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Surfactant assisted liquid phase exfoliation of graphite rod in the production of stable colloidal graphene-surfactant solution

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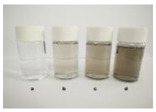
GRAPHICAL ABSTRACT



Graphene-SDS

Graphene-CTAB

ABSTRACT

Surfactant assisted Liquid Phase Exfoliation (LPE) was reported to be the most promising strategy to produce high quality stable colloidal graphene solution. In this study, surfactant assisted LPE was carried out in a two electrode system, using surfactants namely sodium dodecyl sulphate (SDS) and cetyltrimethylammonium bromide (CTAB). The study was carried out at concentrations of surfactant below critical micelle concentration (CMC) which are 0.01M SDS and 0.001M CTAB. The electrochemical process was carried out for 5 hours, at several intercalation potentials of 6V, 7V and 8V with a sequence of intercalation of surfactant onto the graphite anode followed by exfoliation of the surfactant-intercalated graphite electrode when the anode was treated as cathode. The graphene-surfactant suspension was characterized by Optical microscopy, UV-Visible spectroscopy, Nuclear magnetic resonance (NMR) and Raman spectroscopy. UV-Visible spectroscopic analysis indicated an increase in graphene production with increased in intercalation potential while Optical microscope images shows that graphene-SDS was more dispersed than graphene-CTAB at the various intercalation potential employed. The presence of shielding in ^{1}H NMR spectroscopy indicates the interaction of graphene with surfactant. Raman spectra of both graphene-SDS and graphene-CTAB obtained show typical exfoliated graphene band shape affected by the attachment of surfactant molecules confirmed the graphitic configuration. Three peaks in the Raman spectra shown by graphene-surfactant are the D band around 1350 cm^{-1}, the G band 1590 cm^{-1} and the 2D band around 2700 cm^{-1}. The study concluded that graphene-SDS results is a more stable colloidal graphene-surfactant solution compared to graphene-CTAB.

Keywords: Graphene, Liquid Phase Exfoliation, Grapehene-surfactant, sodium dodecyl sulphate, cetyltrimethylammonium bromide.

1. INTRODUCTION

Graphene, a two-dimensional (2D) structure consisting of sp^2 bonded carbon atoms densely packed in honeycomb crystal lattice, has attracted much attention of researches because of its unique structural and superior properties [1,2,3]. It can be wrapped up into zero dimensional (0D) fullerenes, rolled into one dimensional (1D) carbon nanotubes (CNTs) or stacked into three dimensional (3D) graphite [1]. Graphene is the most fascinating materials of the 21st century because its intriguing features, for instance high mobility of charge carriers, unique transport performance, high mechanical strength and extremely high thermal conductivity [2]. These fascinating features are suitable in many application such as flexible devices, high-frequency transistor, energy storage, sensors, biomedical application and composites [2,5,6,8]. Thus, these leads to explosive research in the production of graphene for future application.

Various method have been conducted since the discovery of graphene in 2004 by two scientist, Andre Geim and Konstantin Novoselov, to produced high yield production and less structural defects of graphene [1,2]. Graphene production method can be classified into two approaches which is top-down and bottom-up. The top-down method that are well known include mechanical exfoliation (Scotch tape method) historically used by Geim and Novoselov, reduction of graphene oxide, electrochemical exfoliation, liquid phase exfoliation in the presence of surfactant [4]. The bottom-up approaches include catalytic chemical vapour deposition (CVD), organic synthesis or expitial growth on SiC.

Early days of graphene research, Liquid Phase Exfoliation (LPE) has been anticipated as the most desirable mass-production method for graphene because this method is straightforward and scalable process [3]. This method was carried out by Coleman group in 2008 via sonication of graphite flakes in organic solvent such as N-methyl-pyrrolidone (NMP) and dimethylformamide (DMF). It is well known that exfoliated graphite can form stable colloidal suspension of graphene sheet [5]. In LPE method, the solvent is the most important factor that dominates the production of grahene. Three different routes can enhance the exfoliation process namely in organic solvent, with polymer assistant and with surfactant assistant.

In this study, the synthesis of stable colloidal graphene solution via surfactant assisted liquid phase exfoliation with two electrode system is still in its infancy for highly efficient production without the use of very strong oxidizing and hazardous oxidative condition. The surfactant used in this study is Sodium Dodecyl Sulphate (SDS) and Cetyltrimethylammonium Bromide (CTAB) with different intercalation potential of 6V, 7V and 8V. The electrochemical process includes an electrochemical intercalation of surfactant into graphite and electrochemical exfoliation of surfactant-intercalated graphite electrode by using the electric current as oxidizing and as reducing agent later. The effect of surfactant and intercalation potential on the production of graphene-surfactant are studied. Characterization of graphene-surfactant solution have been carried out by using Optical microscopy, UV-Visible spectroscopy, Nuclear magnetic resonance (NMR) and Raman spectroscopy.

2. EXPERIMENTAL

The method of stable colloidal of graphene solution in this study are based on electrolytic liquid phase exfoliation of graphite rod in different type of surfactant at several intercalation potential of 6V, 7V and 8V. The electrolytic cell was set up by using two high purity graphite rods as the electrode, DC power supply for drive force, SDS and CTAB as electrolyte. The apparatus set up was shown in Figure 2.1. The concentration of SDS and CTAB are fixed below the critical micelle concentration (CMC) which are 0.01M SDS and 0.001M CTAB.

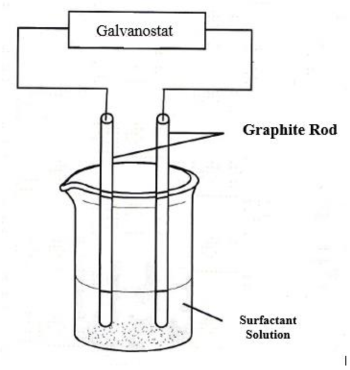


Figure 2.1 Schematic diagram of the experimental set up for liquid phase exfoliation of graphene

A constant voltage of 6V were initially applied between the two electrodes using a DC power supply and the electrochemical reaction was allowed to occur for about 10 minutes. The power supply was then turned off and the anode was treated as cathode and vice versa. The power supply is then turned on to let the electrochemical process to occur for about another 10 minutes. The process was carried out for the sequence of electrochemical intercalation of surfactant into graphite anode followed by electrochemical exfoliation of the surfactant which is intercalated graphite electrode when the anode was treated as cathode. Therefore, the intercalation-exfoliation process for graphite electrode occur at both anode and cathode. This process was repeated for 5 hours of electrolysis. A very stable graphene-surfactant solution was obtained from the electrochemical operation and the product was centrifuged at low speed (15 000 rpm) to remove large agglomerates and to obtain graphene powder. The analysis for the different type of surfactant and significant absorbance of the graphene solution produced from 6V, 7V and 8V electrochemical exfoliation process are analyzed using Optical microscopy, UV-Visible spectroscopy, Nuclear magnetic resonance (NMR) and Raman spectroscopy.

3. RESULTS AND DISCUSSION

3.1. Liquid Phase Exfoliation (LPE) of graphite

Liquid Phase Exfoliation (LPE) of graphite rod was carried out via electrochemical route in the presence of surfactant to yield a stable colloidal graphene solution. The electrochemical process involve a sequence of intercalation of surfactant to graphite electrode (anode) followed by electrochemical exfoliation of the surfactant-intercalated graphite electrode (cathode) where electric current was used as the oxidizing and reducing agent. In this study, the surfactant used is anionic surfactant namely sodium dodecyl sulphate (SDS) and cationic surfactant namely cetyltrimethylammonium bromide (CTAB). The functions of surfactant in the electrochemical process is to prevent them from re-stacking in the solution thus yield a stable colloidal graphene solution [5,8,13]. Electrochemical intercalation of surfactant in graphite was achieved by electrooxidation in surfactant solution according to this reaction.

$$[C_x] + [\text{surfactant}] + y(\text{solv.}) \leftrightarrow [C_x{+}\ \text{surfactant}]y(\text{solv.}) + e^-$$

Where Cx is graphite, and solv. is solvent (water). The surfactant was adsorbed onto the surface of the graphite anode to form surfactant-intercalated graphite electrode, thus it prevent re-stacking of graphene sheets after the exfoliation process. When the graphite anode is treated as the cathode, electrochemical exfoliation of the surfactant-intercalated graphite electrode occurred and a very stable colloidal graphene-surfactant suspension was obtained. Figure 3.1 shows electrochemical route in three-electrode system for the production of graphene [40]. The route as shown in Figure 3.1 is similar with the production of graphene-surfactant for this study.

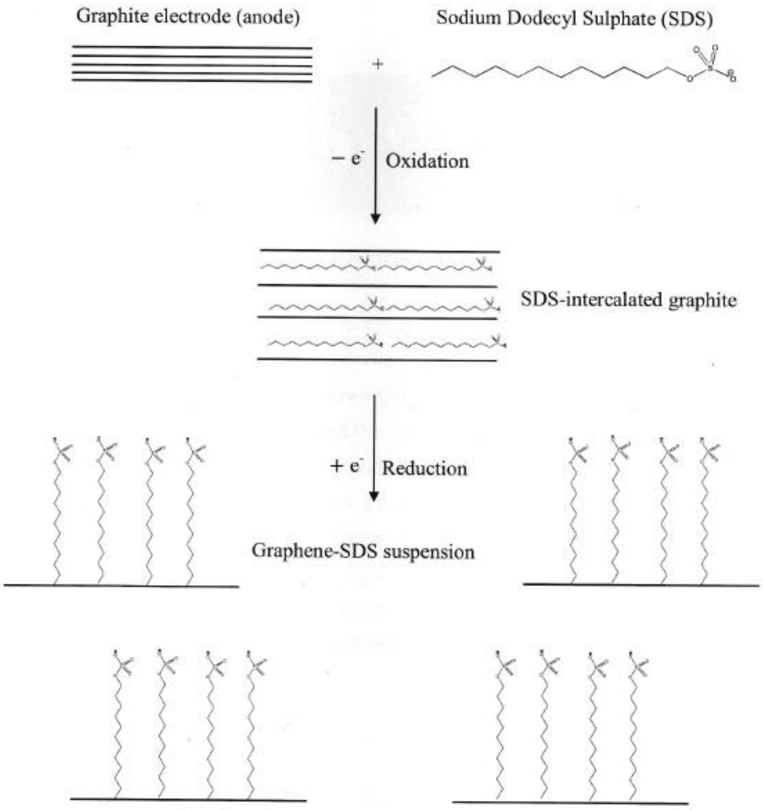


Figure 3.1 The electrochemical route for synthesis of graphene-surfactant solution [9]

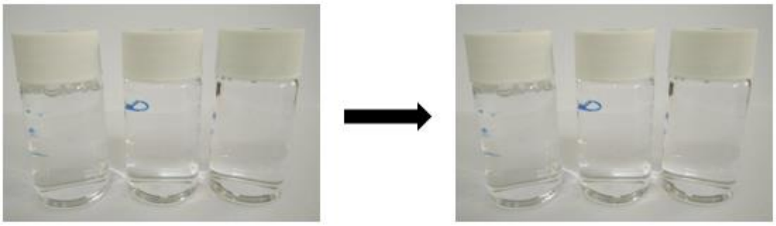
3.2. Effect of Surfactant on the synthesis of graphene

In this study, the surfactant assisted LPE via a two electrode system has shown to promote the stabilization of suspended graphene sheets against aggregation, able to reduce the high surface energy of water and enhance interaction with the highly hydrophobic graphitic surfaces. The surfactant interacts with graphene by surface adsorption, micelle formation or π-π stacking [9]. Ionic surfactants adsorbed onto graphene impart an effective charge by providing electrostatic repulsion to prevent re-aggregation of the graphene sheets [9]. Sodium Dodecyl Sulphate (SDS) and Cetyltrimethylammonium Bromide (CTAB) surfactant are compared in terms of their stability in the dispersion of graphene solution. The concentration of the surfactant are set up below the critical micelle concentration (CMC). Concentration of SDS is 0.01M while concentration of CTAB is 0.001M.

The stability of the graphene-surfactant solution were observed by keeping the colloidal solution in vial for approximately 3 months. Figure 3.2 (a) and Figure 3.2 (b) shows the graphene-surfactant solution after exfoliation process and after 3 months respectively. Based on the Figure 3.2 (b), the graphene-SDS platelets remained suspended. No solids were observed at the bottom of the vial. This indicates that the colloidal graphene-SDS in the solution are stable. Therefore, it can be prove that, both surfactant are able to stabilize the graphene suspension.

(a) (b)

Figure 3.2 Graphene-SDS solution a) after exfoliation process b) after kept about 3 months



(a) (b)

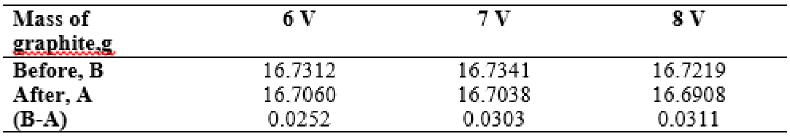
Figure 3.3 Graphene-CTAB solution a) after exfoliation process b) after kept about 3 months

Anionic surfactant such as SDS can acts as highly efficient surfactants because of their hydrophobic surface similar to graphene and the strong π-π interactions between them can facilitate LPE process [9]. The CTAB molecule has quaternary cationic ammonium head group and long alkyl chains as tail which enables the molecule to be adsorbed onto the electron rich graphene surface through electrostatic interactions [9]. The interactions between hydrophobic chains of CTAB molecule on the graphene surface could prevent the restacking and agglomeration of the exfoliated graphene. Therefore, SDS and CTAB are suitable surfactant to stabilize the graphene solution.

3.3. Effect of intercalation potential on the synthesis of graphene

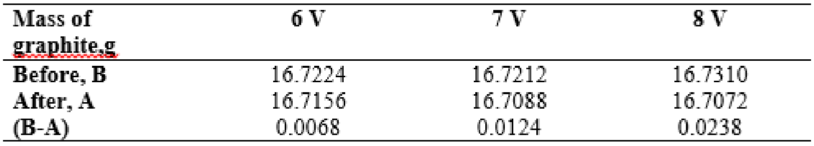
In this studies, the effect of different intercalation potential was studied in the production of stable colloidal suspension of graphene. Intercalation potential of 6V, 7V and 8 V were applied in the electrochemical process. Different surfactant give different effect on intercalation potential on the production of stable colloidal suspension of graphene. The graphite electrode was weighed before and after exfoliation. The difference in weight of the graphite rod indicates the amount of exfoliated products formed. The weight of the graphite electrode used before and after exfoliation with anionic and cationic surfactant are tabulated in Table 3.1 and Table 3.2. The data showed a slight decrease in the weight of graphite electrode used after 5 hour electrolysis. It is also observed that, the higher the intercalation potential used showed an increase in the weight loss of graphite rod also indicating in the increase of exfoliation product.

Table 3.1 The weight of the graphite electrodes before and after electrolysis in SDS solution



Mass of graphite,g	6 V	7 V	8 V
Before, B	16.7312	16.7341	16.7219
After, A	16.7060	16.7038	16.6908
(B-A)	0.0252	0.0303	0.0311

Table 3.2 The weight of the graphite electrodes before and after electrolysis in CTAB solution



Mass of graphite,g	6 V	7 V	8 V
Before, B	16.7224	16.7212	16.7310
After, A	16.7156	16.7088	16.7072
(B-A)	0.0068	0.0124	0.0238

The graphene-SDS suspension obtained is black in colour (Figure 3.4) while graphene-CTAB (Figure 3.5) suspension appears colourless. Figure 3.4 shows that the the colour of graphene-SDS suspension darkened as the intercalation potential increased resulting from the increased the amount of exfoliated product. However, the graphene-CTAB shows almost colourless solution since the amount of product exfoliated was very minimal.

Although the solution is colourless, the weight of graphite rods decrease after the exfoliation as the intercalation potential increases.

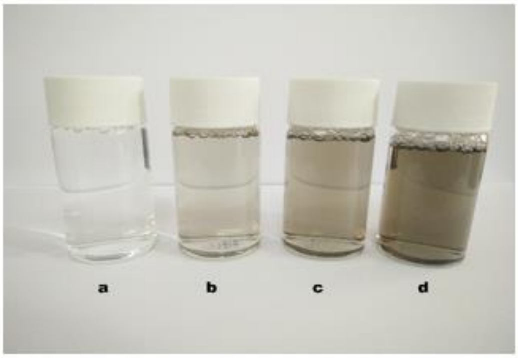


Figure 3.4 a) 0.01M of SDS solution and graphene-SDS solution prepared at different intercalation potential b) 6V, c) 7V, and d) 8V.

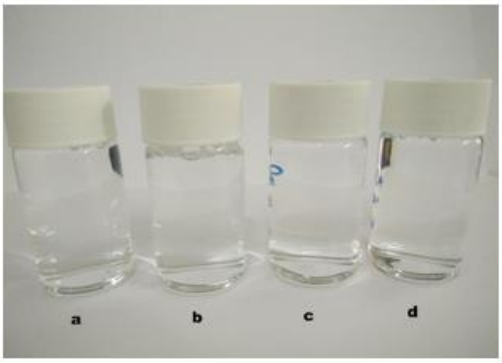


Figure 3.5 a) 0.001M of CTAB solution and graphene-CTAB solution prepared at different intercalation potential b) 6V, c) 7V and d) 8V

The effect of electrochemical reaction is dependent on the voltage applied since the electric current was served as the electro-oxidizing or reducing agent. It can be concluded that the amount of graphene being exfoliated depends on the intercalation potential applied whereby the higher the intercalation potential the greater the amount of exfoliated product.

3.4. Characterization of graphene

The graphene-SDS and graphene-CTAB solutions obtained at different intercalation potential were characterized using Optical Microscope, UV-Visible spectrometer, Nuclear Magnetic Resonance (NMR). Meanwhile, the dried graphene-surfactant powder were used to analyse using Raman Spectroscopy.

3.4.1 Optical microscopy

Optical microscope images only provide qualitative information about the state of dispersion of graphene in aqueous surfactant. The state of dispersion was studied after exfoliation process and after centrifugation for 1 hour at 3000 rpm for both graphene-surfactant solutions with different intercalation potential. Figure 3.6 and Figure 3.7 shows optical images of graphene-surfactant dispersion at different intercalation potential after exfoliation process and after centrifuged.

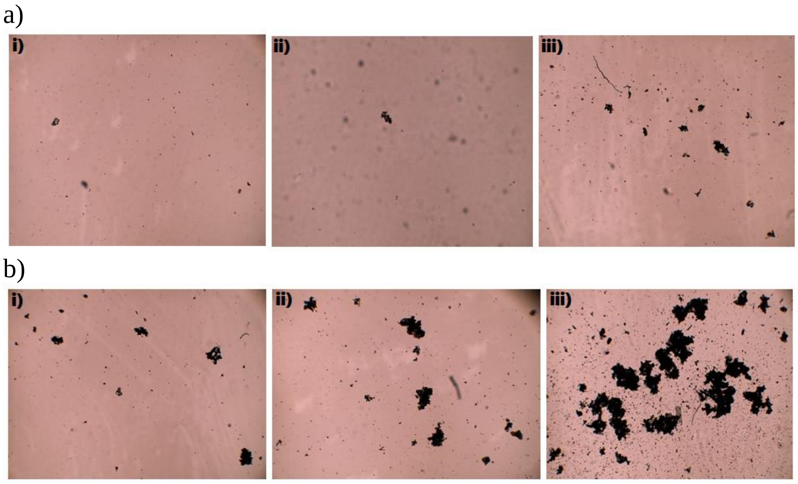


Figure 3.6 Representative optical microscope images of Graphene-SDS solution a) after exfoliation process and b) after centrifugation. Figure a) and b) shows images at different intercalation potential i) 6 V, ii) 7 V, iii) 8 V.

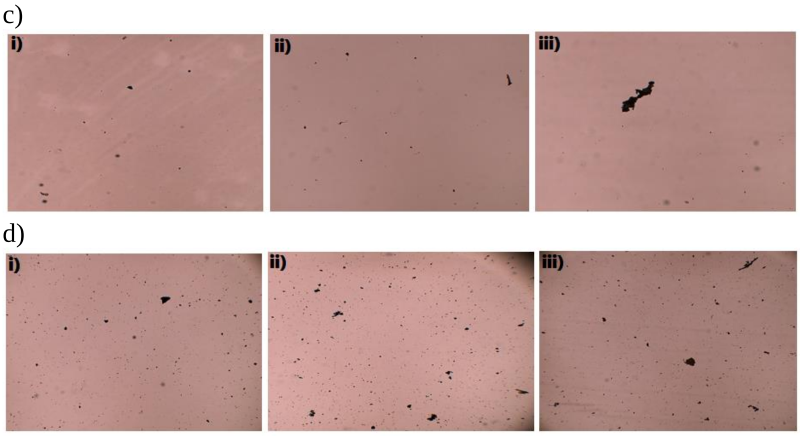


Figure 3.7 Representative optical microscope images of Graphene-CTAB solution a) after exfoliation process and b) after centrifugation. Figure a) and b) shows images at different intercalation potential i) 6 V, ii) 7 V, iii) 8 V.

For graphene-SDS, the amount of dispersed graphene and the aggregates appeared at 6 V and 7 V are very smaller compared to intercalation potential at 8V, the images of dispersed graphene and the aggregates can be seen clearly. After about 1 hour centrifuged, the dispersed graphene become large agglomerates at every intercalation potential. The higher the intercalation potential, the larger the amount of graphene which aggregates.

On the other hand, for the graphene-CTAB, the amount of dispersed graphene is much less compared to graphene-SDS and the size of the dispersed graphene is very small at every intercalation potential. After centrifugation for 1 hour, the amount of dispersed graphene is were more visible and aggregates of the graphene could be observed as intercalation potential increasing.

The effect of intercalation potential in this study, show that the amount of exfoliated product of graphene-SDS greater that graphene-CTAB as the intercalation potential increased. Thus, optical microscopy further confirmed the result as the amount of graphene-SDS produced higher than graphene-CTAB.

3.4.2 UV-Visible spectroscopy

UV-Visible absorption spectra of graphene-SDS and graphene-CTAB suspension at different intercalation potential of 6V, 7V and 8V are shown in Figure 3.8 and Figure 3.9 respectively. These spectra are obtained by subtracting the background of 0.01M SDS and 0.001M CTAB.

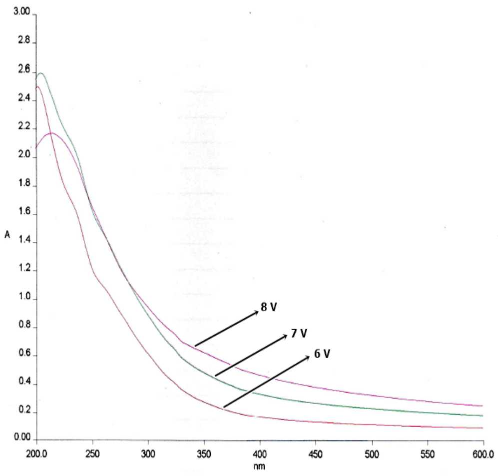


Figure 3.8 UV-Vis spectra of graphene-SDS suspensions prepared at different intercalation potentials with background of 0.01 M SDS

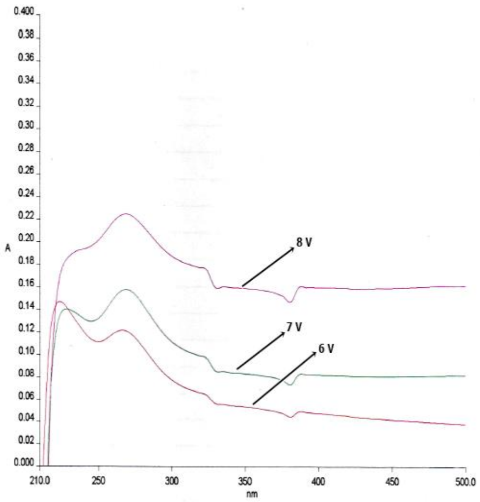


Figure 3.9 UV-Vis spectra of graphene-CTAB suspensions prepared at different intercalation potentials with background of 0.001 M CTAB

Based on the Figure 3.8, UV-Vis spectra for graphene-SDS shows at different intercalation potential have different maximum absorbance. The absorbance increased at 6V and 7V electrolysis due to the increased of graphene concentration in the suspension. While, the absorbance at 8V initially increased then reduce when achieve its maximum absorbance. This is because the smaller amount of suspension produced. The maximum absorbance of 6V, 7V and 8V is at 202 nm, 204 nm and 214 nm respectively.

UV-Vis spectra for graphene-CTAB on Figure 3.9 shows, the absorbance increased as the intercalation potential increased. As the intercalation potential increased, the graphene concentration in the suspension also increased. The maximum absorbance for all peaks is 270 nm corresponding to $\pi \rightarrow \pi^*$ transitions of aromatic C-C bond.

3.4.3 ^{1}H Nuclear magnetic resonance (NMR)

The interaction of graphene with surfactant was proven by ^{1}H (400 MHz) Nuclear Magnetic Resonance (NMR) spectroscopy. Graphene-surfactant suspension was dissolved in D_2O solution and placed into an NMR tube. The spectrum of surfactant was analysed. Graphene-surfactant suspension and surfactant were scanned individually and then the spectra were compared to show the shifts in peak position corresponding to interaction between the surfactant and the graphene. Figure 3.10 (a) and (b) shows the ^{1}H NMR spectra of the graphene-surfactant complexes stabilized with SDS and CTAB respectively compared with the surfactant only spectra.

The spectra of graphene-surfactant are compared with surfactant only spectra shows shifting of peaks representing hydrogens involved in the complexation interaction. Based on the Figure 3.10 (a), graphene-SDS and SDS only shows small shifting while (b) graphene-CTAB and CTAB alone shows significant shifting. The shifting is caused by the shielding effect of the delocalised electrons in the graphene sheet. This occurs when the proton is in close proximity and involved in van der Waals interactions [39]. For graphene-CTAB, two of the methyl groups on the quarternary amine are interacting with the graphene sheets. This can be confirmed by the splitting of the peak into three peak at 2.8 ppm. Both graphene-surfactant shows shifting in the NMR spectrum, thus, indicating the interaction between graphene and surfactant in the solution.

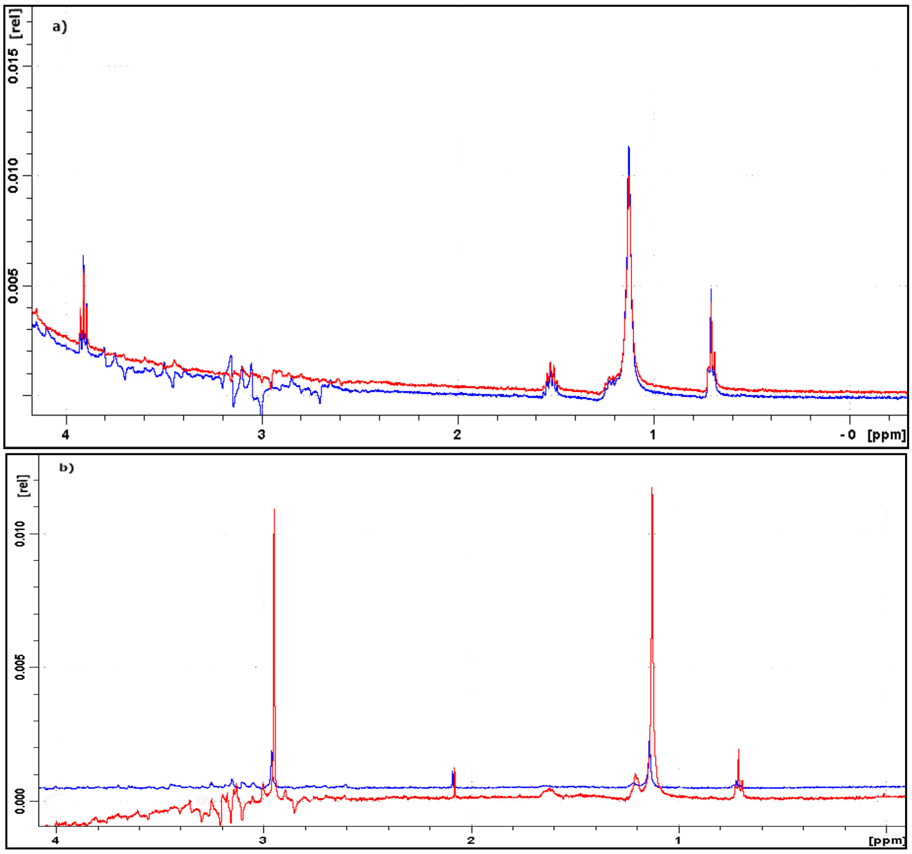


Figure 3.10 ^{1}H NMR spectra of the graphene-surfactant complexes (red) stabilized with SDS (top) and CTAB (bottom) compared with the surfactant only (blue).

3.4.4 Raman spectroscopy

Raman Spectroscopy is used to investigate the graphitic configuration effects on the exfoliated graphene prepared. In addition, it can also determine defect density and estimate the number of graphene layers of graphene sheets. This technique is non-destructive, quick and accurate. The graphene-surfactant obtained under 8V was analysed using Raman Spectroscopy and the spectrum obtained are compared with the graphite spectrum. The comparison is used to verify the presence of graphene.

The spectrum of graphite, graphene-SDS and graphene-CTAB at 8 V intercalation potential are presented in Figure 3.11 and Figure 3.12. There are three remarkable intense peaks in all Raman spectra which are the D band around 1370 cm^{-1}, the G band around 1590 cm^{-1}, and the 2D band is broader between 2700 cm^{-1}. In all sp^2 hybridized carbon materials, the presence of G caused by the stretching of the C-C bond. The intensity of the G band is reduced in the graphene-surfactant when compared with graphite spectrum due to the reduced number of layers. Meanwhile, the D band results from the disorder in the graphene flakes and edge defects such as a “zig-zag” or “chair” shape on the edge. The 2D band present in sp^2 hybridized systems and can be used to estimate the number of layers. Defects in the graphene-surfactant might be due to the disorders created by exfoliation process and by the decrease in the average size of sp^2 domains.

According to many research of graphene, the intensity of 2D band of graphite is higher than intensity of the 2D band of graphene-surfactant as shown in Figure 3.13 [41]. However, in this study, the intensity of 2D band of the graphene-surfactant is lower than the 2D band intensity of graphite. This is due to the attachement of surfactant molecules on the graphene surfaces. In addition, other research report state that the attachment of compound having a chemical doping effect can reduce the intensity of 2D band. Besides, the formation multilayer graphene also can cause the intensity of 2D band much lower than intensity of 2D band of graphite as shown in Figure 3.14. As in the Figure 3.11 and Figure 3.12, it is revealed that I_G/I_{2D} ratio is more than 1, indicating the presence of exfoliated graphene [34,38]. It can be concluded that, the production of graphene in surfactant assisted liquid phase exfoliation of graphite rod with two electrode system is successfully achieved as the Raman result shows positive result on the presence of graphene.

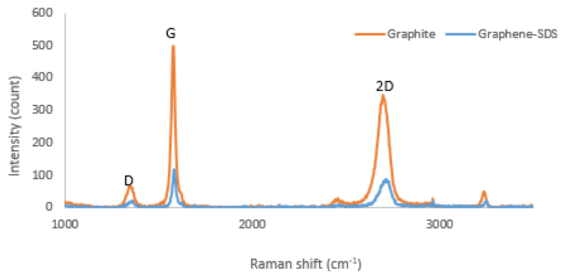


Figure 3.11 Raman shift of graphite (brown) and graphene-SDS (blue)

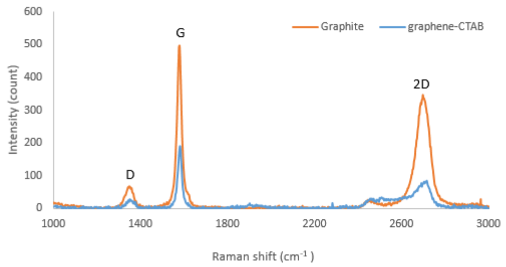


Figure 3.12 Raman shift of graphite (brown) and graphene-CTAB (blue)

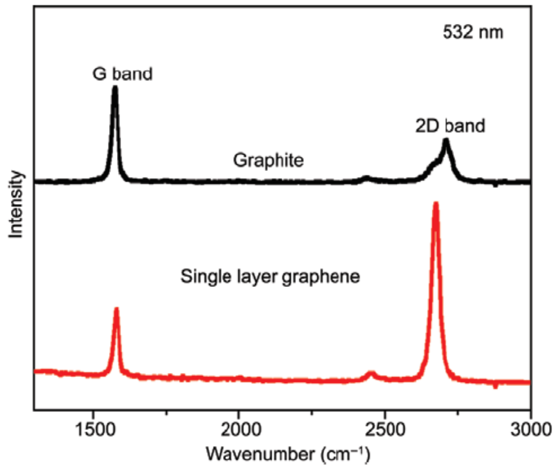


Figure 3.13 Raman spectra of single layer graphene and graphite

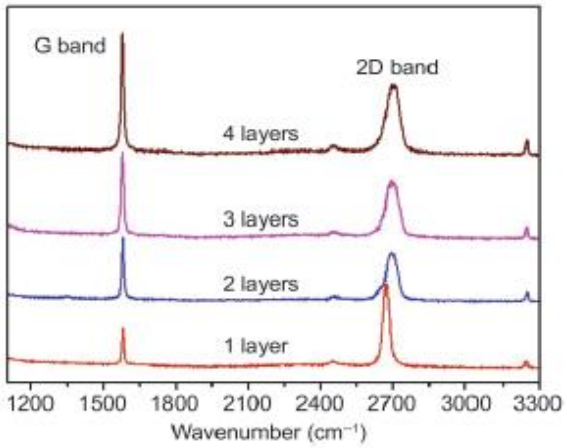


Figure 3.14 Raman spectra with 1,2,3, and 4 layer

4. CONCLUSION

In summary, the production of graphene-surfactant colloidal solution by surfactant assisted Liquid Phase Exfoliation (LPE) with two electrode system was successfully achieved. This technique is very simple, minimal safety requirement and economical. In this method, graphene from high purity graphite rod can be obtained directly as this method does not use strong acid, toxic solvent or hazardous oxidizing conditions. The graphene-SDS and graphene-CTAB suspension remained stable for more than 3 months. Optical microscopy described the dispersion behaviour with graphene-SDS is more dispersed than graphene-CTAB while UV-Vis spectroscopy confirmed being the linear relationship between the concentration of graphene produced and the intercalation potential applied. The presence of shielding in 1H Nuclear Magnetic Resonance indicates the interaction of graphene with the surfactant when the graphene-surfactant spectra is compared with surfactant alone. Raman spectroscopy can detect presence of defects and number of layers. Raman spectrum of graphite and graphene-surfactant is compared to verify the presence of graphene. Three intense peak observed in all Raman spectra is D band around 1370 cm^{-1}, the G band around 1590 cm^{-1} and the 2D band slightly broader between 2600 – 2700 cm^{-1}. From the data obtained, it can be concluded that graphene-SDS results is a more stable colloidal graphene-surfactant solution compared to graphene-CTAB.

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