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# Graphene Oxide Derived from Biomass and Their Potential Photocatalytic Application

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## Abstract

*Recently, abundance of research reported the works related to waste to wealth (WTW) concept. There has been a lot of research done using sources from animal and plant to mimick the synthesis of carbonaceous materials from natural resources. Graphene, the world exciting material also was included in WTW concept where researchers trying to produce from biomass and waste. Graphene oxide (GO), which is in the family of carbon materials is extensively research for their various applications including photocatalyst. Hence, this review focuses on synthesis of GO from biomass, the synthesis of nanocomposites and the photocatalytic activity of GO based nanocomposites.*

**Keywords**: Review, Graphene Oxide, Photocatalytic activity, Biomass, Green synthesis

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## INTRODUCTION

Waste and biomass have potential to be transformed into a value-added nanomaterial. For example, a simple pyrolysis process can convert tea waste into a bio char for fluoride adsorbent [1]. Apart from that, sugarcane and camphor also was used as precursor to synthesis GO and carbon nanotubes [2–4]. Carbon-based structures are the most adaptable materials to be utilized in current technology of sustainable energy as well as natural science. Comparably, carbon based frameworks are gaining attention in green technology such as photocatalysis, biofuels, electroanalysis [5–7]. Realizing their potential, some of well-known scientific awards such as Nobel Prize in Chemistry 1996 and 2008 Kavli Prize have been awarded to carbon related works in respect to the interest of carbon based materials technology and application potential [8]. The newest member in carbon family, which is graphene requires specific methods to produce such as from graphite [9] and natural gas. GO are unique material that have been utilized in photovoltaic, photoelectrochemical, drug delivery, biosensor, and supercapacitor [10–16]. GO also has been utilized to enhance the photocatalytic performance either for Titanium Dioxide ($TiO_2$) [7] or Zinc Oxide (ZnO) nanoparticles [17–19]. However, the challenging part is by replacing these kinds of current precursor material with something that abundant and more environment friendly. Hence, researchers have put enormous amount of efforts to try replacing graphite and natural gas with biomass and waste to synthesis GO.

## Synthesis of GO from biomass

**Table 1: Previous work of GO synthesis from biomass and waste**

| Origin material | Method | Product | Reference | Year |
|---|---|---|---|---|
| PET bottle | Thermal decomposition | GO | [20] | 2017 |
| Oil palm leave<br>Palm kernel shell<br>Empty fruit bunch | Carbonization followed by synthesis of GO | GO | [21] | 2017 |
| Sugarcane bagasse | Single step oxidizing | GO | [3] | 2015 |
| Chitosan | Pyrolysis | N-doped GO | [22] | 2014 |
| Camphor | CVD | Iodine doped graphene | [23] | 2011 |
| Camphor | Chemical Vapor Deposition (CVD) | GO | [2] | 2013 |
| Camphor | CVD | GO | [24] | 2011 |

Table 1 revealed that scientists now have shift their focus in terms of GO synthesis from chemical synthesis to low cost "waste to wealth" synthesis. X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM), transmission electron microscope (TEM), and Raman spectroscopy were classified as a must do analysis for the graphene-based materials synthesized from either biomass or waste.

In the year of 2015, [3] GO have been successfully derived from sugarcane bagasse by using only single step oxidizing method in the muffle furnace. The structure of sugarcane bagasse powder can be easily converted into GO after mix with ferrocene, where the iron catalyzed the graphitic structure of untreated ligno-cellulosic biomass. The finding is supported by the work of [25]. The physical properties of black powder collected then was characterized by XRD, FTIR, Raman, and TEM. XRD result in Figure 1 shows the peak at 2 theta = 11.6 ° indicate the GO with interlayer of 0.76 nm. The result from this work are similar with [26,27]. Raman spectroscopy (Figure 3) give two peaks which are D band (1358 $cm^{-1}$) and G band (1585 $cm^{-1}$). The calculated $I_D/I_G$ ratio give out value of 0.76, indicated low defects in $sp^2$ carbon.

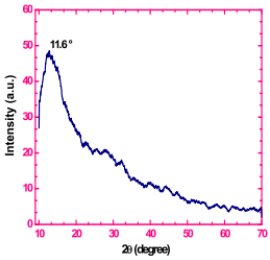


**Figure 1: XRD pattern of GO [3]**

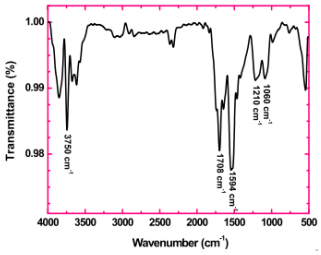


**Figure 2: FTIR spectrum of GO [3]**

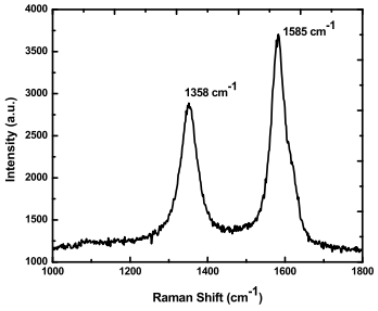


**Figure 3: Raman spectra showing D and G band of GO [3]**

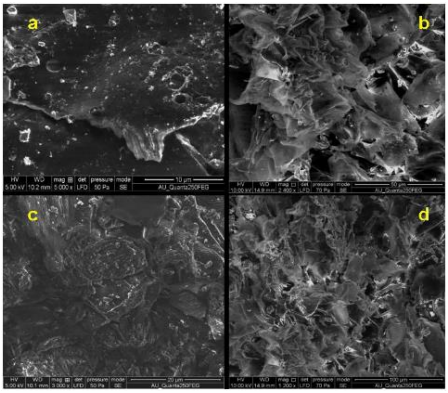


**Figure 4: SEM images of (a,c) GO nano sheet, (b,d) GO flakes [3]**

SEM images in Figure 4 (a,c) show a nano sheet structure of GO. Meanwhile a flake like structure can be seen in Figure 4 (b,d) as there is a disorder in $sp^2$ carbon, which resulting the formation of $sp^3$ during the oxidation process. This is supported by the $I_D/I_G$ ratio in Raman. Figure 5 is HRTEM result of the GO from sugarcane bagasse. Figure 5 (a,b) show the edge of the GO, confirming a few layer of GO formed.

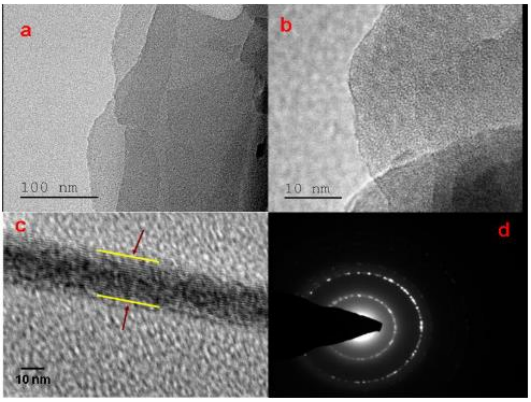


**Figure 5: HRTEM images of (a,b) GO edge (c) Flake structure in GO (d) SAED pattern [3]**

Apart from sugarcane bagasse, solid camphor ($C_{10}H_6O$) also gaining worldwide attention to be used as carbon precursor. Camphor refers to the white crystalline solid material that can easily sublimate at room temperature having melting temperature of 180 °C. The easiest way to obtain camphor is via collection from latex of cinnamomum camphora tree [28]. Several methods and studies has been carried out in respect to the formation of graphene from camphor such as pyrolysis technique, chemical vapour deposition technique, as well as their effect on carrier gas, and different doping material [2,23,24].

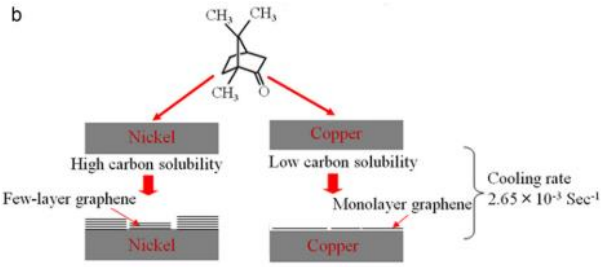


**Figure 6: Mechanism on formation of few layer and monolayer graphene affected by substrate [24]**

Figure 6 shows the study reported by [24] where the formation of monolayer graphene found to be dependent mainly on substrate and carbon solubility. The result obtained was compare with the study by [29], which revealed that copper foil is better in terms of helping the formation of monolayer graphene, while the use of nickel resulted in the formation of bilayers or few layers graphene. In addition, another group of researcher also using camphor precursor in the synthesis but the different is in terms of the effect of gas carrier [2]. In the experiment, they simply varying the composition of argon and hydrogen gas, and their findings indicated that the presence of hydrogen gas are crucial to induce larger domain of GO, C-etching, and avoid defects [30–32].

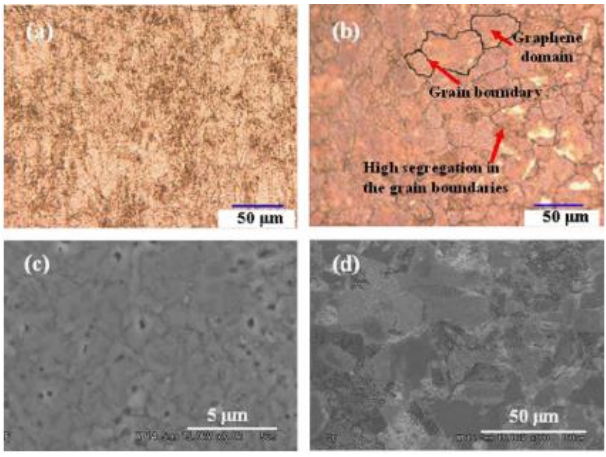


**Figure 7: Optical images of formation of GO in (a) Ar atmosphere, (b) Ar+H2 atmosphere, and SEM pattern of GO grown in (c) Ar atmosphere, and (d) Ar+H2 atmosphere [2]**

Another interesting work reported recently is the conversion from polyethyleneterephthalate (PTE) bottle into GO by using thermal decomposition method [20]. PET bottle is one of the industrial waste that extremely difficult to convert into more valuable product due to poor conductor and unsuitable mechanical and thermal properties [33,34] . Due to high carbon content in PET, several researchers have suggested the use of PET as the precursor to synthesis a high value carbon materials such as carbon nanotubes, carbon microspheres, and activated carbon [35–37]. The as prepared GO from PET bottles showed high carbon content and very low composition of impurities suggested the important factor for the as prepared graphene to be further exploited as photocatalyst.

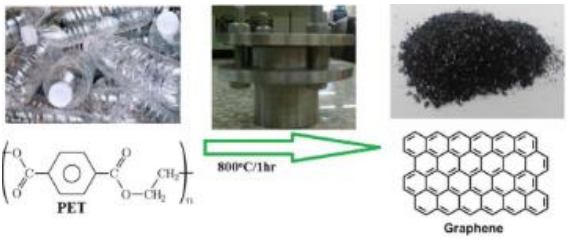


**Figure 8: Schematic diagram of process of synthesis of GO from PET bottles [20]**

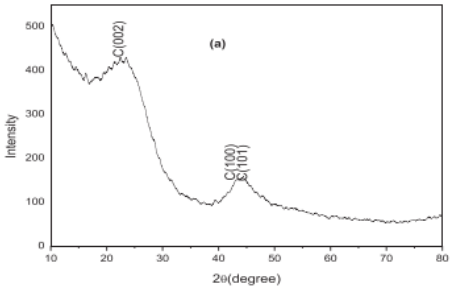


**Figure 9: XRD pattern of GO from PET bottle [20]**

XRD result in Figure 9 shows three peaks that indicate the formation of graphene structure at 26 °, 42.3 °, and 44.3 ° representing (002), (100), and (101). The result was supported by [38,39]The (101) peak also represent the stacking structure of graphene layer [40]. The elemental composition a shown in

energy dispersive X-ray (EDX) (Figure 10) shows high carbon content in the graphene from PET bottles.

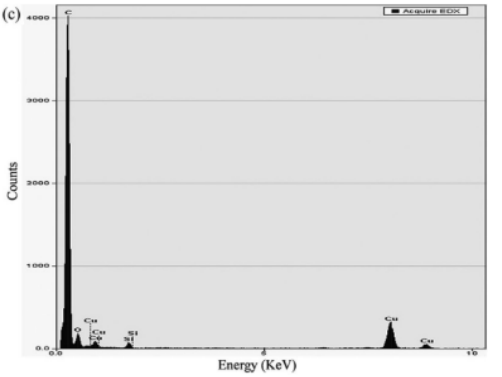


**Figure 10: Elemental composition in GO from PET bottle [20]**

The success of synthesis of GO from biomass could open new doors to synthesis a photocatalyst nanocomposite from biomass. Popular semiconductor materials such as ZnO and $TiO_2$ have a large band gap which is ~ 3.70 eV [41] and ~3.2 eV [42], respectively which will limit their efficiency in UV region due to fast recombination of electron-hole pair. An excellent electron conductor such as graphene is desired for photocatalyst since there are several studies previously reported the successful incorporation of semiconductor materials into graphene increase the efficiency of photocatalyst compared to stand alone ZnO and $TiO_2$ nanoparticles. Therefore, appropriate method or approach need to be considered and wisely chosen to synthesis the nanocomposite. Another approach to produce GO from biomass is first, by converting the biomass into graphite like material by carbonization, then followed by the synthesis of GO using various method such as Hoffman's, Hummer's method, or modified Hummer's method. A work by [21] in 2017 have successfully produced GO from various part in palm oil plant such as oil palm leaf, kernel shell, and empty fruit bunch. Briefly, all the samples was carbonized at high temperature, followed by the synthesis of GO as demonstrated by [43] in 2010.

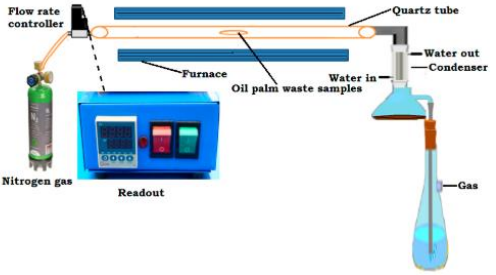


**Figure 11: Schematic diagram of experiment set up for carbonization process [21]**

## Synthesis methods of graphene/zinc oxide (G/ZnO) and graphene/titanium dioxide (G/$TiO_2$)

Hydrothermal are quite popular method to synthesis G/$TiO_2$ nanocomposite [42,44]. The oxygen in graphene oxide (GO) was reduced in hydrothermal method by electron donating from ethanol then produce the Ti-O-C bond formation between nanowire structure of $TiO_2$ and reduced graphene oxide [42,45]. Highlighting the advantage of hydrothermal method over mechanical mixing, work done by [46] shows the sample made from mechanical mixing have lower photocatalytic effect toward methylene blue (MB) solution, which indicate the incorporation of ZnO onto graphene sheets is more successful in hydrothermal process. G/ZnO photocatalyst also received attention, as it overcome the limit of working surrounding in visible light [47]. Among other methods, microwave assisted method are most common to synthesis G/ZnO [19,48,49]. The advantage of microwave heating compared to conventional heating, this method is useful to produce a uniform growth of particle size, aside from reduce the time consume [50–52].

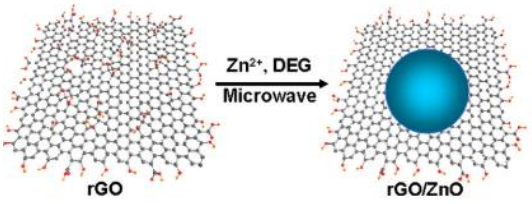


**Figure 12: Illustration of microwave assisted formation of G/ZnO [19]**

Solution method [17] and wet chemical method [53] might have the difference in synthesis process despite the method name could be interpreted as the same. The main difference are the calcination and reflux process that involved in solution method and wet chemical method, accordingly for different purpose. Besides that, hydrothermal [54], solvothermal [55], deposition [56,57], and photochemical method [47] also are common practice to synthesis the nanocomposite.

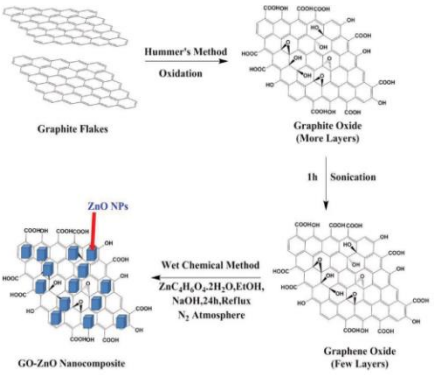


**Figure 13: Schematic diagram of synthesis of G-ZnO [53]**

## Photocatalytic degradation performance of G/$TiO_2$ and G/ZnO nanocomposite

Graphene are becoming popular due to its two-dimensional (2D) structure, large surface area, high electron mobility, and high electron conductivity which have been gaining attention as the main recipe to synthesis a nanocomposite [58,59]. Previously, $TiO_2$ nanomaterials have been studied in photodegradation and energy conversion. However, in the efforts on modify and enhance response towards visible light photocatalyst condition, the $TiO_2$ nanomaterials incorporated into the carbonaceous material such as carbon nanotubes and GO [60,61]. Another material, ZnO also successfully incorporated due to the fact that ZnO is an electron donor while graphene is a good electron acceptor, which results in synergistic effect between these two materials. In addition, the prepared nanocomposite also

effectively inhibit the recombination of electron-hole pairs which in turns will increase the separation of charge carrier [53,55]. The addition of GO also important in the degradation of methylene blue (MB) solution due to p-p conjugation between MB and aromatic regions of graphene [44,62]. In order to get the appropriate ratio of GO and ZnO, [46] have demonstrated that the increase of GO capable in lowering the band gap. However, it can reduce the efficiency of photocatalytic activity due to shielding effect. The outstanding photocatalytic activity found to be correlated to the decrease in opacity and light scattering, so, the increase of irradiation that passing through the reaction suspension solution is desired. However, too much amount of graphene can cause to the blocking the active site of catalyst, resulting decrease the intensity of light passing through [63]. This statement was fully supported by past projects that concluded the ratio of graphene in nanocomposite is beneficial in order to bring out the best performance in the photocatalytic activity [64,65].

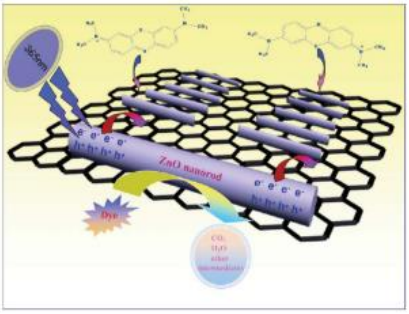


**Figure 14: Proposed mechanism of photocatalytic degradation of MB over G-ZnO in UV light condition [46]**

Another factor that can affect the photocatalytic activity is the adsorption or reactant [66–68]. This can be carried out by adding the photocatalyst into the solution in dark condition. RhodamineB found to be more adsorb toward G-$TiO_2$ nanocomposite, hence with the present of UV and visible light, it led to higher photocatalytic activity. From [44,69], the optimal amount of graphene desired in nanocomposite should

less than 5% to enhance the interaction between graphene and semiconductor material. In terms of stability, three times used photocatalyst of G-ZnO gave a better performance at 97% efficiency compared to GO and ZnO at 21% and 52% accordingly [53]. Surface area also plays an important role affecting the rate of photodegradation. For example, surface area of pure ZnO is much lower than G-ZnO nanocomposite [47]. The higher the surface area can lead the easy adsorption of molecules and harvesting exciting light [70–73].

**Table 2: Previous work of photocatalytic activity of GO nanocomposite**

| Composite | Method | Light source | Catalyst concentration | Photocatalytic performance | Authors | Year |
|---|---|---|---|---|---|---|
| G-ZnO | Photochemical method | UV, visible | 0.01 g/L | 90.00% in visible<br>99.99% in UV<br>At 120 min | [47] | 2018 |
| G-ZnO | Solution method | UV | 1.00 g/L | 99.99% at 20 min | [17] | 2017 |
| G-ZnO | Precipitation method | UV | 0.50 g/L | 99.99% at 75 min | [7] | 2016 |
| G-ZnO | Wet chemical method | Visible light | 1.00 g/L | 99.99% at 120 min | [53] | 2016 |
| G-ZnO | Hydrothermal method | UV | 0.214 g/L | 99.99% at 40 min | [46] | 2013 |
| G-ZnO | Microwave method | Visible light | 0.125 g/L | 99.99% at 20 min | [19] | 2012 |
| G-$TiO_2$ | Hydrothermal method | UV,Visible | - | 95.00% at 120 min for UV<br>70.00% at 120 min for visible light | [69] | 2011 |
| G-$TiO_2$ | Chemical method | Solar light | 1.00 g/L | 35.00% at 180 min | [74] | 2010 |

## CONCLUSION

To conclude, this review was carried out with intention to provide readers with an overview of potential of GO derived from biomass, and their importance as photocatalyst. With various method available to synthesis GO and semiconductor nanocomposite, this review also highlighted the comparisons between a few methods and their effect towards photocatalytic activity. However, there are not significant differences in terms of efficiency in comparing the synthesis method. It depends on the availability of apparatus and the simplicity of the process so that researchers could have numbers of choices. GO are proven to be essential to improve the performance of ZnO and $TiO_2$. With a study on the right of amount of GO incorporated in $TiO_2$ and ZnO was conducted, this paper provide reader with the information such as shielding effect due to having too much GO in the nanocomposite. Since there were a lot of works have been done with similar purpose, this review can provide a gap which researchers overlook by gathering some of interesting projects to be discussed.

Materials scientists need to be more creative in the future for the sake of innovation without causing harm to the environment and to be able to sustain the resources. There are a lot of things need to be considered to before creating an innovation that can contribute to the modern technology such as the source of materials, the emission of harmful gas as well as reducing the toxic byproducts in the process. Researchers need to concern about the environment safety as top priority than anything else. This is the massive challenge to us, scientists to be innovative while to ensure planet Earth does not suffer from our technology race.

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