Malaysian Journal of Microscopy 10: 84-91 (2014) ISSN: 1823-7010

ELECTROCHEMICAL SYNTHESIS AND CHARACTERIZATION OF STABLE COLLOIDAL SUSPENSION OF GRAPHENE USING TWO-ELECTRODE CELL SYSTEM

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The present work reports the synthesis and characterization of graphene via electrochemical exfoliation of graphite rod using two-electrode system assisted by Sodium Dodecyl Sulphate (SDS) as a surfactant. The electrochemical process was carried out with sequence of intercalation of SDS onto the graphite anode followed by exfoliation of the SDS-intercalated graphite electrode when the anode was treated as cathode. The effect of intercalation potential from 5 V to 9 V and concentration of the SDS surfactant of 0.1 M and 0.01 M were investigated. UV-vis Spectroscopic analysis indicated an increase in the graphene production with higher intercalation potential. Transmission Electron Microscopy (TEM) analysis showed a well-ordered hexagonal lattice of graphene image and indicated an angle of 60° between two zigzag directions within the honeycomb crystal lattice. Raman spectroscopy analysis shows the graphitic information effects after the exfoliation process.

Keywords: graphene, sodium dodecyl sulphate, electrochemical exfoliation, two-electrode, UV-vis spectra

INTRODUCTION

Graphene, which represents a class of the two-dimensional crystalline material based carbon, has a number of unique and intriguing properties for fundamental researches and applications [1-3]. Its properties include high mobility of charge carrier [2], unique transport performance [4] with a number of remarkable mechanical [5] and electrical properties. These intriguing properties make graphene attractive for many technological applications including graphene-based nanoelectronic devices [6, 7], transparent conductive film [8, 9], nanocomposite materials [10-12], biosensors [13, 14], energy storage devices [15], and catalyst support in fuel cells [16, 17].

The synthesis of graphene can be achieved by various approaches including chemical synthesis [18-20], chemical vapor deposition [21-23], solid-state carbon source deposition [24], nanotube unzipping [25, 26], electrochemical synthesis [27–31], and mechanical exfoliation of graphite also known as scotch tape or micromechanical cleavage [1]. The latter method introduced by Geim and Novoselov gives low yield of graphene. The principle of chemical synthesis of graphene based on Hummer's

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method requires a strong oxidizing condition which may contribute to some structural defects of the graphene obtained [31, 32]. Moreover, the above mentioned methods except surfactant-assisted electrochemical synthesis, usually produce non-dispersible graphene either in aqueous solution or in some organic solvent [33]. Previous studies have shown that the synthesis of graphene by surfactant-assisted electrochemical exfoliation of graphite using three-electrode cell system yield a very stable graphene suspension [27]. The use of the surfactant in the production of graphene is probably attributed to the presence of interactions between the ionic solutions (such as sulphate [34], nitrate [35], fluoride [36], perchlorate [37] and lithium [38]) and the graphite. The electrochemical method is simple, economical and environmentally safe compared to other methods. However, it only produces small amount of graphene that may present structural defects. The electrochemical synthesis of graphene can be achieved either in two-electrode or three-electrode cell system. The use of a three-electrode cell system has been claimed to have a true control of the intercalation and exfoliation potential as opposed to the use of two-electrode cell system. However, the usage of the two-electrode cell system may efficiently allow the electrochemical exfoliation process to simultaneously occur on both graphite anode and cathode. In this work, the synthesis of graphene suspension via electrochemical technique using two-electrode cell system and Sodium Dodecyl Sulphate (SDS) as a surfactant was undertaken. Special goal of this work is to optimize the electrochemical method of graphene synthesis for large scale production and low structural defects.

EXPERIMENTAL

The electrolytic cell was set up using two high purity graphite rods (∅ = 3 mm, 99.999%, Aldrich) as the electrodes, galvanostat (DC power supply, Witeg) and sodium dodecyl sulphate (SDS) (Aldrich) dissolved in Milli-Q ultra-pure water as the electrolyte (0.1 M). A constant voltage of 5 V was initially applied between the two electrodes using a DC power supply and the electrochemical reaction was allowed to occur for intercalation process of SDS into the graphite anode. The exfoliation of SDS-intercalated graphite occurred when the anode was treated as cathode, producing an extremely stable graphene-SDS suspension. Both intercalation and exfoliation process for the graphite electrodes occurred accordingly towards both anode and cathode. This intercalation-exfoliation process was repeated for 5 hours of electrolysis. The graphene-SDS solution obtained from this electrochemical procedure was then centrifuged at low speed (1000 rpm) in order to remove large agglomerates. The experiment was repeated by using 6 V, 7 V, 8 V and 9 V of intercalation potentials to study its effect on the production of graphene. The experiments were carried out in similar way to that reported by Alanyalioglu and co-workers [27] but using two-electrode cell system. The experimental procedure was repeated using 0.01 M of SDS at various intercalation potentials. The quantitative analysis for the concentration and significant absorbance of the graphene solution produced from the electrochemical process were analyzed using UV-vis spectrometer (Perkin Elmer, Lambda 25). The crystal structures and morphological information of the graphene were analyzed by Transmission Electron Microscopy (TEM) (Philips, Technai 20). Raman spectra of the graphite rod and GSDS powder were collected using inVia Raman Microscope (Renishaw) with an excitation laser of 514 nm.

RESULTS AND DISCUSSION

Electrochemistry

Based on the experimental findings, a stable graphene solution was obtained via the electrochemical process with sequence of intercalation of SDS to the graphite electrode (anode) followed by electrochemical exfoliation of the SDS-intercalated graphite electrode (cathode) where the electric current is used as the oxidizing and reducing agent. During the intercalation process, the surfactant was adsorbed onto the surface of the graphite anode to form SDS-intercalated graphite electrode and prevented the graphene sheets from re-stacking after the exfoliation process. When the graphite anode is treated as the cathode, the electrochemical exfoliation of the SDS-intercalated graphite electrode occurred and a very stable graphene-SDS suspension was obtained [27].

Figure 1(aii – avi) shows the graphene-SDS colloidal solution prepared by various intercalation potential of 5 V, 6 V, 7 V, 8 V and 9 V electrolysis, respectively. The colour of these graphene-SDS solution showed increasing amount of exfoliated product as the colour of the colloidal solutions darkened with increasing intercalation potential in comparison with the clear solution of 0.1 M SDS (ai). The graphite rods used at the different intercalation potentials are shown in Figure 1(b). The increase of the exfoliation effect after five hours with increasing intercalation potentials is clearly visible on the graphite rods. This feature might give some significant information on the structural and morphological effects on both graphite rods used and graphene produced. Lee *et al*. [29] reported the novel surface modification of graphite, providing a high surface area with surface roughness analysis of 2-D graphene nanosheets synthesis by electrochemical exfoliation of graphite.

Compared to 0.1 M of SDS, the electrochemical process was much slower using 0.01 M of SDS with much lower current flow through the electrolytic cell. Thus, the amount of graphene produced using 0.01 M of SDS is lower due to slower intercalation-exfoliation process. The product obtained also yields a very stable solution in which there is no precipitation except the small amount of the large agglomerates produced during the exfoliation process.

UV-Vis Spectroscopy

The UV-vis absorption spectra of GSDS solution produced at different intercalation potentials of 5 V, 6 V, 7 V, 8 V and 9 V using 0.1 M of SDS are shown in Figure 2(a). The maximum absorbance at about 270 nm was obtained for each spectrum which corresponds to the π to π^* transition of aromatic C-C bond [27, 39]. The relationship between absorbance at 270 nm with the concentration of GSDS solution also indicates the increase in absorbance with increasing intercalation potential. It can be seen from Figure 2(a) that the absorbance increases gradually at 6 V and 7 V electrolysis due to the increase in graphene concentration in the suspension. However, the absorbance of the GSDS solution prepared at 7 V, 8 V and 9 V electrolysis only showed a slight increase indicating that the intercalation potential at 7 V gives an optimum value for the production of GSDS solution using 0.1 M of SDS. The UV-vis spectra obtained when using 0.01 M of SDS are shown in Figure 2(b). The maximum absorbance are obtained at about 214 nm, clearly different from that obtained in Figure 2(a) using 0.1 M of SDS.

According to Woodward-Fieser rule for dienes [40, 41], compound having a chromophore (a group or unsaturated system responsible for UV absorption), 214 nm is the standard wavelength for heteroannular diene(transoid). The effect on the intensity and wavelength of the chromophore depends on the presence of auxochrome, subtituents which increase the intensity of the UV absorption and wavelength. Based on the model structure of graphene which is graphically illustrated in Figure 3, considering the parent chromophore of the transoid as the repeating units of the graphene lattice, no auxochrome is attached

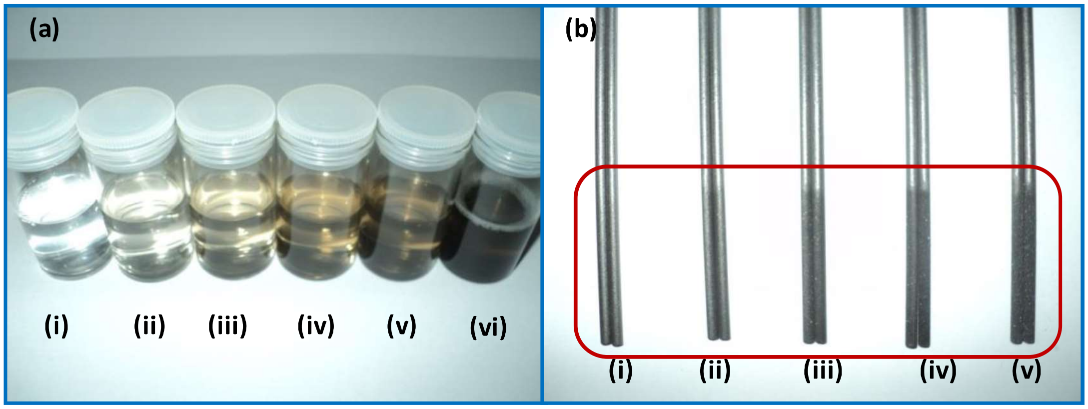

Fig. 1: *(a) 0.1 M of SDS solution (i) and graphene-SDS solution prepared at different intercalation potentials (ii) 5, (iii) 6, (iv) 7, (v) 8, and (vi) 9 V. (b) Graphite rods used after 5 h electrolysis at various intercalation potentials (i) 5, (ii) 6, (iii) 7, (iv) 8 and (v) 9 V.*

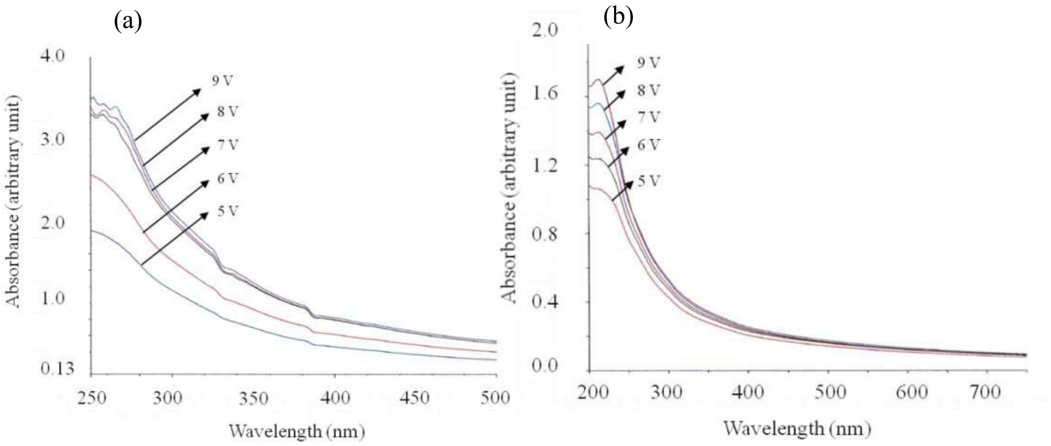

Fig. 2: *UV-vis absorption spectra of graphene-SDS suspensions prepared at different intercalation potentials with background of 0.1 M SDS (a) and 0.01 M SDS (b.)*

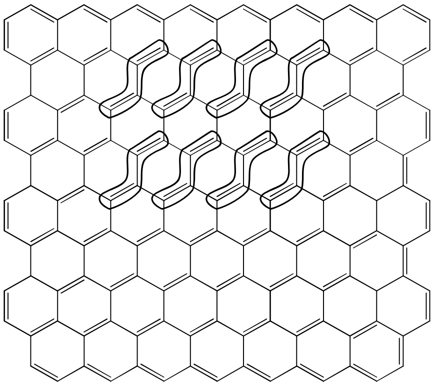

Fig. 3: *Model structure of graphene with transoid as repeating lattice*

which indicate the possible wavelength of the UV absorption is 214 nm similar to the maximum absorbance obtained in Figure 2(b). This rules usually applies to simple and non-complex structure, but for graphene structure, a Fieser-Kuhn rule [42] (another empirical rules used to calculate maximum absorption of a very long chemical chain structure or polyenes) is not applicable with the complex structure of graphene as no maximum wavelength appears at visible region. In addition, UV-vis spectra obtained in Figure 2 shows a linear relationship between the absorbance and the intercalation potential, whereby the increase in the applied potential indicates a constant increase in the concentration of the product obtained when using 0.01 M of SDS.

Transmission Electron Microscopy

product obtained using a potential of 7 V and 0.1 M of SDS was analyzed using Transmission Electron Microscopy (TEM). The TEM images of the graphene-SDS solution prepared are shown in Figure 4. A well-ordered hexagonal graphene lattice is clearly seen in Figure 4(a) and a very thin and transparent layer of hexagonal lattice can also be seen in bottom-right corner in Figure 4(b). The angle between two zigzag directions exist in the graphene hexagonal lattice and is of the order of 60° as shown in Figure 4(b). Similar pattern of the angle can also be seen in Figure 4(a) at about 60 – 70° and also indicates the AA' stacking structures formed of the graphene at the stacked layer (less transparent region) of the clearly seen hexagonal graphite lattices.

Raman Spectroscopy

Raman spectroscopic analysis was carried effects on the exfoliated graphene prepared. Raman spectra for both graphite rod and GSDS powder prepared at 7 V electrochemical process are presented in Figure 5. There are three significant peaks can be observed around 1350 cm^{-1}, 1590 cm^{-1}, and 2700 cm^{-1} represent the D band, G band and 2D band respectively. The D band may correspond to sp^3 bonds present at graphene edges or structure defects, while G band represent the planar configuration of the sp^2 bonds [43, 44].The 2D peak is the D band overtone which due to two phonons at opposite momentum [45]. The higher D band for GSDS spectrum may shows the increase of defect formation, but we suggest that it results from the graphene edges configuration. Indeed, the small size area of the graphene obtained (as observed by TEM), results in high detection of edges through the spot size of Raman beam. The GSDS spectrum displays a 2D band shape similar to graphene bilayers obtained by Liu *et al*. [46], but it might be expected that the mixture of graphene with different numbers of layers are produced. Besides, the G band to 2D band intensity ratio (I_G/I_{2D}) is usually not lower that 1 in the scope of exfoliated graphene process [46]. This supported by the raman spectra obtained by Alanyalioglu *et al.* [27] and Liu *et al.* [46]. We believe that the low intensity effect of the 2D was due to attachment of SDS molecules on the graphene surfaces. As some groups report, the attachment of compounds having a chemical doping effect (hole- or electron-doping) on the graphene surface can markedly reduce the intensity of the 2D band [46-48].

CONCLUSIONS

The synthesis of graphene sheets using the common surfactant, Sodium Dodecyl Sulphate, via electrochemical process can be achieved. The electrochemical synthesis using two-electrode cell system technique is simple, economical and environmentally safe. The method of electrochemical intercalation and exfoliation can directly produce graphene from the high purity graphite rod and substantially avoid the collateral damage of graphene as it is not aided by the use of super-strong acid or hazardous oxidizing conditions.

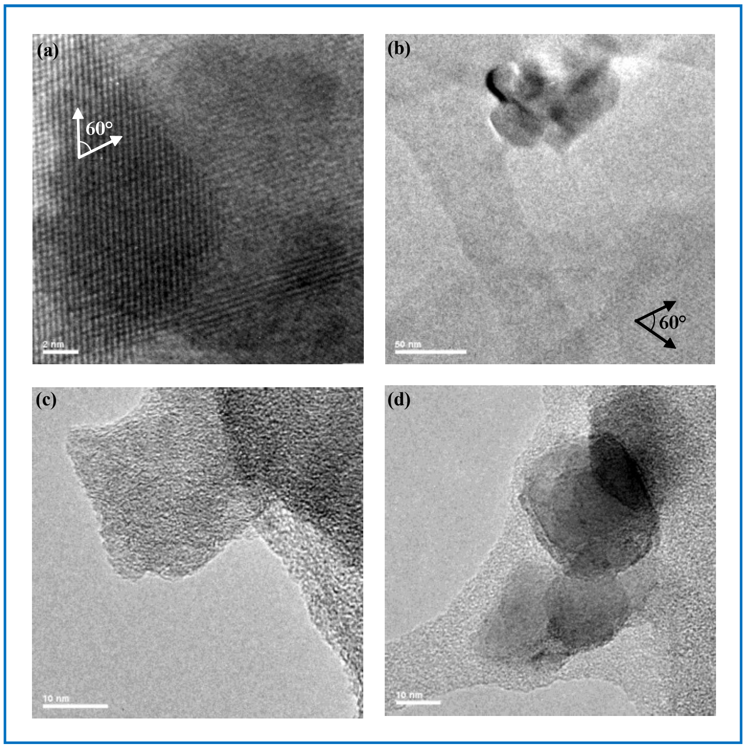

Fig. 4: *TEM images of (a) well-ordered hexagonal lattice, (b) A thin, ordered and relatively transparent of graphene hexagonal lattice showing 60° of angle between two zigzag direction. (c) TEM image of single layer of graphene with stacked and folded effect at the shaded region, and (d) Small width surface of relatively transparent graphene layer.*

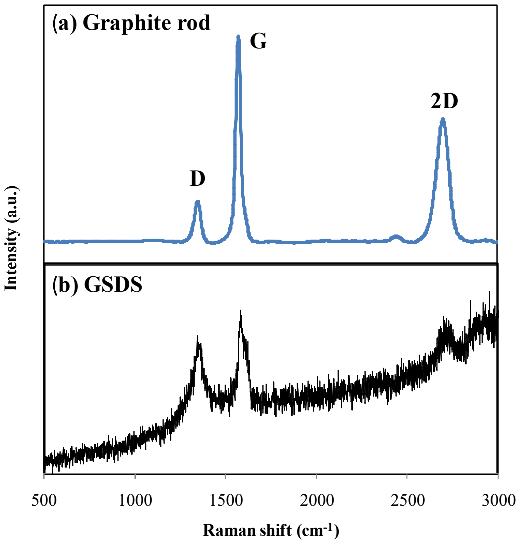

Fig. 5: *Raman spectra of (a) graphite rod and (b) GSDS powder*

UV-vis spectrometer confirmed the linear relationship between the intercalation potential applied and the concentration of graphene produced and indicated that 7 V electrochemical possess an optimum value for synthesis of graphene using 0.1 M of SDS. The TEM analysis indicates the presence of relatively transparent, thin, and well-ordered hexagonal lattice (scale bar = 2 nm), for the electrochemical synthesis using 0.1 M SDS and at a voltage of 7 V. Raman analysis shows the effect of graphitic information of the GSDS after the electrochemical exfoliation process and indicates the significant graphene band shape. We believe this work paves the way towards a large-scale production of graphene using two-electrode cell system with surfactant-assisted of SDS.

ACKNOWLEDGEMENTS

This study was supported by the Fundamental Research Grant Scheme (4F234), Ministry of Higher Education, Malaysia and Universiti Teknologi Malaysia.

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