PHYSICAL INVESTIGATION OF THIONINE-GRAPHENE NANOCOMPOSITE SYNTHESIZED USING DIFFERENT CONCENTRATIONS OF GRAPHENE OXIDE

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Abstract

Nanomaterials such as graphene is popular amongst researchers because of its capability to increase electrical conductivity. In some researches, graphene was composited with thionine to induce stability when dispersed in water-based solvents especially in fabricating electrodes for biosensor applications. In this research, the concentration of graphene in the Thionine-Graphene (Th-G) nanocomposite was varied to observe the stability of the composition produced. Different concentrations of graphene oxide (GO), 0.1, 0.3, 0.6 and 0.9 mg/mL were mixed with 2 mM thionine producing different Th-G samples and were observed through Scanning Electron Microscopy (SEM). Ultraviolet-visible spectroscopy (UV-vis) characterization were used to investigate the π-π interaction of graphene with thionine and to confirm the presence of both molecules in the samples. Physical observation of Th-G nanocomposite with 0.1mg/mL of graphene physically appeared to be most stable. While the UV-vis investigation confirms the presence of π-π interaction hence further proves the stability of the nanocomposite containing 0.1 mg/mL of GO when the absorbant peaks of graphene and thionine were the most prominent compared to the other samples.

Keywords: Absorbance, Graphene, Nanocomposite, Spectroscopy, Thionine-Graphene

Introduction

Graphene is a single atomic layer of carbon with a large surface area. It is an emerging superstar material used in many fields of study due to its incredible characteristics such as great mechanical strength, good electrical conductor and can withstand high temperature (Kim et al., 2008; Novoselov et al., 2004; Z. Yang, Ye, Zhao, Zong, & Wang, 2010). However, its hydrophobicity causes obstacles especially when handling with water-based solvents. In water, graphene molecules agglutinate causing inconsistency in obtaining homogeneity. GO is a less hydrophobic derivative of graphene that can be easily dispersed in water-based solvents due to the formation of hydrogen bonds between surrounding water molecules with the polar functional groups of GO attaining a stable GO suspension (Zou et al., 2016). The oxygen-containing functional groups on its edges make it more soluble and can easily be modified chemically. This beneficial attribute gives the ability for GO to absorb other molecules such as dye and were reported to be of high performance (Zhao, Ren, & Cheng, 2012). Other than that, the abundant functional groups at the edges of GO surface can also act as active sites for other functionalization and hybridization with other nanomaterials (Guo et al., 2014; Li et al., 2013).

Researchers have used graphene with other materials such as thionine in order to obtain stable water-based dispersion. Thionine, a tricyclic heteroaromatic molecule has been used to cater for the hydrophobicity of graphene (Zhu, Luo, & Wang, 2012). The hydrophilic molecule forms π-π stacking force with graphene making it disperse well in water-based solvents while preserving the intrinsic properties of graphene since it involves non covalent bonding. There were numerous researches done on the application of thionine to stabilize graphene (Chen, Zhai, Lu, Zhang, & Zheng, 2011; Liu, Wei, Zheng, Xu, & Zhou, 2014; Sun, Fu, Deng, & Wang, 2013; Zhu et al., 2012). Thionine was proven to be a good stabilizer for the hydrophobicity of intrinsic graphene. UV-vis was used to investigate the π-π interaction between thionine and graphene. This type of characterization requires well dispersion of graphene.

In this work, different concentrations of GO, 0.1, 0.3, 0.6 and 0.9 mg/mL were employed to produce the different Th-G nanocomposite samples through similar method (Zhu et al., 2012) to avoid bias results. However, vacuum filter was used instead of centrifugation to decant excess thionine. The samples were first physically observed to identify the difference in stability of the dark dispersion produced between the samples with different initial GO concentrations . SEM were also operated to support the physical observations in micro level. The samples were then characterized using Fourier-transform Infrared Spectroscopy (FTIR) to confirm the successfulness of the nanocomposition. UV-vis characterization was being done to investigate how different concentration of GO affects the π-π interaction between the thionine and graphene molecules in the Th-G nanocomposite.

Materials and Method

The GO was prepared via green synthesis route (Kamisan et al., 2015) while Th-G samples were prepared through procedure reported by Zhu et al. (2012). There were four samples being produced with different concentrations of GO, 0.1, 0.3, 0.6 and 0.9 mg/mL. The production of Th-G nanocomposite was initiated with the ultrasonication of different amount of graphite oxide with distilled water depending on the concentration intended. In order to obtain 0.1, 0.3, 0.6 and 0.9 mg/mL, a total of 5, 15, 30 and 45 mg of graphite oxide was mixed with 50 mL of distilled water and ultrasonicated, respectively. Later the mixtures were centrifuged to remove any residues and the supernatant produced was GO.

Concurrently, 10 mL of the 2 mM thionine was prepared and was mixed with GO and was stirred vigorously for 12 hours. After successful mixing, 600 µL of 26% hydrazine hydrate was added into the mixture and was further stirred for another 10 minutes. The mixture was then heated under reflux at 95˚C for one hour. After heating, the stable dark dispersion was filtered using the vaccuum filter and kept in sample flasks. The steps were repeated for every different concentrations of GO.

The microstructure of the samples were observed using SEM (Phenom XL) and elemental detection using Energy Dispersive X-ray Spectroscopy (EDX). FTIR was done (Perkin Elmer FTIR Model Spectrum 400) with 4 cm^{-1} resolution. The sedimentation stability was further observed via UV-vis (Cary 5000 - V1.12) investigation. The working wavelength range was done between 800 nm to 200 nm at a scan rate of 600 nm/min. A 2 mL of each of the samples were filled into the cuvettes and absorbance were taken and recorded.

Result and Discussion

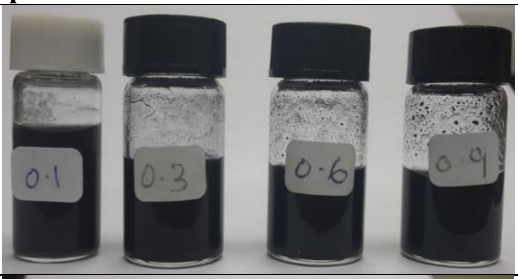
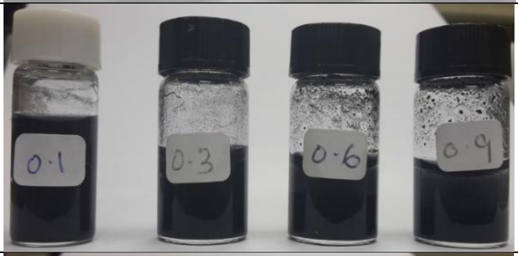
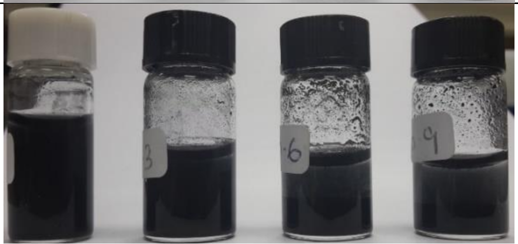
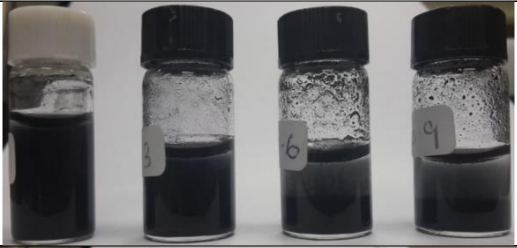
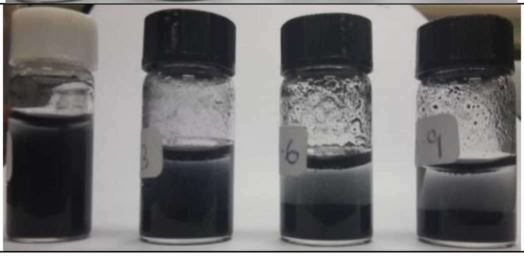
Dispersal Stability

All of the four samples with different concentrations of graphene was physically observed. All of them appeared black as a sign of successful oxygen removal by reduction agent and the restoration of the sp2 structure of graphene (Guardia et al., 2012; Wallace et al., 2008). Early inspection in Th-G samples with 0.1 and 0.3 mg/mL of GO produced a stable homogenous dispersal in the water solvent. However, in the samples with 0.6 and 0.9 mg/mL of GO produced dark clumps. In 0.6 mg/mL GO, a few dark clumps were found to disperse in the water but in the sample with 0.9 mg/mL GO, numerous clumps with various sizes were observed and some of the large aggregates were found immediately at the bottom of the flask. These clumping phenomenon happened when there was a high concentration of GO in the sample indicating that the aggregate suppression activity of thionine failed to stabilize the clumping of graphene molecules eventhough thionine was an excess. When the thionine composited with a lower concentration of graphene molecules, the right electrostatic repulsion forces occurred and the whole Th-G species will appear as a stable dark dispersion (Sun et al., 2013). During application of Th-G with 0.9 mg/mL GO by using small tipped pipette, the larger clumps clogged the tip and causing inefficiency in characterization. Stability and homogeneity of the dark dispersion is crucial so that a more efficient application can be performed.

The stability of the dark dispersions of all for samples were then investigated. Within 4 minutes time frame, observation has been made to identify the behaviour of the dispersion. According to **Table 1**, one can observe that the sample with 0.1 mg/mL GO abide with the electrostatic repulsion forces and remained stably dispersed throughout. The 0.3 mg/mL GO sample started to lose its formation in the second minute while the 0.6 and 0.9 mg/mL GO samples at the very first minute. By the end of 4 minutes, the latter two samples expressed sediments at the bottom of the sample flasks leaving only a small portion of dispersion in the solvent. Homogenous reformation of all the samples were obtained with a simple mechanical agitation.

In the production of Th-G nanocomposite, graphene was reduced from GO with the presence of thionine. GO has the ability to absorb thionine molecules due to the polar functional groups on its surface. However, without thionine association, graphene aggregated as a result of van der Waals interaction between surrounding graphene molecules in the sample. As a result, a great reduction of the surface area of the graphene leads to the reduction of the ability to absorb other molecules such as thionine (Zhao et al., 2012; Zou et al., 2016). This causes it to coagulate and not appearing as colloidal suspension.

Table 1 Time lapse of sedimentation process for Th-G nanocomposite samples with different GO concentrations 0.1 mg/mL, 0.3 mg/mL, 0.6 mg/mL and 0.9 mg/mL in the span of 4 minutes

Time	Th-G suspension
0 minute	
1 minute	
2 minutes	
3 minutes	
4 minutes	

Microscopy Observation

As to support, SEM was operated to monitor the physical characteristic of all four samples. Based on observation made on **Figure 1**, it is clear the higher the concentration of GO, the more intense the graphene structures can be observed. Samples with 0.1 and 0.3 mg/mL of GO displayed relatively smaller aggregates as compared to the other two samples with higher concentrations of GO. EDX characterization was done to inspect the percentage of elements in the samples. Results exposed that the atomic concentration percentage of nitrogen element in each sample of 0.1, 0.3, 0.6 and 0.9 mg/mL were 21.70%, 21.13%, 16.94% and 16.47% respectively. Here nitrogen element can represent the material thionine as graphene does not contain any nitrogen element. Presumption can be made that the sample with 0.1 mg/mL of

GO contained the highest amount of thionine composited with the graphene. As a result, the high amount of thionine induced stability to graphene. Conflicting with the other samples containing higher concentrations of GO, the lesser amount of thionine composited resulting the large aggregates of graphene unstabilized.

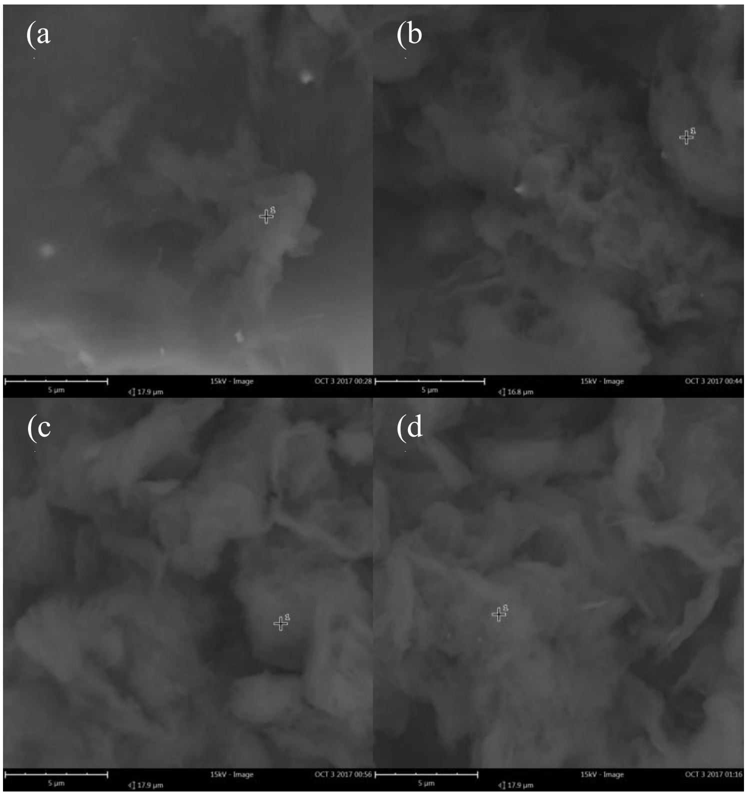


Figure 1 SEM images of Th-G with (a) 0.1 mg/mL, (b) 0.3 mg/mL, (c) 0.6 mg/mL and (d) 0.9 mg/mL GO

Chemical Bonds Investigation

FTIR was conducted to investigate the successfulness of the composition of thionine with graphene in every samples. The FTIR spectrum in **Figure 2** shows all of the samples with different concentrations of graphene expressed prominent peaks at 1633cm^{-1} and broad combined peaks at 3288cm^{-1} and 3354cm^{-1}. At the wavelength of 1633cm^{-1}, the samples expressed the C=C bond of the graphene while the peaks at wavelengths 3288cm^{-1} and 3354cm^{-1} denotes for the stretching of asymmetric N-H bond which is expressed by the thionine in the sample (Ciriza et al., 2015; Ibrahim et al., 2017; S.-T. Yang et al., 2010). All of the samples did not express a peak at wavelength 1644cm^{-1} which denotes for carbonyl (C=O) stretching vibration when graphene forms amide bond with other molecules (Wang, Shen, Wang, Yao, & Park, 2009). This proves that no covalent bonding occurred but only π-π interaction between the two materials. Furthermore, through FTIR, GO expresses two prominent peaks at 1373cm^{-1} and 1070cm^{-1} which denotes for carboxyl (COOH) and C-O bonds (Yu et al., 2015). The absence of these two peaks suggested that graphene was successfully reduced from GO in the presence of thionine.

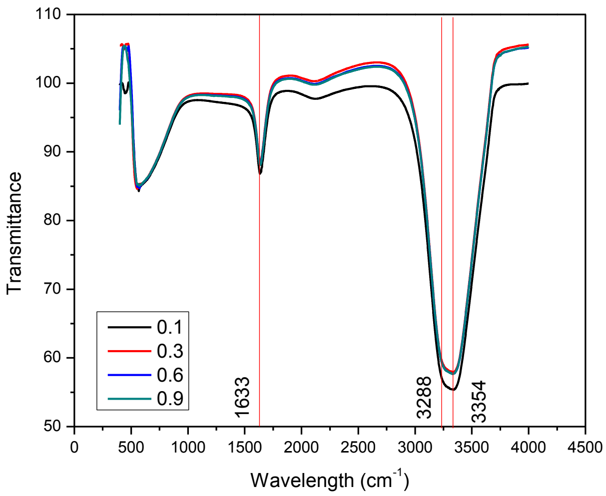


Figure 2 FTIR spectrum of Th-G nanocomposite with different concentrations of GO

UV–Vis Spectroscopy

The absorption spectrum was carried out using UV-Vis spectroscopy to investigate the interaction between the thionine and graphene molecules in Th-G nanocomposite. As shown in **Figure 3**, graphene expressed its characteristic band at 286 nm which is due to the π-π* transition of aromatic C=C bonds which suggests that the nanocomposition happened without disrupting the intrinsic properties of graphene during the interaction with thionine. Thionine in the other hand expressed its characteristic band in the visible light region at 650 nm which corresponds to the n-π* transitions of C=N bond (Liu et al., 2014). Having both prominent bands in a sample proves the successfullness of the interaction and composition of both graphene and thionine molecules. Observing Figure 3, 0.1 mg/mL GO sample has the highest absorption intensity due to the stability of the dispersion during the characterization. As an addition, prominent peaks of graphene in 286 nm wavelength and 650 nm of thionine were obtained. 0.3 mg/mL GO sample expressed more peaks but not prominent. Only two recognisable peaks related to subject which were graphene and thionine but expressing them in a more broad and non-prominent manner. In lower absorption intensities were the 0.6 and 0.9 mg/mL GO samples. Thionine peaks at 650 nm wavelength can be observed but graphene peaks seem flattened or unrecognisable. This may due to the nonhomogenous condition where the large clumps reside.

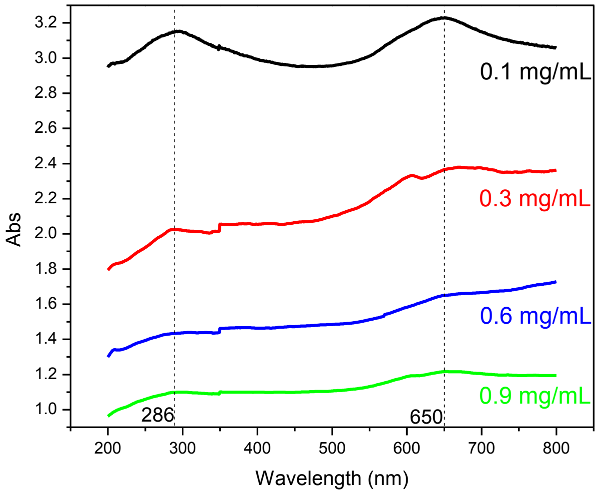


Figure 3 UV-Vis characterization of Th-G samples with different GO concentrations

The sedimentation during characterization may also caused due to the lack of absorption by the graphene molecules. During UV-vis characterization, the clumps reside in the 0.6 and 0.9 mg/mL GO samples sedimented quickly due to gravity pull. According to the result potrayed in Figure 3, we can conclude that the clumps were made up mostly of graphene molecule. As a result of the sedimentation of the clumps, graphene peaks failed to be expressed in the UV-vis spectrum.

Conclusion

Th-G nanocomposite with different concentrations of GO were successfully being produced based on the FTIR spectrum. According to physical observation, the samples with 0.6 and 0.9 mg/mL produced dark clumps which shows inefficient interaction between graphene and thionine molecules. The UV-vis investigation shows significant peaks of graphene and thionine in sample with 0.1 mg/mL GO which shows a good interaction of both components in the nanocomposition. The samples with 0.3, 0.6 and 0.9 mg/mL GO shows a more broad thionine peaks. The latter two samples showed almost unacknowledgable graphene peaks altogether due to its nonhomogeniety. Hence, Th-G nanocomposite with 0.1 mg/mL of GO is the most physically efficient concentration to be used in other applications.

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Conflict of interests

Author hereby declares that there is no conflict of interests with any organization or financial body for supporting this research.

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