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Three different types of tea as surfactant in liquid exfoliation of graphite: green tea, black tea and oolong tea

F S Ismail[1,*], K Yusoh[1], A S Zainal Abidin[1], A H Abdullah[1] and Z Ismail[2]

[1] Faculty of Chemical and Process Engineering Technology, Universiti Malaysia Pahang, Lebuhraya Tun Razak, 26300 Kuantan, Pahang, Malaysia

[2] Faculty of Manufacturing Engineering,Universiti Malaysia Pahang, Lebuhraya Tun Razak, 26600 Pekan, Pahang, Malaysia

*E-mail: fadwa_wawa@yahoo.my.

Abstract. Liquid phase exfoliation (LPE) with surfactant-assisted is a method to produce graphene that used water and surfactant as solvent. Tea is one of possible surfactants that can be used in LPE of graphite as it reduced the surface tension energy of water (72.75 mJ m^{-2}) to ~40 – 50 mJ m^{-2} which is suitable level to exfoliate graphite. Three different types of tea were used as surfactant through one-step production of graphene which were green tea (GT), black tea (BT) and oolong tea (OT). The exfoliation of graphite in each tea solutions were successful as the UV spectra of supernatant samples show peak at 270 nm which indicates the C – C bond of graphene flakes. Morphology analysis (AFM) of resulted graphene samples show that graphene sheets have sharp edges caused by sonication process. The effect of sonication time was being investigated in this work. Green tea has higher exponent factor of time (1.715) compare to black tea (1.033) and oolong tea (0.762) due to high quantity of small molecules of polyphenols present in green tea solution. Thus, it is better to used GT as surfactant in LPE of graphite compare to BT and OT.

1. Introduction

Tea (*Camellia sinensis*) is one of most consumed beverages by over two-third of the world population after water. In the past 2000 years, tea which originated from China has gained the world's taste [1]. Mostly, tea being consumed as green tea (GT), black tea (BT) and oolong tea (OT) as beverages. 80% of tea are processed as black tea, meanwhile 20% of tea manufactured as green tea and 2% of tea as oolong tea [2]. Those type of tea are produced varies manufacturing process. Green tea unfermented tea that produced by drying and steaming the fresh leaves without oxidation process. It has more catechins than black tea and oolong tea. It also composed of certain minerals and vitamins which increase the antioxidant potential [1]. Black tea is fermented tea. The fresh leaves are left to wither and caused the moisture content in the leaves to be reduced. Then, the withered leaves are crushed and rolled to initiate fermented process of the tea polyphenols and produce black tea [3]. Whereas, oolong tea is manufactured by rolling and firing the tea leaves in short time to end the oxidation process and dry the leaves. Oolong tea is also known as semi fermented tea [3]. Tea has been used as reducing agent to produce graphene from graphene oxide [4]. Rather as reducing agent, tea also has been proven to be one of possible surfactant to exfoliate graphite in LPE method. In Ismail et al. [5] research, graphene has been successfully produced by using black tea as surfactant in LPE of graphite assisted by kitchen mixer. It also proof that polyphenols that contain in tea acts as stabilization agent for graphene in water. Thus,

most of graphene sheets does not clumping back to form graphite.

Graphene is two-dimensional (2D) of carbon allotropes building block. It is a promising material due to its own peculiar electric properties as well as outstanding mechanical and thermal properties. Graphene had been used as nanofiller in the composite matrix to enhanced the properties of bulk composite [6]. The production methods of graphene can be divided into bottom-up and top-down approach. Bottom-up process such as chemical vapor deposition (CVD), epitaxial growth and reduction of CO produce high quality of graphene. However, the cost of production for these process is extremely expensive and the yield production is low. Meanwhile, separation or exfoliation of graphite and graphite derivatives is used in top-down process to produce graphene or modified graphene sheets. Liquid phase exfoliation (LPE) is one of top-down process that has potential to produce large scale of graphene with low production cost. LPE of graphite can be divided into two solvent-assisted and surfactant-assisted exfoliation. Most of researches about solvent-assisted exfoliation method used solvents which are toxic to organ and irritant to eye such as N-methyl-2-pyrrolidone, N,N-dimethylformamide and ortho-dichlorobenzene [7]. Thus, the another alternative method is to used water as solvent in LPE method. Surfactant is needed to tune the water surface energy (72.75 mJ m^{-2}) to a suitable level for exfoliation of graphite (~ 40 mJ m^{-2}) [8]. Direct LPE of graphite in water-surfactant solution to produce dispersed graphene has attracted more attention as it is a simplest, non-toxicity and eco-friendly method.

There are three steps involves in LPE process which are dispersion of graphite in a solvent, exfoliation of graphite and purification of graphene [8]. There were several methods that been used to aided the exfoliation of graphite in LPE such as high-shear mixing, high-pressure exfoliation, vortex-fluid exfoliation, kitchen mixer and sonication [5]. In this research, graphite has been exfoliated in solvent aided by ultrasonication to extract individual layers [9]. In Ciesielski et al. [8] graphite had been successfully exfoliated to produce graphene sheets by using sonication method. During ultrasonication, sound is transmitted through solvent and created cavitation bubbles [10]. Formation, growth and implosive of these cavitation bubbles induce the exfoliation of graphite in solvent. When the graphite was exfoliated into graphene sheet, surfactant diffused into newly exposed interfaces to stabilize the graphene sheets from aggregation [11]. Sonication process can be carried out by a probe-type ultrasonic homogenizer. In the previous research, tea was used as an agent to reduce graphene oxide to graphene [12]. Rather than two step production of graphene, graphene was produced directly from industrial graphite using LPE method and three types of tea (green tea, black tea and oolong tea were used as surfactant solution in this paper.

2. Materials and Methods

2.1. Materials
Industrial graphite flakes (332461) was purchased from Sigma Aldrich (Malaysia), commercial black tea leaves (TeaBoh brand), green tea leaves (TeaBoh brand) and oolong tea leaves (Da Hong Pao).

2.2. Tea concentration
The brewing process of each tea solution must be kept in constant condition because the concentration of tea polyphenols can be effected greatly by the effect of temperature, time taken for brewing process and volume of ultrapure water. In this work, 5 g of tea was measured by analytical balance and was put into a beaker with 200 ml of ultrapure water. The solution with tea was heated with a hotplate equipped with thermal control at 120 $^{\circ}$C for 30 minutes. After being heated, the solution was filtered using small sieves.

2.3. Exofoliation of graphite
Graphene was prepared by liquid exfoliation of graphite in water-surfactant solution aided with probe-type ultrasonic homogenizer at ~70 W. 2 g of graphite was sonicated in 200 ml of water-tea solution for 90 minutes. After sonication, the resultant supernatant was collected in tubes (50ml) and centrifuged at 5000 rpm for 30 minutes. After centrifugation, 15 ml of upper dispersant was collected from the tube which is graphene. Ultra-pure water was used to wash graphene for 6 times and it was filtered by using filter paper. Finally, graphene was dried in vacuum oven that set at 100 $^{\circ}$C for 24 hours.

2.3. Graphene's characterization

Ultra-violet spectroscopy was used to measure the spectroscopy of blank tea solutions and exfoliated graphene in the resulting supernatant. The resulted supernatants after centrifugation and washing process are concentrated. Thus all supernatant samples were diluted with ultrapure water for the dilution factor of 10. The absorbance measurement for diluted supernatant samples and blank tea solutions were determined by using *Shidmazu UV Spectroscopy* from 800 nm to 200 nm. For morphology analysis, *Park Systems Atomic Microscopy (AFM)* was used to obtained images of graphene sheets in supernatant samples. Imaging was done in tapping mode using silicon cantilevers with spring constant of 3 to 10 N m^{-1} and resonance frequency of 110 to 190 kHz at ambient temperature and pressure with a scanning raster rate 1 Hz. Images were analyzed using *Molecular Imaging* software and properties profiles were obtained from topography images that have been levelled by first-order plane subtraction.

3. Results and Discussion

3.1. Characterization of graphene

3.1.1. Ultra-violet spectroscopy. After preparation of three different teas (BT, GT and OT) solutions in approximately same condition, the UV spectrum of those blank tea solutions were taken as shown in figure 1. Based on figure 1, solid line indicates UV spectrum for green tea solution reached the maximum value at 283 nm. Meanwhile, dashed line which represent UV spectrum of oolong tea reached the maximum value at 311 nm and uv spectrum of black tea solution (small dashed line) at 341 nm. The differences of maximum values was due to the different concentration of polyphenols present in each tea solution [13]. Thus, BT has higher polyphenols content than GT and OT solutions.

UV spectra of resulting supernatant were taken after being washed for 6 time with ultrapure water as shown in figure 2. Based on figure 2, all three spectra have shown UV peak at 270 nm. Durge et al. [14] claims that the UV peak at 270 nm (cyan region) indicates the C-C bond of graphene flakes. Thus, those peaks in figure 2 indicates successful exfoliation of graphite in each tea solution to produce graphene flakes. There is intense peak at 200 nm (yellow region) for G_{GTea} spectrum compare to G_{BTea} and G_{OTea} spectrum. This peak is attributed for remaining of unbound tea polyphenols in collected sample solution [9]. Green tea contains high concentration of simple polyphenols (catechins) than complex polyphenols. Whereas, black tea and oolong tea undergoes oxidation process that change simple polyphenols (flavonoids) into more complex structure of polyphenols (theaflavins and thearubigins) [1]. In reasonable explanation, most of simple polyphenols in green tea solution have tendency to stay in supernatant sample after it being centrifuge because it has less density than complex polyphenols.
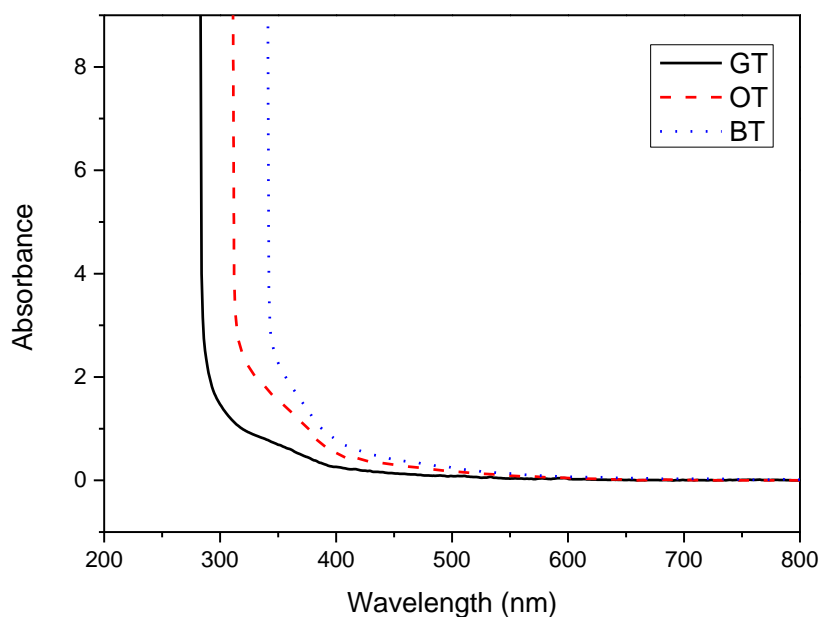
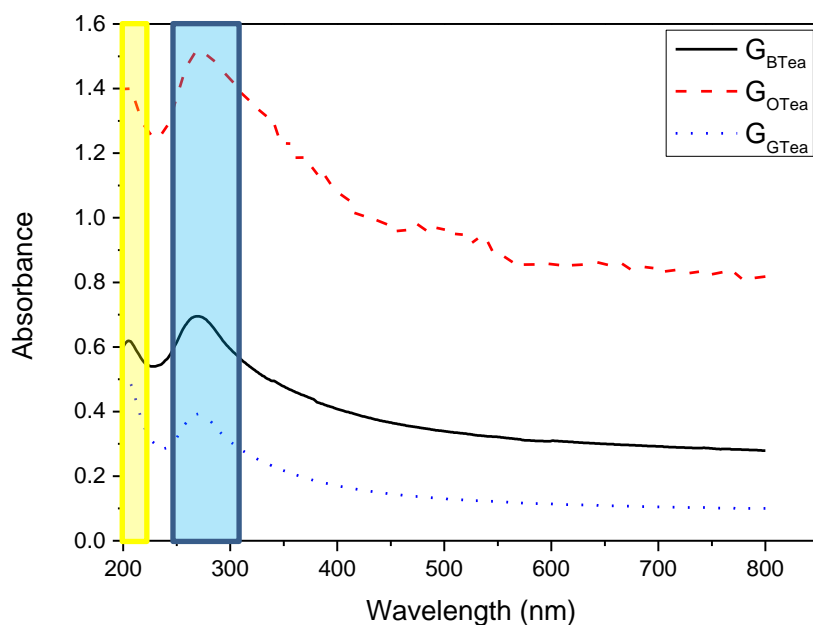**Figure 1**. UV spectrum of blank black tea (BT) solution, green tea (GT) solution and oolong tea (OT) solution

Figure 2. UV spectra of washed G_{Gtea}, G_{Otea} and G_{Btea} supernatant.

3.1.2. Atomic force microscopy (AFM)
The morphology study of those graphene was investigated by using *Atomic force microscopy (AFM)*. Figure 3 shows AFM images of G_{Gtea}, G_{Otea} and G_{Btea}. In figure 3, white color of flakes represent graphene sheet and brown color is for substrates. As shown in figure 3, there were many graphene sheets

been distributed in those three samples. All three AFM images for G_{Gtea}, G_{Otea} and G_{Btea} in figure 3 shows the graphene sheets have sharp edge caused by the effect of fragmentation during sonication process by homogenizer. The same effect of sonication on the graphene sheets had been seen in Durge et al. [15] research work. The lateral sizes of graphene sheets in figure 3 are different than each other. Thus graphene that produce using LPE of graphite does not have uniform lateral size unlike chemically modified graphene [16]. Using bare eyes, graphene sheets in figure 3(a) and figure 3(c) have larger lateral size compare to figure 3(b). This may be due to sonication effect in sample for figure 3(c) is high compare to figure 3(a) and figure 3(b). Based on Botas et al. [17] study, the lateral sizes obtained from AFM images for graphene oxide sheets is decreased when the power of sonication and sonication time increased [17].
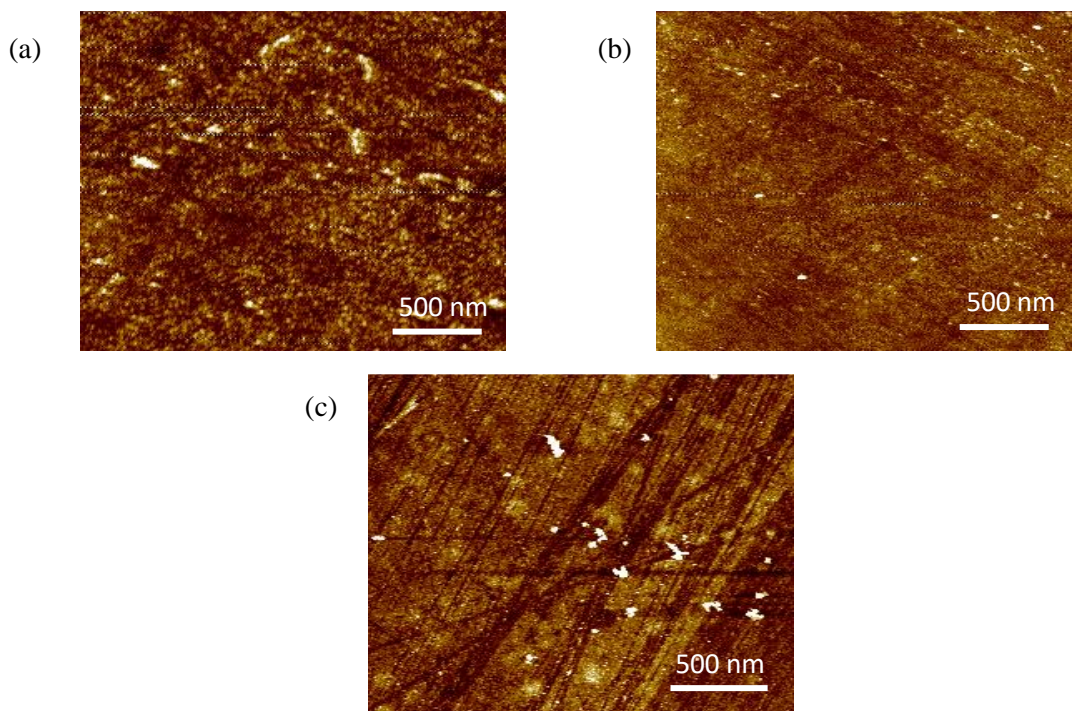

Figure 3. AFM images of (a) G_{Gtea}, (b) G_{Otea} and (c) G_{Btea}.

3.2. Effect of sonication time. The efficiency of graphene production can be improved by investigate several crucial parameters. One of important parameter that usually being investigated is production time [18]. Thus, the effect of sonication process was determined in this research work. 200 ml of BT, OT and GT solutions were prepared and mixed with 2 g of graphite. The duration of sonication time was varied between 15, 30, 45, 60, 75, 90 and 105 minutes. As the result, figure 4 shows the relationship between sonication time and concentration of G_{Gtea}, G_{Otea} and G_{Btea}. In all three relationship graphs on figure 4 shows that the yield concentration of graphene are increased as sonication time increased. Those data are consistent with other previous graphene production research [19]. This shows that sonication can be used to exfoliate graphene and as the time of sonication increased, the yield of graphene production also increased. Figure 5 shows log-log graph of G_{Gtea}, G_{Otea} and G_{Btea} against time. The exponent factor of time as function of graphene concentration can be determined by the gradient of log-log graph of graphene concentration against time [20]. Based on figure 5, G_{Gtea} has higher exponent factor of time (1.715) compare to G_{Otea} (1.033) and G_{Btea} (0.762). Based on UV spectrum in figures 2, GT has high concentration of polyphenols attached to graphene compare BT and OT. In addition, GT has simpler and smaller component of polyphenols. Small molecules of polyphenols acts as efficient surfactant because its can easily attach and locate between the layers of graphite to facilitate the exfoliation of graphene [6]. Small molecules of surfactants also packed tightly and increase its density on the graphene surface so that it can prevent graphene from aggregating and accumulating [21]. Thus

higher concentration of graphene will be produced using GT as surfactant in LPE of graphite for fixed sonication time compare to BT and OT.
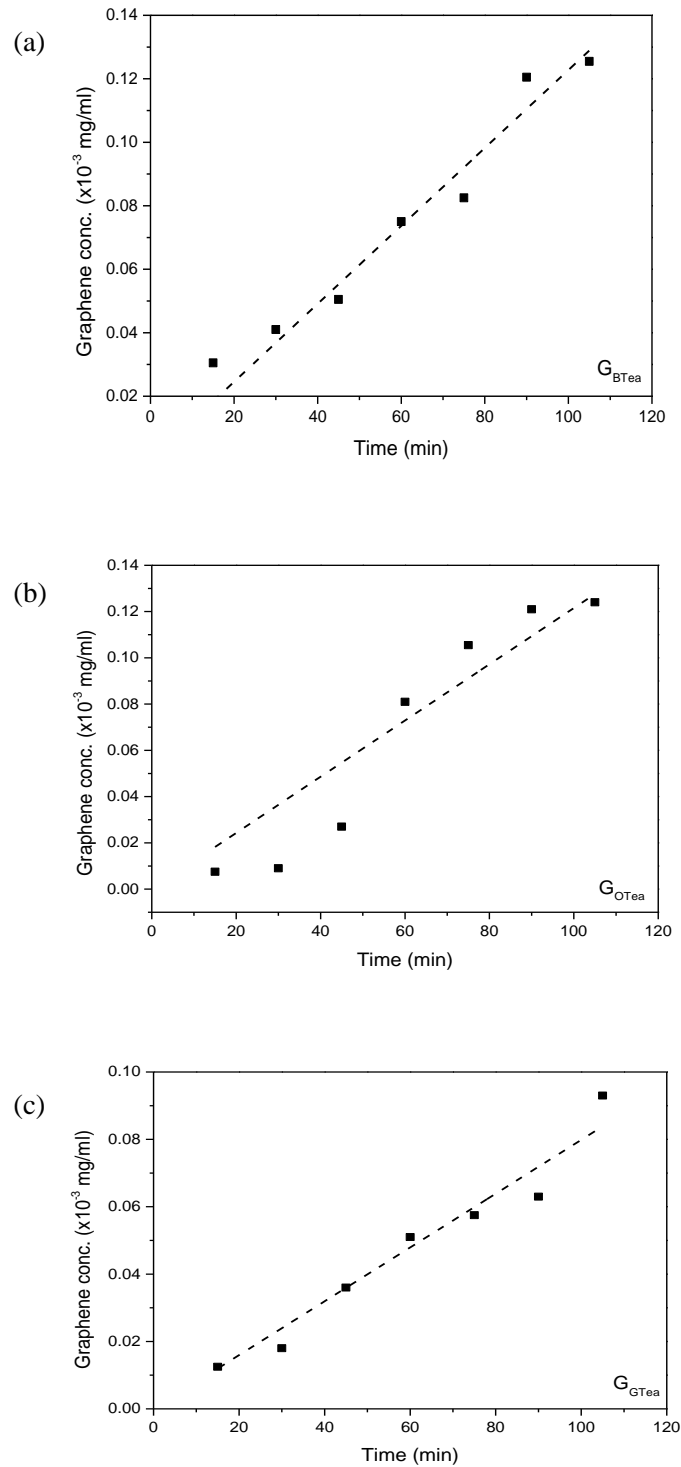

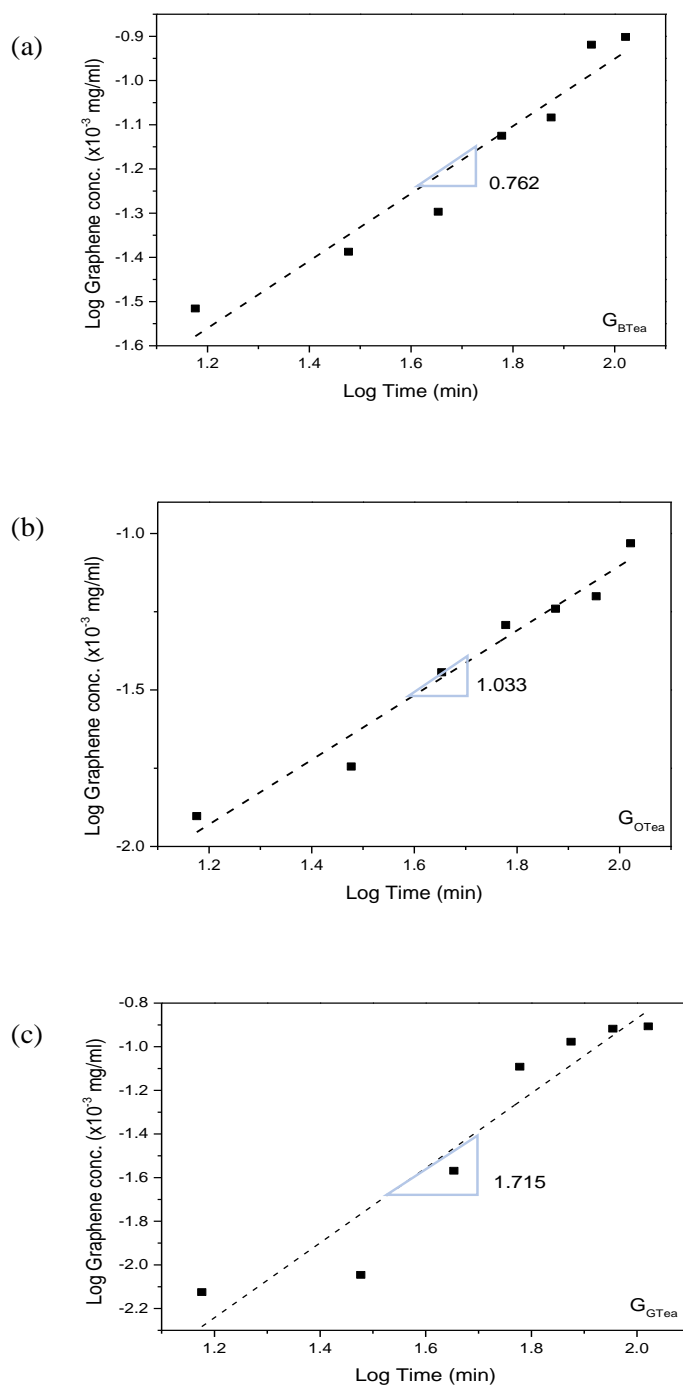**Figure 4.** Relationship between time and yield concentration of (a) G_{BTea}, (b) G_{OTea} and (c) G_{GTea}.

Figure 5. Log-log graph of yield concentration of (a) G_{BTea}, (b) G_{OTea} and (c) G_{GTea} against time.

4. Conclusion

In conclusion, this work has shown that direct exfoliation of graphite in GT, BT and OT solution can produce a few layers graphene. The presence of graphene after exfoliation of graphite in each tea solutions has been determined by using UV spectroscopy and the morphology study on those graphene was conducted by AFM. The effect of sonication time on the production of graphene using three different tea solutions as surfactant is discussed in this work. As the time taken for graphite to sonicated in surfactant solution increased, the yield of graphene concentration is increased. GT has shown highest

exponent factor of time (1.715) than BT and OT. This is due to small components of polyphenols that present in green tea. Thus, it is better to used green tea compare to black tea and oolong tea as surfactant in LPE of graphite in order to get high yield of graphene.

Acknowledgements

References

[1]   Cabrera C, Artacho R and Gimenez R 2006 Beneficial effects of green tea - A review *J. Am. Coll. Nutr.* **25**(2) 79–99

[2]   Kushwaha U K and Kushwaha U K S 2016 Health Benefits of Black Rice *Black Rice* **4**(2) 151–83.

[3]   Harbowy M E and Balentine D A 2007 Tea Chemistry *CRC. Crit. Rev. Plant Sci* **16**(5) 415–80.

[4]   Krane N 1993 Preparation of Graphene Selected Topics in Physics : Physics of Nanoscale Carbon *Growth Lakel* **4**(4) 1–5.

[5]   Ismail Z, Abu Kasim N F, Abdullah A H, Abidin A S Z, Ismail F S and Yusoh K 2017 Black tea assisted exfoliation by kitchen mixer allow one-step production of graphene *Materials Research Express* **4** 11

[6]   Abidin A S Z, Yusoh K, Jamari S S, Abdullah A H, and Ismail Z 2016 Enhanced performance of alkylated graphene reinforced polybutylene succinate nanocomposite *AIP Conf. Proc.* **1756** 1–6

[7]   Cui X, Zhang C, Hao R, and Hou Y 2011 Liquid-phase exfoliation, functionalization and applications of graphene *Nanoscale* **3** 2118-26

[8]   Ciesielski A and Samorı P 2014 Graphene via Sonication Assisted Liquid-phase Exfoliation *Chem Soc Rev* **43** 381-98

[9]   Ismail Z and Yusoh K 2016 Facile method for liquid-exfoliated graphene size prediction by UV-visible spectroscopy *AIP Conference Proceedings* **1756** 070002

[10]   Ginsburg E, Kinsley M D, and Quitral A 1998 The power of ultrasound *Adm. Radiol. J* **17**(5) 17–20

[11]   Uysal Unalan I, Wan C, Trabattoni S, Piergiovanni L and Farris S 2015 Polysaccharide-assisted rapid exfoliation of graphite platelets into high quality water-dispersible graphene sheets *RSC Adv.* **5**(34) 26482–90

[12]   Ban F Y, Majid S R, Huang N M, and Lim H N 2012 Graphene Oxide and Its Electrochemical Performance *Int. J. of Electrochem. Sci.* **7** 4345–51

[13]   Atomssa T and Gholap A V 2011 Characterization of caffeine and determination of caffeine in tea leaves using uv-visible spectrometer *African J. Pure Appl. Chem.* **5**(1) 1–8

[14]   Durge R, Kshirsagar R V, and Tambe P 2014 Effect of sonication energy on the yield of graphene nanosheets by liquid-phase exfoliation of graphite *Procedia Eng.* **97** 1457–65

[15]   Durge R, Kshirsagar R V and Tambe P 2014 Effect of Sonication Energy on the Yield of Graphene Nanosheets by liquid-phase exfoliation of graphite *Procedia Engineering* **97** 1457-65.

[16]   Park S and Ruoff R S 2019 Chemical methods for the production of graphenes *Nature Nanotechnology* **4** 45–47

[17]   Botas C, Perez-Mas A M, Alvarez P, Santamaria R, Granda M, Blanco C and Menendez R 2013 Optimization of the size and yield of graphene oxide sheets in the exfoliation step (Mexico: Instituto Nacional del Carbon, CSIC) *Carbon* **63** 576-78

[18]   Paton K R 2014 Scalable production of large quantities of defect-free few-layer graphene by shear exfoliation in liquids *Nat. Mater.* **13**(6) 624–30.

[19]   Fan J, Shi Z, Ge Y, Wang J, Wang Y and Yin J 2012 Gum arabic assisted exfoliation and fabrication of Ag–graphene-based hybrid *J. Mater. Chem.* **22**(27) 13764

[20]   Lotya M, King P J, Khan U, De S and Coleman J N 2010 High-Concentration, Surfactant-Stabilized Graphene Dispersions *ACS Nano* **4**(6) 3155–62

[21]   Zhang K 2017 Direct exfoliation of graphite into graphene in aqueous solution using a novel surfactant obtained from used engine oil *J. Mater. Sci* **53** 2484-96