (100) are observed in the graphene sample which showed the absence of regularly stacked graphitic structure (Figure 3 (b)) (Muramatsu et al., 2014).

**Corn stalk core-derived graphene**

Cellulose biomass is a promising material that can be used to generate sustainable bio-fuels as alternative energy for fossil fuel. Besides that, it can also supply reproducible raw materials for production of chemical products like surfactants, pigments and polymers (Xu et al., 2016). Corn stalk is one of the ample agricultural wastes that is made up of a cortex and a core. The cortex is made up of cellulose and lignin while corn stalk core (CSC) is primarily hemicellulose and lignin and cellulose. CSC is naturally porous, which can form a large surface area of carbon, which is an excellent property for electron transfer and easier for ion diffusion in carbon matrix (Cao et al., 2016).

Liu and coworkers have synthesized CSC-GO via assembly mechanism (freeze-dried process) where GO is firstly prepared by using modified Hummer’s method (Figure 5) (Liu et al., 2018). From the SEM images, it shows that the freeze-dried GO exhibits monolithic structure and after the addition of CSC, the surface of CSC is covered with GO (Figure 6) (Karim et al., 2006). After the addition of CSC, the layers of GO are distracted and stripped into thinner layer (Cong et al., 2011).

On the other hand, Ge and teammates have prepared citric acid functionalized magnetic graphene oxide coated corn straw (CA-rGOCS) via solvothermal system (Ge et al., 2016). It is reported that CA has successfully grafted into mGOCS due to the formation of peak around 1756 cm\(^{-1}\) on FT-IR spectrum, which is belong to CA (Li et al., 2013). Raman spectrum indicates that the \(I_D/I_G\) ratio is reduced when the amount of CS added into the mixture is increased, concluding that the order of carbonaceous material structure and \(sp^2\) cluster size are increased (Ouyang et al., 2015).

**Plastic waste-based graphene**

Plastic is one of the abundant wastes that found on the earth which includes plastic bottles, plastic bags and plastic sheets, which can cause a serious waste of resource and environmental pollution (Cui et al., 2017). Therefore, there are a lot of alternatives to convert this waste into carbon based material. Study conducted by Essawy and teammates reported that, graphene is successfully obtained from polyethylene terephthalate (PET), which is used enormously in pharmaceutical, food and soft drink bottles and containers industries (El Essawy et al., 2017). Usually, PET waste is eliminated using incineration, chemical recycling or feedstock recycling to produce gaseous and liquid products and carbon-enriched materials (Mishra et al., 2003). However, as PET contains high amount of carbon and negligible content of mineral impurities, it is favorable to turn this material into carbon based material such as carbon nanotubes, carbon microspheres and activated carbon (Mendoza-Carrasco et al., 2016).

Based on the study, the SEM image exhibits a fiber network morphology with void space, which can provide access for porosity (figure 7) (El Essawy et al., 2017). The graphene produced shows a diffraction pattern at 2\(\theta\) = 26, 42.3 and 44.3\(^{\circ}\) which corresponded to (002), (100) and (101). The result indicates that the graphene is highly amorphous (Zhang et al., 2016). On the other hand, the Raman spectrum indicates that there are two bands found which are G-band (1596 cm\(^{-1}\)) and D-band (1360 cm\(^{-1}\)). G-band is formed by the interaction with other layers or due to external disorder that breaks the hexagonal symmetry of graphene. Meanwhile, the formation of D-band indicates a highly disordered graphite arrangement (El Essawy et al., 2017). Thus, the intensity ratio \((I_D/I_G)\) obtained is relatively low, 1.13 which means that the prepared graphene is highly disordered (Sergienko et al., 2009).

**Fig. 5** Illustration of assembly mechanism between GO and CSC (Liu et al., 2018).

**Fig. 6** SEM images of (a) freeze-dried GO (b) \(ZnCl_2\) treated CSC (c) CSC-GO (Liu et al., 2018).

**Fig. 7** SEM image of graphene derived from PET (El Essawy et al., 2017).

On the other hand, Sharma and colleagues have produced a high quality single crystal graphene on polycrystalline Cu foil using solid waste plastic as carbon source in an ambient pressure (AP) chemical vapor deposition (CVD) process (Figure 8) (Sharma et al., 2014). They claimed that, graphene obtained via this method provides much...
better opportunity to grow large-area high quality monolayer graphene (Li et al., 2009, 2011). This statement is proven by the Raman spectrum where a very small defect on the graphene is shown by the low intensity of D-band. Meanwhile, G-band and 2D band are found at 1590 cm\(^{-1}\) and 2700 cm\(^{-1}\), respectively. Based from the results, it confirms that the graphene produced in this study is single layer as the 2D-band has a higher intensity than G-band (Sharma et al., 2014).

Besides that, Chui and coworkers reported that they have prepared graphene foil (GF) via solid-state CVD (Cui et al., 2017). Based on the characterization, Raman spectrum shows that the G-band of the material is intense and narrow, indicating a good crystallinity and high graphitization (Pimenta et al., 2007). On the other hand, low I\(_{D}/I\_G\) shows that the defect on the sample is relatively less. The XRD analysis further supports the Raman results where peak at 2\(\theta = 26.7^\circ\) reveals a high graphitization of graphene (Cui et al., 2017).

**Application of waste and biomass derived graphene**

Nowadays, it is vital for researchers to develop energy-related materials and devices to meet the global energy demand (Dawoud et al., 2007). Graphene has received tremendous attention and its properties have been studied extensively such as room temperature quantum Hall effect (Bhuyan et al., 2016), optical (Nasrollahzadeh et al., 2015) and mechanical properties (Potts et al., 2011). Owing to its unique properties, graphene has been attracted to be applied in various applications which include dye removal (Elsaghoum et al., 2017), adsorption of heavy metals (Mattilainen et al., 2010), supercapacitors (Chen et al., 2014) and many more. Herein, we summarize some of the recent studies concerning the applications of waste and biomass derived graphene in dye removal, adsorption of toxic and heavy metals, gas storage, high performance supercapacitors, electrochemical sensor and fuel cell.

**Dye removal**

Water pollution and inadequate access to clean water are some of the most pervasive environmental problems that afflicting people throughout the world. Synthetic dyes contain some components or moieties that can be toxic, carcinogenic, teratogenic or mutagenic to aquatic life and humans, that consequently will cause danger (Konicki et al., 2011). Among all techniques, adsorption is considered as an effective alternative due to its low cost, simplicity of design, ease of operation, insensitivity to toxic pollutants and smaller amounts of harmful substances (Peng et al., 2017).

Chitosan-gelatin/graphene oxide (CGGO) has been synthesized and the adsorption performance on lead ion (Pb\(^{2+}\)) is studied. Zhang reported that, higher GO content can gradually increase the adsorption capacity of Pb\(^{2+}\) (up to 90%) (Zhang et al., 2011). Khasbataar and teammates claimed that this is likely due to the existence of carboxyl groups which are effective chelating groups for metal ions (Khasbataar et al., 2008).

**Gas storage**

Carbon dioxide (CO\(_2\)) has been the main greenhouse gas that leads to global warming and climate change (Nowrouzi et al., 2018). To date, various of efforts are being undertaken to reduce the greenhouse gas concentration that is mostly emitted from the combustion of fuel in vehicles and burning of coal in power plants (Yoon et al., 2011). Among all techniques, adsorption is considered as an efficient alternative due to its low energy requirement and cheap (Shafieeyan et al., 2010).

Ekhlasi and colleague have studied the graphene that derived from populus wood biomass (PWB) as adsorbents for CO\(_2\) capture using different amounts of KOH as activating agent. Based on the report, they stated that the optimum KOH/HC ratio is found to be 3:1 as the maximum CO\(_2\) adsorption capacity can be reached up to 9.86 mmol CO\(_2\)/g (Ekhlasi et al., 2018). This can be explained by the fact that the increased in activation ratio will cause the micropores and mesopores to be enlarged. Hence, the adsorption capacity of CO\(_2\) will be enhanced (Cazorla-Amorós et al., 1996).
High performance supercapacitors

Supercapacitors is one of the energy storage devices that received tremendous attention due to its high power densities, long cycling life and fast charge-discharge rate (El-Kady and Kaner, 2013). Supercapacitors can be classified into two categories: electrochemical double-layer capacitors (EDLCs) and pseudocapacitors (Simon et al., 2014). Hence, Fan and teammates have conducted a study on N-doping cotton derived carbon frameworks incorporated with reduced graphene oxide (NCCF-rGO) that is prepared from direct carbonization of commercial cotton for supercapacitors. NCCF-rGO shows that it has excellent capacitance retention as no changes is observed when it is bent under different angles (Figure 10). In addition, it also shows a better energy storage capability and displays a high energy density of 20 Wh/kg at a power density of 4000 W/kg (Fan et al., 2017).

CONCLUSION

Waste and biomass derived graphene is another promising material that can be applied in many applications, yet the synthesis method is still challenging. Therefore, several studies need to be carried out to justify the best method in order to produce graphene with the most satisfying characteristics. In addition, production of graphene using biomass precursors will possibly reduce the disposal issue of the material. Furthermore, based on this review, most of the approaches are scalable, efficient and cost effective, making graphene as suitable to be applied in many applications such as water filtration, supercapacitors, fuel cell and gas adsorption.

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