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Effect of electrolyte concentration on the synthesis of graphene by electrochemical exfoliation process

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Abstract. Graphene can be produced from graphite rod of a battery by electrochemical exfoliation process in acidic electrolytes. This process is simple, safe, fast, cheap and produces graphene in large scale. Parameters to be controlled during the process are the concentration of the electrolytes and potential for exfoliation. The synthesized graphene was characterized by Raman Spectroscopy and Field Emission Scanning Electron Microscopy (FESEM). From the results, it was found that graphene synthesized with 90:10 volume ratio had better yield, lowest interlayer distance, less oxidation and minimum defect of graphene.

1. Introduction

Graphene as a single layer of sp²-hybridized carbon, is rightly proclaim for its superlative material properties. It has been demonstrated both as a novel building block and as an additive for a wide range of multifunctional materials [1][2]. In recent years, exfoliation of graphene has been investigated various processes such as by mechanical, chemical, thermal, electrical or through electrochemical[3][4]. These are known as top-down processes. Electrochemical exfoliation is a promising process for synthesizing graphene from graphite. It is cheaper, greener and potentially capable of mass production with few layers of graphene. In this process, an applied voltage drives ionic species to intercalate into graphite lattices where they form gaseous species that expand and exfoliate into individual graphene sheets [5]. The quality and quantity of the synthesized graphene (graphene layer numbers, O contents, lateral size, edge or sheet defects) can be obtained by controlling the process parameters (applied electrical potential, current, processing time, composition of electrolytes) [6][7].

Thus, in order to investigate the effect of electrolyte acidity concentration by using different H₂SO₄:KOH volume ratios (90:10, 80:20 and 70:30) at room temperature, this paper describes specifically the quality and microstructural properties of the synthesized graphene using Raman Spectroscopy and FESEM.

2. Experimental

The starting reagents were H₂SO₄ (SigmaAldrich, 95%), KOH (Scharlau) and IPA (HmbG Chemicals, 99.8%). Deionized water was used throughout the experimental process. The required graphite rod was obtained from a dry cell battery with a diameter of 0.8 cm, a length of 5.7 cm and weight of 4.90 g as shown in Figure 2(a).



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2.1 Electrochemical exfoliation.

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Electrolytes with different H_2SO_4 :KOH volume ratios of 90:10, 80:20 and 70:30 were prepared by mixing 0.1 M H_2SO_4 and 0.1 M KOH solution by using a magnetic stirrer. Prior to electrochemical exfoliation process, graphite rod was pre-treated by immersing in the electrolyte for 24 hours. All processes were carried out at room temperature.



Figure 1. Electrochemical exfoliation set-up for graphene synthesis.

Electrochemical exfoliation process was carried out in an electrochemical cell. The cell was composed of a graphite rod and a platinum (Pt) plate immersed in an electrolyte. It was connected to a DC power supply as shown in Figure 1, with graphite rod acts as anode (using positive bias) and Pt plate as cathode (using negative bias). Exfoliation was conducted by applying +2.5 V (low voltage) for 5 min followed by +10 V (high voltage) for 10 min. The sample was left to settle for 5 hours before filtration process. The graphene fragments at the top of the solution were filtered using a vacuum pump and PTFE filter membrane with pore size of 0.2 μ m. During the filtration process, graphene fragments were rinsed with IPA and deionized water. The filtered samples were dried overnight.

2.2 Material characterization

Raman Spectroscopy measurements were performed using Renishaw InVia Reflex spectrometer in the range of 100 to 3300 cm⁻¹ with excitation laser of 532 nm to analyse the number of layers and defect of the synthesized graphene. The graphene powders were dropped cast onto a glass slide for measurement. Renishaw WiRE 5.0 software was used for the analysis, background correction and peak fitting.

The microstructural observations were conducted on Carl Zeiss GeminiSEM 500 FESEM using a secondary electron detector operating at 15 kV. The microscope was coupled with an energy dispersive X-Ray spectrometer (EDS) for elemental analysis. Samples were not coated prior to imaging in the FESEM. Samples were prepared by sprinkling the powders onto a silicon wafer fixed to a FESEM sample holder.

3. Results and discussion.

The mechanisms behind electrochemical exfoliation depend principally on the type of potential applied: anodic or cathodic. Anodic exfoliation involves the intercalation of anions as well as other co-intercalating species involved in the reaction mixture into the graphite lattices.

For anodic potential, a positive bias withdraws electrons from the graphite (anode), creating a positive charge. On the other hand, a negative bias allows electrons to the Pt (cathode), creating a

negative charge. This negative charge drives the reduction of water molecules at the cathode, producing hydroxyl ions (OH⁻¹). OH⁻ can attack graphite (anode) at the edges and grain boundaries [8]. This oxidation at anode leads to the expansion of graphite layers at the edges, opening up the lattices for intercalation by sulfate ions (SO_4^{2-}) and also possibly more water molecules [9]. After the electrochemical intercalation and expansion of graphite, the gaseous species (e.g. SO_2 and O_2) produced (e.g. from oxidation of water molecules and from reduction of SO_4^{2-} anions) will then exfoliate and separate the graphite lattices into graphene [10].

Figure 2(b) shows a reduction in size of graphite rod after electrochemical exfoliation with a diameter of 0.5 cm, a length of 5.6 cm and weight of 4.18 g. The initial low voltage applied to the graphite rod helps to expand the graphite lattices to allow the OH⁻ enters between the graphite lattices. When a higher voltage is applied, the graphite is exfoliated into two types of fragments. Sediment at the bottom of the electrolyte consisting of thick graphite sheets while the sample floating on the surface of the electrolyte is predominantly graphene of thinner thickness.



Figure 2. Graphite rod (a) before and (b) after exfoliation.

Figure 3 shows the Raman spectrum for all the samples. From the spectra, D peak is located at ~1360 cm⁻¹, G peak is located at ~1590 cm⁻¹ and 2D peak is located at ~2700 cm⁻¹. The intensity of the D peak depends on the disorder of the graphene. The G peak represents the E_{2g} phonons vibrations mode in the centre of the Brillouin Zone and is a characteristics peak of carbon material [5]. The I_D/I_G ratio, which gives information about the amount of defects in graphene, was found to be 0.42, 0.75 and 0.94 for sample with H₂SO₄:KOH volume ratios of 90:10, 80:20 and 70:30 respectively. This ratio allows to distinguish graphene from multi layered graphite [11]. The intensity I_{2D}/I_G ratio, which represents the number of graphene layers, for 90:10, 80:20 and 70:30 with H₂SO₄:KOH volume ratio was 1.15, 0.19 and 0.15 respectively. Based on these results, electrolyte concentration by using 90:10 H₂SO₄:KOH volume ratio showed the highest number of graphene layers with minimum defects.



Figure 3. Raman spectra of samples with H₂SO₄:KOH volume ratios of 90:10, 80:20 and 70:30.

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Figure 4. FESEM micrographs of samples with H₂SO₄:KOH volume ratios of (a) 90:10, (b) 80:20 and (c)70:30.

The surface morphology and cross section of the samples were characterized by using FESEM. From Figure 4, it can be seen that the lateral size of graphene sheets is quite large with almost similar average diameters of 200 nm for the samples. The layering of graphene in image of 90:10 is more prominent compared to 80:20 and 70:30. Images shown in (a) and (b) exhibit both layering and folded structures while images in (c) shows platelet-liked crystalline form of carbon, which is similar to graphite.

Table 1 shows the summarized data of EDS analysis of the synthesized graphene in terms of carbon content (atomic %), oxygen content (in atomic %), and the ratio of carbon to oxygen composition. Oxygen content increases, whereas carbon content and C/O ratio decreases when using H_2SO_4 :KOH volume ratio from 90:10 to 70:30 indicating that less chemical oxidation occurs when using high concentration of acidic electrolyte during electrochemical exfoliation.

Sample	C (%)	0 (%)	C/O ratio
90:10	87.0	13.0	6.7
80:20	83.8	16.2	5.2
70:30	72.5	27.5	2.6

Table 1. EDS analysis of the synthesized graphene samples.

4. Conclusions.

In conclusion, we have successfully synthesized graphene by electrochemical exfoliation of graphite rod employing different concentration of acidic electrolyte. Electrochemical exfoliation with higher concentration of electrolyte (H_2SO_4 :KOH volume ratio of 90:10) leads to better yield, less oxygen content and minimum defect of graphene. Selection of a suitable electrolytes is thus important to tune

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the quantity and quality of the graphene. The present study provides a proficient approach to synthesize cost effective and high-quality graphene.

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