Exfoliation of charcoal by electrochemical method to synthesize few layers graphene sheets

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Abstract. Graphene is a new 2D carbon nanomaterial that has unique properties for several applications. However, the synthesis of large quantity of graphene is a key challenge for researchers. Previous conventional methods such as Chemical Vapour Deposition (CVD) and epitaxial growth resulted in low production rate and high cost. The research on the electrochemical exfoliation by using charcoal as an electrode is still remains unknown as most researchers employed graphite to produce graphene. The electrochemical exfoliation of charcoal and graphite rod is easy to operate and less time-consuming in the synthesis of few layers graphene sheets. An electrochemical cell consists of charcoal/graphite (as anode) and copper foil (as cathode) which immersed in several types of electrolytes was developed. The surfaces of exfoliated graphene sheets were observed as wrinkle, flaky and layered structures. Fourier transform infrared spectroscopy (FTIR) showed the presence of oxygen functional groups in the exfoliated graphene sheets while the characteristic peak of GO showed up at 2θ = 9-10° was not seen clearly in all XRD spectrums. The results proved that high amount of exfoliated graphene sheets was formed but less amount of graphene oxide (GO) was produced in the electrochemical exfoliation process.

1. Introduction

In 2004, Geim’s group first mechanically exfoliated the monolayer graphene with one-atom-thick plate of carbon from graphite [1]. In 2010, Andre Geim and Konstantin Novoselov were awarded The Noble Prize in Physics for the project titled “ground-breaking experiments regarding the two-dimensional material graphene” [2]. Since the discovery of “scotch tape” method by Geim’s group, numerous researches have been sparked in the worldwide due to its extraordinary properties and depletion of indium (In) [3]. The extraordinary properties such as excellent electrical conductivity and high charge carrier mobility are the some of the attractions and thus, the synthesis and application of graphene become the main research of the researchers [3]. Graphene is a two-dimensional (2D) carbon allotrope in the crystalline form that possesses single-layer of sp² hybridisation atoms and in a honeycomb lattice arrangement [3]. Graphene has different structures with other carbon allotropes such as diamonds and fullerenes but possesses similar chemical composition. Graphene has been widely used to make plenty of electronic devices. The applications that have been utilized the graphene sheets are fuel cells, capacitors and sensors [3]. On the other hand, graphene oxide (GO) is a compound that mainly consists of carbon, hydrogen and oxygen functional groups. The chemical structure of the GO was same as graphite oxide which comprises many oxygen functionalities on its carbon basal plane and edges [3]. GO consists of monolayer or few layered stacked structure while graphite oxide consists of multilayer stacked structure like graphite [3].
Several methods have been established for producing graphene such as epitaxial growth [4], Chemical Vapour Deposition (CVD) [5] and electrochemical exfoliation of graphite [6]. However, synthesis of large quantities of graphene is a key challenge to researchers. The first method, “scotch tape” method has been developed to produce good quality of monolayer graphene but resulted in low production rate. Other techniques such as CVD and epitaxial growth require expensive cost production. Furthermore, chemical exfoliation method such as Hummers’ method involves the use of hazardous chemicals such as KMnO₄ and thermal reduction needs a lot of electricity to reduce GO to graphene sheets which take long process. Thus, a more effective method such as electrochemical exfoliation of charcoal and graphite is preferable to synthesize few layers graphene sheets. The electrochemical techniques are more beneficial as compared to other techniques for the mass production of high-quality graphene [7]. It is easy to operate, cheap and less time-consuming. Therefore, electrochemical production of graphene in single stage or multiple steps and followed by electrochemical reduction of graphene oxide (GO) have gained extensive interest from researchers. Consequently, number of researches based on electrochemical methods have been significantly increased in the last decade [8].

In this paper, we demonstrated the synthesis of few layers graphene sheets by using electrochemical exfoliation method. The effect of types of electrolytes and anodes on the exfoliated graphene sheets were investigated using several characterization methods. The results obtained from the characterization methods such as Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and scanning electron microscopy (SEM) were discussed in this paper.

2. Methodology

In current research, the graphene sheets were prepared by using the electrochemical exfoliation technique. The materials, chemicals and method used in the research were described in detail. After the synthesis of the graphene sheets, the characterization on the exfoliated graphene sheets will be carried out.

2.1. Materials

In this research, the raw materials were charcoal (anode), graphite rod (anode) and copper foil (cathode). BBQ Grade Charcoal Coconut Shell Briquettes with purity 98.0% was ordered from The Clorox Company. Copper foil (alfa aesar, VWR Singapore) with purity 99.999 % and graphite rod (pencil core) was bought in stationery shop. The following chemicals were ordered from Sigma-Aldrich and used without further purification: copper (II) sulfate pentahydrate (CuSO₄·5H₂O), sodium sulfate decahydrate (Na₂SO₄·10H₂O, ACS Reagent, ≥ 99.0%), sulfuric acid (H₂SO₄, ACS Reagent, 95.0 - 98.0%) and hydrochloric acid (HCl, ACS reagent, 37%).

2.2. Methods

In this work, 125 mL of 0.2 M Na₂SO₄ electrolyte was prepared by mixing 64.438g of Na₂SO₄·10H₂O powder mixed with the deionized (DI) water and stirred for 10-15 mins. The electrochemical cell was prepared by using two electrodes where the copper foil was used as the cathode and a charcoal was used as the anode. Both electrodes were immersed into 125 mL of Na₂SO₄ electrolyte. Then, the electrochemical process was carried out by applying optimized DC voltages for 25 mins. After exfoliation of charcoal for 25 mins, the exfoliated graphene sheets were collected and filtered to remove electrolytes
from graphene sheets by using filter paper with a diameter of 9 cm. After filtration, the filter paper with black samples were dried at room temperature. After dried, the graphene powder was extracted by using a spatula. The final product, graphene powders were put into a crucible for drying in an oven (Memmert) at 80 °C for 24 hours. The same procedures will be repeated by using graphite rod as an anode and different electrolytes such as Na_2SO_4, H_2SO_4 and CuSO_4 solution. The voltage was applied at 3.0 V, 6.0 V, 9.0 V, 12.0 V and 15.0 V, respectively for 25 mins. One sample only was synthesized using CuSO_4 solution at 15.0 V for 25 mins.

3. Results and discussions

3.1. Fourier transform infrared spectroscopy (FTIR)

All samples names: A, B, C, D and E are based on the descriptions as shown in the Table 1. From the FTIR analysis (Figure 1), the exfoliated graphene samples were mainly composed of hydroxyl groups, alkyn, alkene and sulfate ions. In the FTIR spectra, a broad and intense peak was noticed at the wavelength of 3624 cm\(^{-1}\) was assigned to the O-H stretching of the alcohol groups. Moreover, the O-H stretching of the carboxylic acids was presented at the wavelength of 2541 cm\(^{-1}\), 2888 cm\(^{-1}\) and 2976 cm\(^{-1}\). Besides, the characteristic peaks showed up at wavelength of 2177 cm\(^{-1}\), 2000 cm\(^{-1}\) and 840 cm\(^{-1}\) were attributed to the presence of alkyn groups (C≡C), aromatic compound (C-H) and alkene groups (C=C), respectively. In addition, the presence of the free (nonbonded) sulfate ion, SO_4^{2-} at the wavelength of 624 cm\(^{-1}\) was observed because of the absorption of SO_4^{2-} ions in the electrolyte occurred on the surface of the exfoliated graphene sheets [9].

| Samples | Types of Anodes | Types of Electrolytes |
|---------|-----------------|-----------------------|
| A       | Charcoal        | Na_2SO_4              |
| B       | Graphite Rod    | CuSO_4                |
| C       | Graphite Rod    | CuSO_4                |
| D       | Graphite Rod    | H_2SO_4               |
| E       | Graphite Rod    | Na_2SO_4              |

Some functional groups presented in graphene sheets synthesized using charcoal do not presented in the graphite. For spectrum A (charcoal), there was no significant peak presented at the wavelength of 1594 cm\(^{-1}\) and 1250 cm\(^{-1}\). In the spectrum A, the characteristic peaks showed up at the wavelength of 1749 cm\(^{-1}\) and 1465 cm\(^{-1}\) was assigned to the aliphatic C=O stretching of esters group and C-H bending of the alkane, respectively. On the other hand, in B to D spectrums, the peak presented at the wavelength of 1594 cm\(^{-1}\) and 1250 cm\(^{-1}\) was ascribed to the C=C stretching of the cyclic alkene and an aromatic C=O stretching of esters, respectively. H_2SO_4 is a strong acid and demonstrated high exfoliation rate than other electrolytes [1]. For CuSO_4, high voltage of 15.0 V was applied in the exfoliation process of the graphite rod. When a high voltage was applied, more positive charges were produced at the graphite rod (anode) as compared
with low voltage. This large number of positive charges attracted the anions and encouraged more anions were intercalated into the graphene layer. Thus, resulted in high exfoliation rate and CuSO₄ was as effective as H₂SO₄. The graphene oxide (GO) sheets were successfully produced through the exfoliation of charcoal and graphite rod which was well-evidenced by the presence of O-H peaks.

Figure 1. FTIR spectra of exfoliated graphene samples using different types of electrolytes.

3.2. X-Ray Diffraction (XRD)

For all the exfoliated graphene samples, a strong and sharp peak was observed at 2θ = 26.2° or 26.5° along the (002) orientation (Figure 2). This (002) peak confirmed the presence of graphite structure with d-spacing of 0.3395 nm or 0.3356 nm between the different graphene layers [10], [11]. In XRD spectrum of A, lowest peak intensity can be seen at 2θ = 26.2° with d-spacing of 0.3395 nm, along the (002) orientation with ICSD File 01-075-1621 (Reference pattern 98-001-7130). It is due to the incomplete exfoliation of charcoal as charcoal was brittle and easily broken down during the exfoliation process. Thus, the exfoliation duration of charcoal was shorter than graphite rod. On the other hand, the XRD spectrum of E has a higher peak intensity at 2θ = 26.2° as compared with spectrum A even the same electrolyte of Na₂SO₄ was used in the exfoliation. Therefore, higher crystalline structure of graphite (spectrum E) was retained as compared with charcoal (spectrum A).

The XRD pattern of B and C are almost similar because of the same electrolyte of CuSO₄ was used in the exfoliation. A peak showed up at 2θ = 36.20° with (111) orientation in samples B and C was attributed to the cuprite [12]. This indicates the presence of contaminant due to the used electrolyte. However, cuprite was not detected in FTIR results. Sulfuric acid is known as a strong oxidation acid but the oxidation process took place was mild and created less damage on the honeycomb lattice of graphene [9]. Thus, high quality of graphene can be obtained through the exfoliation method. The characteristic peak of GO appeared at 2θ = 9-10° [10, 13] was not seen clearly in all XRD spectrums due to less amount of GO sheets were produced in the exfoliation process. However, the presence of GO with broad O-H peak was well evidenced by the FTIR result as shown in Figure 1. The degree of oxidation on the charcoal and graphite rod is significantly affected by the types of electrolytes and anodes.
Figure 2. XRD patterns of exfoliated graphene samples.

3.3. Scanning Electron Microscopy (SEM)

Figure 3(a) and (b) reveal the SEM micrographs of exfoliated graphene sheets by using two different types of anodes with the same electrolyte of Na₂SO₄. Wrinkle and flaky structures can be observed after the exfoliation [14]. It was reported by other researchers that mild oxidation of graphite induced the formation of defects at the stacked graphene sheets, which appeared as wrinkles in the pile [3, 15]. In addition, few layers of irregular shape flakes were observed. This layered structure implies that the charcoal and graphite were exfoliated to form low amount of GO but high quantity of graphene sheets which correlated with above XRD results [16]. The surfaces of samples in Figure 3(a) and (b) were almost similar with flaky structure. This is because of charcoal and graphite rod have the same basic structure. However, charcoal composes slightly more disordered phase [17] and porous structure [18] than graphite. This caused the charcoal was easily exfoliated into irregular small and big particles during the exfoliation process, resulting incomplete and faster exfoliation rate than graphite rod. Thus, besides large particles were formed, very tiny pieces charcoal was noticed on the surface as marked in red circle in Figure 3(a). On the contrary, graphite rod has stacked and higher uniformity structure due to the strong interlayer covalent bonding as compared with charcoal [19]. Therefore, the exfoliation of graphite rod to form proper graphene sheets was happened in lower rate as compared with charcoal.

Figure 3(c) and (d) indicate the SEM micrographs of graphene sheets synthesized by using CuSO₄ at the low and high voltages respectively. Wrinkled and layered structure can be observed in Figure 3(c) whereas crumpled structure was seen in Figure 3(d) [20]. Furthermore, more exfoliated layers can be observed in Figure 3(d) than Figure 3(c). In this experiment, different voltages were applied to synthesize samples B and C by using the same electrolyte of CuSO₄. When a high voltage of 15.0 V was applied for longer time of 25 mins, more positive charges were supplied at the graphite rod (anode) as compared to low voltage. Consequently, higher amount of positive charges attracted higher quantity of anions to
intercalate into graphite rod, resulting in higher exfoliation rate, thus more exfoliated layers was produced. The SEM micrograph of sample D consisted of multilayers of irregular shape flakes (Figure 3(e)). This is because of the mild oxidation of graphite dislocated the sp² carbon chain of the stacked graphene sheets and caused the defects. Thus, a small increase in distance between adjacent sheets is expected due to the oxygen functional groups were attached at the edge and basal plane of the graphene sheets [3, 15].

![Figure 3. SEM micrographs of (a) sample A, (b) sample E, (c) sample B, (d) sample C and (e) sample D at magnification of 5KX respectively.](image)

An EDX analysis was carried out to obtain the elemental composition in the graphene sample (Figure 4). Carbon and oxygen were the main elements traced in all samples. By using charcoal as an anode, the percentages of carbon and oxygen were 86.80 at% and 12.79 at%, respectively (Figure 4(a)). In addition, for graphite rod, the elemental compositions of carbon and oxygen were noticed at 71.87 at% and 27.75 at%.
at% respectively as shown in Figure 4(b). Besides, a small percentage of platinum were detected in all samples due to the coating of the platinum layer on the sample before SEM imaging. The percentage of oxygen as found in EDX is correlated with the amount of oxygen functional groups on GO and displayed by the characteristic GO peaks in FTIR [21, 22]. Since the sample E shows higher percentage of oxygen thus, more oxygen functional groups were believed attached to the basal and edge of the GO sheets as compared with the sample A. Therefore, sample A (synthesized by using charcoal as anode) contained a lower amount of oxygen functional groups as compared with other samples.

From the EDX analysis of sample B, the percentages of carbon (80.96 at%) and oxygen (18.65 at%) were detected whereas sample D shows the percentages of carbon and oxygen were 76.12 at% and 23.34 at%, respectively. Sample D (H$_2$SO$_4$) has a higher percentage of oxygen thus, more oxygen functional groups were attached onto the edge and basal plane of GO sheets as compared with sample B (CuSO$_4$). This is because of sulfuric acid, a strong oxidation acid caused more oxidation than that of CuSO$_4$ [9]. Thus, at high voltage, CuSO$_4$ was more efficient in exfoliation with much less oxidation on the graphene sheets than sulfuric acid.

![Elemental composition of (a) sample A (b) sample E, (c) sample B and (d) sample D.](image)

**Figure 4.** Elemental composition of (a) sample A (b) sample E, (c) sample B and (d) sample D.

4. Conclusion

The electrochemical exfoliation of charcoal and graphite by using different electrolytes was studied. Exfoliated graphene sheets were characterized by FTIR which showed the GO sheets were successfully produced in low amount in the exfoliation of charcoal and graphite rod. The XRD analysis confirmed the
presences of graphite structure in all samples and less amount of graphene oxide (GO) was produced in the exfoliation process. For the SEM analysis, wrinkle and flaky structures can be observed due to the exfoliation. The layered structure as observed in the SEM micrographs indicates that low amount of GO but high quantities of graphene sheets were produced. The EDX spectra demonstrates carbon and oxygen were the main elements traced in all graphene samples. Overall, it was found that graphite rod is more efficient to be used to form proper graphene sheets than charcoal during the exfoliation process. All electrolytes showed near similar performance in exfoliation based on the obtained results.

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