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Preparation and characterization of graphene oxide from tea waste and it's photocatalytic application of TiO$_2$/graphene nanocomposite

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Abstract

In the present study, the conversion of tea waste biomass was carried via carbonization at high temperature and further used as starting material to produce graphene oxide (GO). The oxidation and exfoliation of graphitized carbon was successfully achieved using modified Hummer's method. The as synthesized GO have been loaded with titanium dioxide (TiO$_2$) using hydrothermal method to produce nanocomposite of rGO/TIO$_2$. The prepared nanocomposites were characterized by means of XRD, FTIR, Raman and FESEM analysis. The evaluation for rGO/TIO$_2$ nanocomposite photocatalytic activity was carried out based on degradation of methyl orange (MO) under the ultraviolet (UV) light irradiation. Results obtained using FTIR results revealed the successful oxidation of graphitized carbon with the presence of carboxyl and hydroxyl group. FESEM images suggested the changes of surface morphology from graphite flakes structure into few layers of graphene sheets. Therefore, it can be indicated that tea waste suitable to be sustainable alternative of graphite for the synthesis of GO. Moreover, GO obtained has immense potential for degradation of various water pollutions. Photocatalytic activity experiment inferred that the importance of optimum ratio between reduce GO to TiO$_2$ materials which can resulted in difference in the degradation efficiency; rGO/TiO$_2$ 1:8 > rGO/TiO$_2$ 1:4 > TiO$_2$ > rGO/TiO$_2$ 1:6 > rGO/TiO$_2$ 1:10.

Introduction

The current research interest worldwide focusing on green based nanomaterials synthesis is growing at a remarkable rate. Green nanotechnology has appeared as a flexible platform which capable in providing efficient, cost-effective, simple and environmentally tolerable solutions to the global sustainability disputes facing by our society. Based on the current trend, the use of biomass as the raw material in producing nanomaterials have been considered as bio-based economy and green options to deal with the problems associated with local and global pollutions. Agricultural waste biomass for example progressively attracted global attention as a low- cost resources for the synthesis of nanomaterials. Tea waste is the form of sweepings, fluffing or tea fibre is highly disposed from household and restaurants daily. Considering the abundant waste available and based on several works previously conducted by in turning waste to wealth by deriving waste biomass into usable materials, there is possibility in turning tea waste into new materials.

Synthesis of carbon-based material is one of the alternatives to reduce and elucidating waste related biomass issues. Several researchers demonstrated the capability in converting the biomass into a graphitized carbon materials from coconut shell powder and wood (Wachid *et al* 2014, Wang *et al* 2008). In addition, the abundance of tea waste can be turn into a valuable material and having the ability to be use in the synthetic oil production as well as an adsorbent for waste water (Uzun *et al* 2010, Amarasinghe and Williams 2007). Tea waste also was considered as adsorbent for fluoride contained in contaminated water (Swapnila *et al* 2018). Tea waste having compounds as tea such as polyphenol, caffeine, amino acids and tannins while tea leaves contains cellulose, hemicelluloses, lignin, tannins, and proteins (Hussain *et al* 2018). Previous researcher reported that due to the

abundance of lignin, hemicellulose and cellulose, graphitic carbon still can be produce but it requires high temperature pyrolysis (Thompson *et al* 2015, Wang *et al* 2008).

Graphene started to gain interest since the successful theoretical work conducted by Wallace in 1947 where single layer of carbon description was used as a model system for all sp^2 carbon system. This is the starting point of comparing the structure of graphite, carbon nanotubes, and other sp^2 carbon (Saito *et al* 2011). There are several studies reported the possibility to synthesis GO from biomass and waste. Some researchers reported the used of biomass such as cow bone, soot, sugarcane bagasse, chitosan, polyethyleneterephthalate (PET) bottle, and camphor to synthesis GO (Kalita *et al* 2010, El Essawy *et al* 2017, Somanathan *et al* 2015, Lavorato *et al* 2014, Akhavan *et al* 2014). Herein, waste biomass in terms on tea waste revealed its potential as low cost and temperature in preparing GO. The preparation of chemically modified graphitized biomass using modified Hummer's method was mimicked by normal route to synthesis graphene oxide (GO). In addition, simply increasing the oxidation time, it resulted the similar structure of GO derived tea waste with the one prepared from commercial graphite.

GO is the result of exfoliation and oxidation of graphite which can be synthesized by several well-known method such as Hummer's method, modified Hummer's method, single step oxidizing, thermal decomposition, and chemical vapor deposition (CVD) (Arthi *et al* 2015, Somanathan *et al* 2015, Amir Faiz and Che Azurahanim 2019, Marcano *et al* 2010). The carbonization of biomass at high temperature leading to the formation of graphitic carbon structure. Chemical modification of graphitic carbon structure using strong oxidizing agent such as sulphuric acid (H_2SO_4), potassium permanganate ($KMnO_4$), and sodium nitrate ($NaNO_3$) will further increase the surface area due to present of hydroxyl group such as COOH, OH, and C–O (Liu *et al* 2011). Reduced GO refers to the complete separation process of carbon layer to form either single or multilayers of graphene (Arthi *et al* 2015).

Due to their unique properties of two dimension of graphene including large surface area, high electron conductivity and mobility, thus it is very preferable as part of any composite that requires any of these features. One approach to improve the performance of a GO for application as photocatalytic can be achieved simply by incorporating GO with metal oxides of interest such as a second material which postulated to have synergistic effects and syntagmatic benefits resulting in enhancing the photocatalytic performance. Therefore, further study should be implemented to understand the sensing mechanism and physics behind performance improvement.

A reviewed published reported that by mixing graphene with titanium dioxide (TiO_2) capable to produce more efficient photocatalyst performance (Amir Faiz and Che Azurahanim 2019). TiO_2 was known as good photocatalyst. However, fast recombination of electron and hole inhibit the full potential of TiO_2 as photocatalyst. Thus, the addition of graphitic carbon structure such as graphene will prevents the fast rate of recombination and extend the reaction time of excited electron with organic compound of pollutant. Although the photocatalysis of GO/TiO_2 has been well investigated but very few papers reported the investigation of rGO synthesized from biomass decorated with TiO_2 and their photocatalytic effect. Hence, it would be worthwhile to explore the nanocomposite properties of the rGO/TiO_2 in conjunction with their photocatalytic effect of following decoration with TiO_2.

In this presented study, the rGO/TiO_2 composite gas sensors were fabricated by a simple hydrothermal method and their photocatalytic performance of prepared nanocomposite was evaluated through the degradation of methyl orange dye.

Experimental design

Chemical reagents

Chemical reagent used in this study were purchased from Sigma Aldrich and used as obtained. Tea waste were collected from local restaurant in Serdang area. Experimental solutions (stock solution and dilutions) were all prepared using deionized water. As and when required, pH adjustments were achieved through 0.1 M HCL and 0.1 M NaOH.

Carbonization of tea waste

The collected tea waste was dried and pestle to form a smooth powder. 3 g of dried tea waste was then carbonized at 650 °C under argon (Ar) atmosphere with 50 sccm gas flow rate for graphitization purpose. The holding time was set for 3 h and the gas was continuing to flow until the temperature of sample was below 100 °C. The procedure was repeated using different temperature at 750 °C and 850 °C. The yield for carbonized sample recorded for 650 °C was 2.3 g and no difference in yield for carbonized sample at 750 °C and 850 °C, respectively which is 2.17 g.

Synthesis of graphite oxide and reduced graphene oxide (rGO)

The as prepared carbonized sample was oxidized using modified Hummer's method (Arthi *et al* 2015). In this process, 2 g of carbonized sample was used as a replacement of commercial graphite. The mixture of sodium nitrate ($NaNO_3$), carbonized sample, and concentrated H_2SO_4 were then added with ($KMnO_4$) very slowly in the controlled temperature condition. Finally, hydrogen peroxide (H_2O_2) was added and the yellowish solution started to appear. The prepared solution was then washed with 10% hydrochloric acid solution (HCL), followed by centrifuged at 6000 rpm
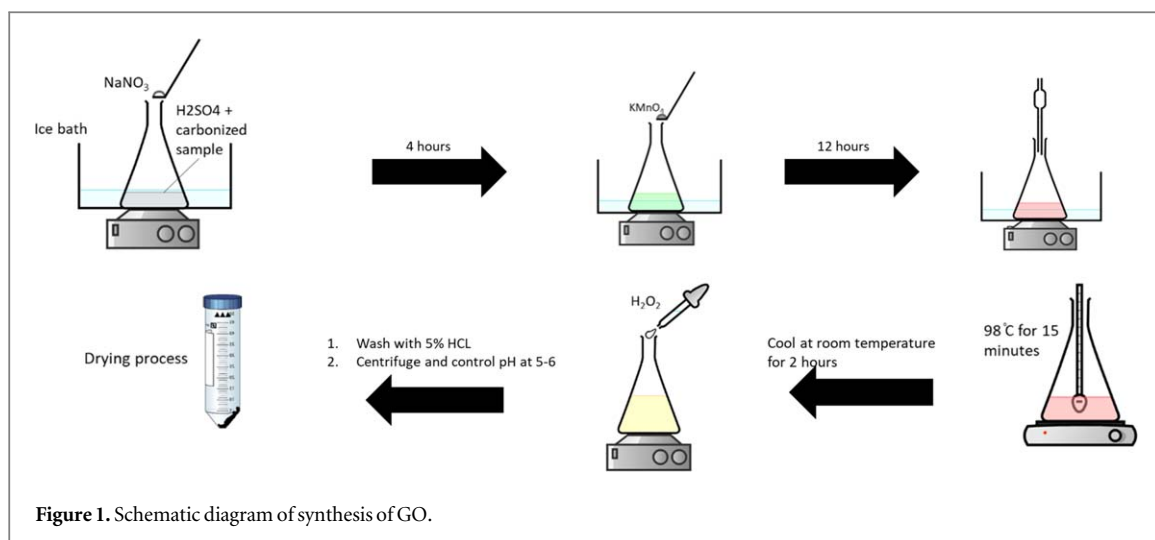
Figure 1. Schematic diagram of synthesis of GO.

Table 1. Amount of GO and TiO_2 used in synthesis of different ratio of rGO/TIO_2 nanocomposite.

Catalyst	GO (mg)	TiO_2 (mg)
rGO/TiO_2 1:4	20.00	80.00
rGO/TiO_2 1:6	14.30	85.70
rGO/TiO_2 1:8	11.11	88.90
rGO/TiO_2 1:10	9.09	91.00

for 20 min a few times until the pH achieved 5 or above. Then it was rinsed with deionized (DI) water and left to dried overnight in the oven. The fluffy black powder was then collected. This method was capable to yield 2.4 g of graphite oxide from 2 g of starting material. The flow of the process was illustrated in Figure 1 below.

To synthesis of reduced graphene oxide (rGO), the black powder collected previously was then put into the bed reactor furnace and heated at 250 °C under Ar gas atmosphere for 30 min.

Synthesis of rGO/TiO$_2$ nanocomposite

TiO_2 powder and graphite oxide was sonicated separately in DI water to ensure each element was completely dissolved in the solution. The sonication will further exfoliate the layer of graphite oxide to form monolayer structure of GO. Then the solution of TiO_2 and GO was mixed and stirred for 30 min before mixing solution was put into the Teflon lined autoclave reactor. The reactor was put in the oven at temperature of 100 °C for 17 h. The resulting solution was washed and dry in the oven overnight to get grey color powder. Different ratios of TiO_2 was incorporated onto graphene sheet find the optimum ratio for rGO/TiO_2 photocatalyst nanocomposite. The amount of TiO_2 and GO was carried out in (w/w) ratio (refer to Table 1).

Photodegradation of methyl orange (MO)

The photodegradation of MO was carried out using rGO/TiO_2 nanocomposite as catalyst and ultraviolet (UV) lamp as the energy source. UV lamp (20 Watt) was used to irradiate the solution where 10 ppm of MO was prepared in 1000 mL beaker. The catalyst was dispersed into the MO solution (1 mg/20 ml). To check the degradation, the time interval for collecting each sample was set to be 20 min. The sample collected was firstly centrifuged at 6000 rpm to remove any catalyst. The rate of degradation was analysed using UV–vis spectrometer Shimadzu 1280 single beam.

Characterization of samples

XRD (x-ray diffraction)

XRD is one of the crucial characterizations to observe the crystallinity of the GO. XRD was performed using Shimadzu x-ray Diffractometer 6000 equipped with Cukα radiation at wavelength 1.5406 Å. The scanning angle was done in the range from $2\theta = 5°$ to $80°$.
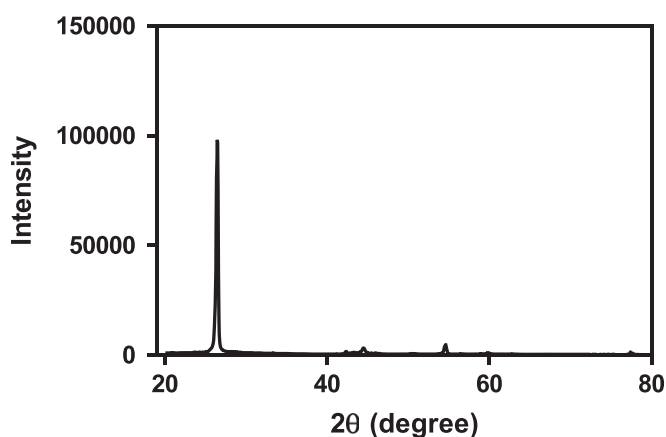
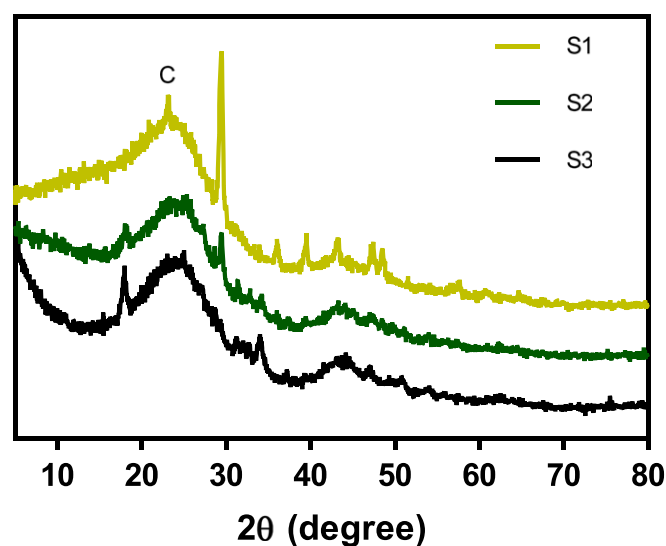**Figure 2.** XRD result of commercial graphite.

Figure 3. XRD result of S1, S2, and S3.

Raman spectroscopy

Raman analysis is very important when dealing with any carbon material to study their degree of graphitization. Besides, Raman also can be used to study the disorder of arrangement in sp^2 carbon structure in graphene. Raman characterization was achieved using Raman spectroscopy Witec Alpha 300R wavelength 480 nm.

Fourier transform infrared spectroscopy (FTIR)

To determine the functional group presence and the bonding presence in the sample, the samples was characterized using FTIR PerkinElmer Spectrum GX. The wavelength of the scanning was done at the range from 500 to 4000 cm^{-1}.

Field emission scanning elecron microscope (FESEM)

FESEM was done using FEI NovaSEM 400. The powdered samples were casted on the aluminium plate and silver ink and dried for a few minutes before taken for imaging process. The accelerating voltage was done at 5.00 kV. The images were observed at magnification from 5000X to 100 000X. The purpose for the FESEM analysis was to study the morphology of the graphitized samples and GO. The surface of the GO after adding TiO_2 also was observed using FESEM to determine the successful incorporation of TiO_2 covering the surfaces of GO.

UV–visible (UV–vis) spectrometer analysis

The photocatalytic performance of catalyst was determined using UV–vis spectrometer (Dynamica Halo DB-20S). The MO solution after each 20 min in the cuvette was put into the UV–vis spectrometer. The reading of absorbance was recorded at 464 nm for all samples.
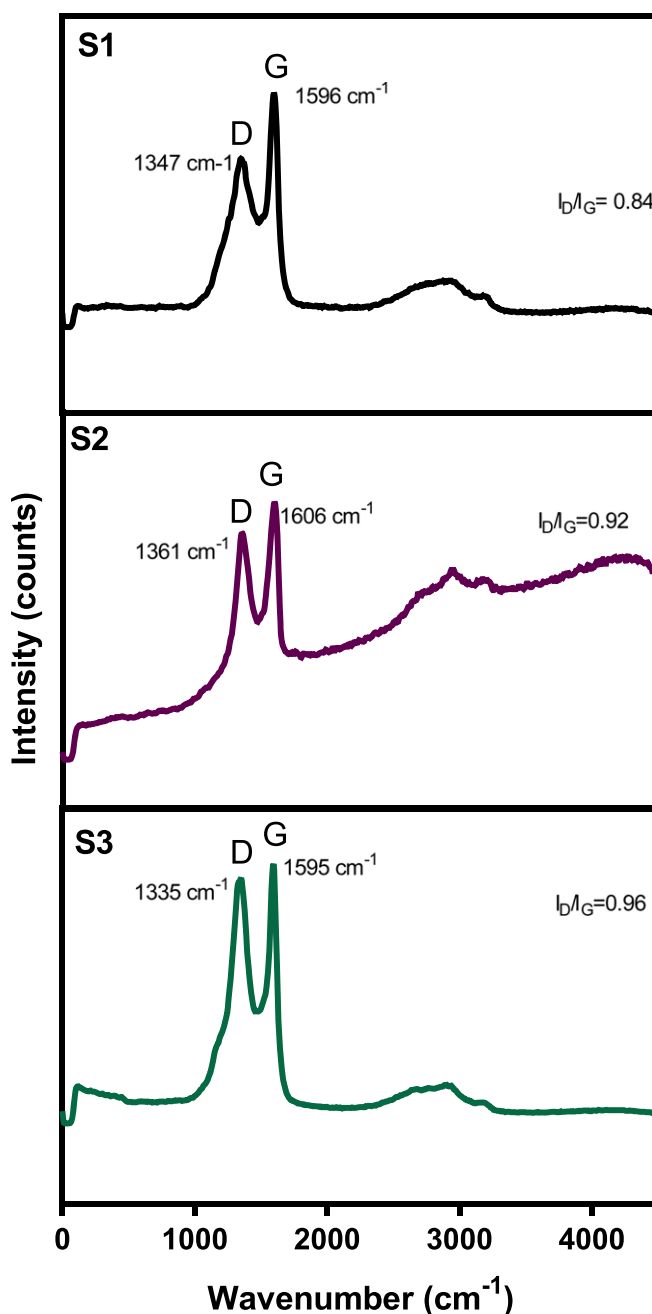
Figure 4. Raman spectra of S1, S2, and S3.

Result and discussion

In this study, the dried tea waste was carbonized at three different temperature which consist of 650 °C, 750 °C, and 850 °C. These were then denoting as S1, S2, and S3. The XRD figure of commercial graphite was inserted in figure 2 as comparison with these three prepared samples. The synthesis of GO was achieved using modified Hummer's method (Arthi *et al* 2015) and was denoted as S1G. All the samples were analyzed by means of XRD, FESEM, Raman spectroscopy, and FTIR. The synthesis of rGO/TiO$_2$ nanocomposite was characterized using FESEM. The photocatalytic performance of the nanocomposite was characterized using UV–vis spectrometer (Dynamica Halo DB-20S).

XRD analysis
XRD (figure 3) is useful to check the graphitization of the graphite and graphite oxide produced. To differentiate between graphite, graphite oxide, and rGO structure, Bragg's Law equation can be used to determine the interspace layer between each plane. The XRD result of S1 shows the shift of 3.21° to the left from the commercial graphite which is from $2\theta = 26.37°$ to 23.16°. The prominent peak for all carbonization
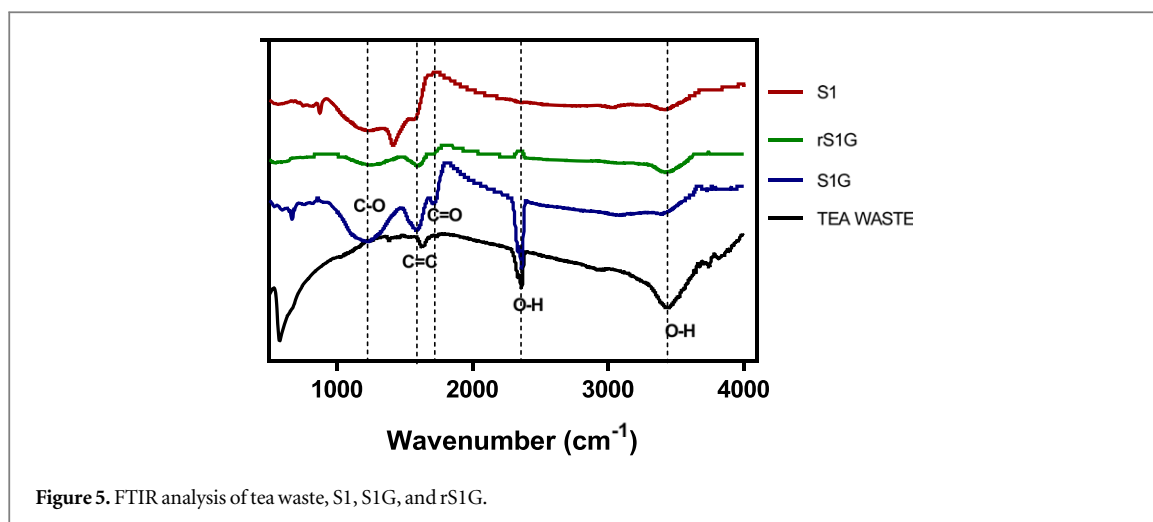
Figure 5. FTIR analysis of tea waste, S1, S1G, and rS1G.

temperature become narrower as the temperature increased. This is due to the structural ordering of carbonized tea waste and increase in the graphitization (Bernard *et al* 2010). However, there are no explanation for the phenomenon of disappearing of peak at 29.46°. Krishnamoorthy and co-workers also reported the similar shifting of the peak in XRD and Raman spectroscopy analysis which postulated to have related to the degree of oxidation of the carbon structure (Krishnamoorthy *et al* 2013). The G band in figure 4 shows that peak at 1596 cm^{-1} which different from commercial graphite which is normally at 1570 cm^{-1}. The shifting in XRD and Raman spectroscopy was related to the presence of hydroxyl group in S1, S2, and S3.

Raman analysis

Raman spectroscopy is a non-destructive tool that are popular to determine the structure of carbon materials such as graphitization, defects, and layer of graphene formed. D and G band are the most basic features in determining the characteristic of sp^2 carbon, which is D band and G band indicate the graphitic and defects features, respectively. Raman analysis was performed for S1, S2, and S3 (figure 4). The analysis revealed that the spectrum of commercial graphite normally shows the peak indicated to the D and G band at 1354 cm^{-1} and 1570 cm^{-1} respectively (Krishnamoorthy *et al* 2013).

For S1, S2, and S3, the G band was shifted to 1596 cm^{-1}. The shifting of the G band may be due to the incomplete reduction of oxygen and formation of oxidized graphite like structure (Krishnamoorthy *et al* 2013). By simply increasing of heating temperature, the intensity of D band at 1356 cm^{-1} also increased. However, there is no difference in terms of degree of oxidation since no changes in the wavelength shifted for all three samples, meaning the temperature does not affect the oxidation of graphite. Nevertheless, the increase of temperature from S1 to S3 led to increase of I_D/I_G ratio. I_D/I_G ratio is the ratio calculated from the intensity for both D and G band. The higher number of I_D/I_G ratio means higher the defects of the carbon structure and more disorder in sp^2 carbon formation. Due to the connection of I_D/I_G ratio with heating temperature can be seen clearly, it suggested that increasing heating temperature affects the defects of sp^2 carbon structure.

FTIR analysis

To study the functional group presence in the samples along the process. The FTIR spectrum of S1, S1G, and rS1G was shown in figure 5. The absorption band corresponding to oxygen functional group existence does increase after S1 was converted into S1G by modified Hummer's method. This finding correlated with the purpose of the exfoliation and oxidation of graphitic carbon, inserting oxygen functional groups between interspace layer of exfoliated carbon layer to form GO structure. The peak at 1232 cm^{-1} (Marcano *et al* 2010) represent C-O stretching vibration started to appear after the carbonization of tea waste and become more prominent with the presence of oxygen increase the intensity of the peak. However, the reduction of S1G into rS1G weaken the bond as oxygen has been eliminated thus the peak decreased. The peak at 1577 cm^{-1} represent C=C stretching vibration (Arthi *et al* 2015) became more prominent at S1G and the intensity decrease at rS1G as the bond has weakened when the carbon layer has been exfoliated. As the low temperature reduction of S1G into rS1G, the prominent oxygen containing functional group absorption band at 1232 cm^{-1}, 1705 cm^{-1}, 2345 cm^{-1}, and 3422 cm^{-1} are decreased in intensity, proving a successful to eliminate the oxygen functional group to restore the graphene like structure.
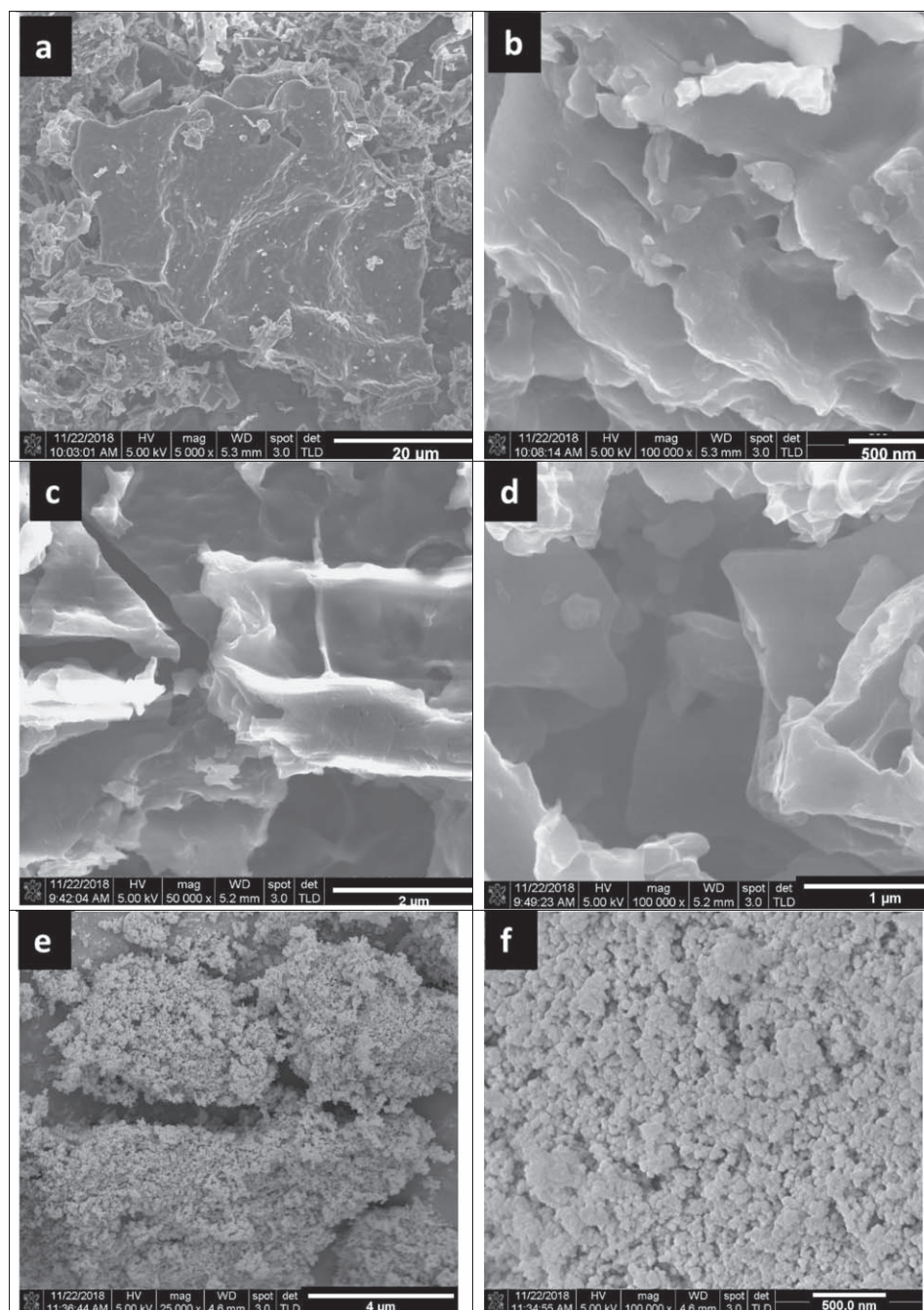
Figure 6. FESEM images of S1 (a) and (b), S1G (c) and (d), GO/TiO$_2$ (e) and (f).

FESEM analysis

Figure 6 shows the FESEM images of S1 (a), (b) and S1G (c), (d). As can be seen in (a) and (b), the images show the result after carbonization of tea waste took place, resulting a clear formation of graphite flakes. As the magnification increased to 100 000X (b), it can be seen the image is the very closely stacked layer of layer graphite. The exfoliated and oxidized of S1 into S1G resulted in the images (c) and (d). The magnification of 50 000X and 100 000X show the formation of GO wrinkled and multiple layer of carbon sheet. During the oxidation process, the stacked graphite structure (a), (b) was exfoliated and oxygen functional group have been inserted between planar. Hence, the images of the product can be seen clearly in (c) and (d) where the few layers of graphene sheets clearly seen when the magnification increased. The synthesis of rGO/TiO$_2$ was done using hydrothermal method. The images produced (e) and (f) shows the successful incorporation of TiO$_2$ nanoparticles onto the surface of the synthesized GO.
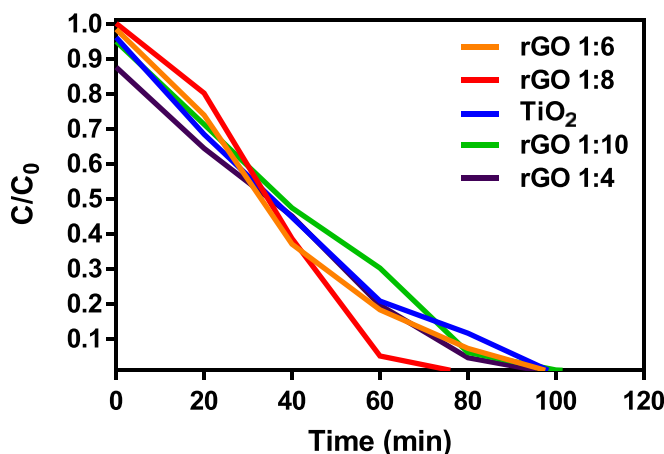
Figure 7. Rate of photodegradation of MO at different ratio of rGO/TIO$_2$ catalyst.

Photodegradation of methyl orange (MO)

The photocatalytic performance of catalyst was determined using UV-Vis. Figure 7 demonstrated the rate of photodegradation performance for each sample versus time. From the data illustrated, rGO/TiO$_2$ 1:8 shows the most excellent performance out of the ratios in order of rGO/TiO$_2$ 1:8 > rGO/TiO$_2$ 1:4 > TiO$_2$ > rGO/TiO$_2$ 1:6 > rGO/TiO$_2$ 1:10. It can be seen the addition of graphene is crucial to prevent fast recombination of electron-hole pair. As the amount of graphene increased, the efficiency increase due π-π interaction and the 2D plane structure of graphene demonstrated the ability of graphene to increase the efficiency of semiconductor materials such as ZnO and TiO$_2$ as photocatalyst (Žerjav *et al* 2017, Cho *et al* 2015, Qin *et al* 2017). However, the weight ratio of GO and TiO$_2$ is crucial as well. Excessive amount of graphene decreased the efficiency due to shielding effect. The graphene blocked the active site of TiO$_2$ thus decrease the ability of light passing through (Amir Faiz and Che Azurahanim 2019, Li *et al* 2011, Zhang *et al* 2012).

Conclusion

The as synthesized graphitized tea waste has been successfully prepared and oxidized using modified Hummer's method. The inserted hydroxyl group such as OH, C=O, and C–O as proven by FTIR results. The morphology of the graphitized tea waste and GO was observed by FESEM resulting in changes from graphite flakes into a few layers of graphene sheets. The incorporation of TiO$_2$ nanoparticles was achieved using simple hydrothermal method and FESEM images revealed the successful decoration or incorporation of TiO$_2$ nanoparticles on the surface of the graphene sheets. Various ratios of weight of GO to TiO$_2$ have been prepared to investigate the optimum ratio of TiO$_2$ capable to be incorporated onto the surface of GO. The dependency of photocatalytic performance towards the ratio of GO and TiO$_2$ also successfully showed in the present study. The photocatalytic evaluation revealed that the order of efficiency of the prepared nanocomposite are as follows; of rGO/TiO$_2$ 1:8 > rGO/TiO$_2$ 1:4 > TiO$_2$ > rGO/TiO$_2$ 1:6 > rGO/TiO$_2$ 1:10. The loading of GO at 11.11% from the total weight of the rGO/TiO$_2$ nanocomposite capable in inhibit the fast recombination of electron and resulted in more efficient photocatalytic performance compared to the use of TiO$_2$ alone. As a result, this work is beneficial to prepare low cost photocatalytic nanocomposite materials to be used in degradation of various water pollutions.

Acknowledgments

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