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Short Communication

Graphene Oxide and Its Electrochemical Performance

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In this study, graphene oxide (GO) was synthesized from graphite flakes using simplified Hummer's method. Field Emission Scanning Electron Microscopy (FESEM) image showed that the GO nanosheets had an average area 7000 μm^2 with lateral dimension of up to 150 µm. The X-Ray Diffraction (XRD) pattern revealed a (002) diffraction peak, signifying the successful synthesis of GO. GO solution was cast on an aluminum (Al) foil placed in a petri dish and left to dry to form an electrode made up of GO film on the Al foil (GO-Al). It was found that GO-Al exhibited equivalent series resistance (ESR) close to that of the Al foil.

Keywords: Capacitance, Electrochemistry, Graphene, Simplified Hummer's Method

1. INTRODUCTION

Graphene is a one atom layer thick carbon sheet. Graphene exhibits many interesting electronic, optical and mechanical properties due to its two-dimensional (2D) crystal structure. The charge carriers of graphene (i.e.: electron) move ballistic in the 2D crystal lattice of graphene; hence it possesses high conductivity despite it being an organic compound [1]. Graphene is a building block because it can be wrapped up to form fullerene, rolled-up to form carbon nanotube or stacked up to form graphite. All of the variation from graphene exhibit interesting electrical properties.

Graphene can be produced by using mechanical approach as demonstrated by Novoselov and Andre Geim. Graphene produced using this method possesses the highest quality compare to the graphene produced by other methods [2]. However, the amount of graphene produced by this method is small and is suitable for research purposes only [2]. Therefore, an alternative method is needed to mass produce graphene. One of the alternative methods is chemical oxidation.

In general, chemical oxidation method produces graphene by first introducing functional groups such as carbonyl, hydroxyl and peroxyl in between carbon layers of graphite. These functional groups weaken the Van der Waals bond between the carbon layers which cause the graphene layers to peel off layer by layer from graphite [3]. The resulting graphene oxide (GO) can be reduced to graphene by adding hydrazine into the GO solution [3].

The criteria for batteries for electronics devices in these days are long-lastingness in spite of extensive usage and fast charging rate during recharging. Therefore, supercapacitors are incorporated inside the batteries to comply with the criteria. Electrochemical supercapacitors are passive and static electrical energy storage devices where extremely fast charging rate is the main property. The properties of supercapacitors are high power capabilities, fast charge propagation, charge-discharge process occuring within seconds, long cyclic life, low maintenance, and low self-discharging [4]. Supercapacitors also exhibit larger energy density compared to conventional capacitors.

The electrodes of the supercapacitor are normally made of porous carbon but recently, the researchers start to investigate the possibilities of using graphene as electrodes [4]. This is because graphene-based materials haves shown interesting properties such as high surface area, high conductivity and capacitance and low production cost [4]. Large area graphene is highly desirable as it significantly reduces high intersheets contact resistance as compared with small area graphene [5].

In this work, graphene oxide (GO) was synthesized using the simplified Hummer’s method, which would produce GO with large lateral dimension in scalable quantity [6]. It was characterized using field emission scanning electron microscopy, x-ray diffractometer and Fourier transform infrared spectroscopy. GO was used as an electrode material because it is the crucial derivative of graphene [7]. GO was adhered onto aluminium (Al) foil to investigate its electrochemical behaviors.

2. EXPERIMENTAL

2.1 Materials

Graphite flakes were purchased from Asbury Graphite Mills, Inc (Asbury, N J). Sulfuric acid (H_2SO_4, 98%), potassium permanganate ($KMnO_4$, 99.9%) and hydrogen peroxide (H_2O_2, 30%) were purchased from Merck (Darmstadt, Germany).

2.2 Synthesis of graphene oxide

Graphene oxide (GO) was exfoliated from natural graphite flake via Simplified Hummer’s method. In a typical synthesis, graphite flake was added to a solution which contained strong oxidizing agents (90% sulphuric acid and 10% phosphoric acid) and stirred with a magnetic stirrer. Nine grams of potassium permanganate was added slowly to the mixture during the stirring process. The mixture was allowed to stir for 3 days. After stirring, the mixture was transferred slowly to another bottle which contained ice and 20 ml of hydrogen peroxide. The resulting GO solution was washed several times with hydrochloric acid and distilled water using a centrifuge.

2.3 Characterization

Field emission scanning electron microscopy (FESEM) images were obtained on a FEI Nova Nano SEM 400 operated at 10.0 kV. The crystalline phase was determined using a Phillips X-ray diffractometer (XRD) employing a scanning rate of $0.033^{o}s^{-1}$ in a 2θ range from 5^{o} to 80^{o} with Cu Kα radiation (λ = 1.5418 Ǻ). Chemical bonding was analyzed using a Perkin Elmer Fourier Transform infrared spectroscopy (FTIR). The spectra (% transmittance with wavenumber) were recorded.

2.4 Preparation of graphene oxide-aluminium electrode

GO was dispersed in distilled water to achieve a concentration of 0.5 mg/ml. Then, the GO solution was cast directly on top of the aluminium (Al) foil in a petri dish and was dried in an oven at 40^{o}C. The dried GO on the Al foil (GO-Al) was then cut into two rectangular shapes and used as working electrodes. The electrodes were then sandwiched and separated by a filtrate paper soaked with sodium sulphate solution. The combination was clamped using microscope glass slides and small clippers as shown in Fig. 1. Cyclic voltammetry measurement was performed on the electrodes in the voltage range of 0-1 V using a module electrochemical workstation (Autolab PGSTAT-12). The potential scan rate was set at 0.1 V/s. Electron Impedance Spectroscopy (EIS) measurement was also carried out in the range of 50 Hz – 5 MHz by using an LCR Hi-Tester (HIOKI 3531).

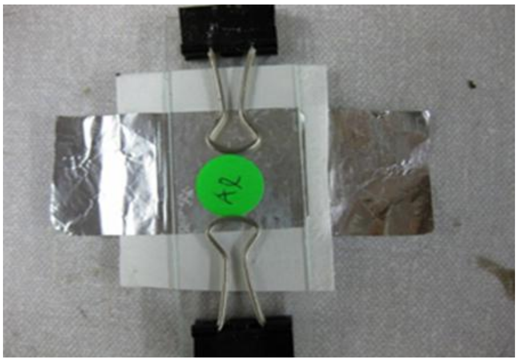

Figure 1. The electrochemical analysis set-up.

3. RESULTS AND DISCUSSION

Fig. 2a shows the FESEM image of graphite flakes with an average lateral size of 1 mm.

Upon oxidation, graphite oxide was exfoliated to GO, resulting in a gel-like solution as shown in Fig. 2b. The average area of the GO nanosheets is 7000 μm^2 with dimension of up to 150 μm as shown in Fig. 2c.

Fig. 3 shows the XRD patterns of graphite and GO. The peaks indexed at (101) at 50.68^{o}, (004) at 54.62^{o}, (110) at 59.84^{o} and (112) at 71.56^{o} signify the crystalline structure of graphite. The distinguishable (002) peak of graphite at 26.56^O has an interplanar distance, d_{002}, of 0.334 nm. This implies that graphite is a highly oriented carbon material. Meanwhile, the XRD pattern of GO shows an intense and sharp peak centered at 10.24° which corresponds to an interplanar distance of 0.80 nm. The increase in interplanar distance of GO is due to the existence of oxygen functional groups and some other structural defects [7].

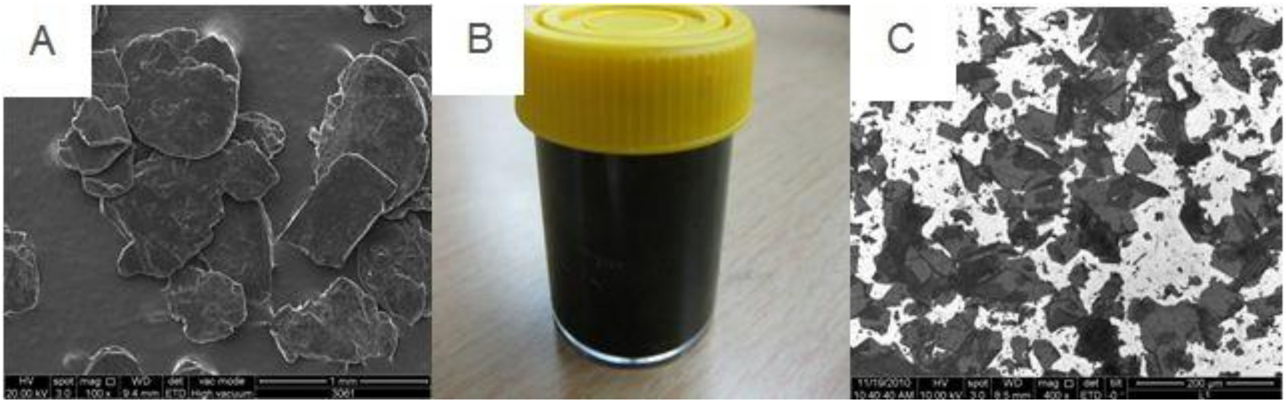

Figure 2. (A) FESEM image of graphite, (B) gel-like solution of graphene oxide and (C) FESEM image of graphene oxide.

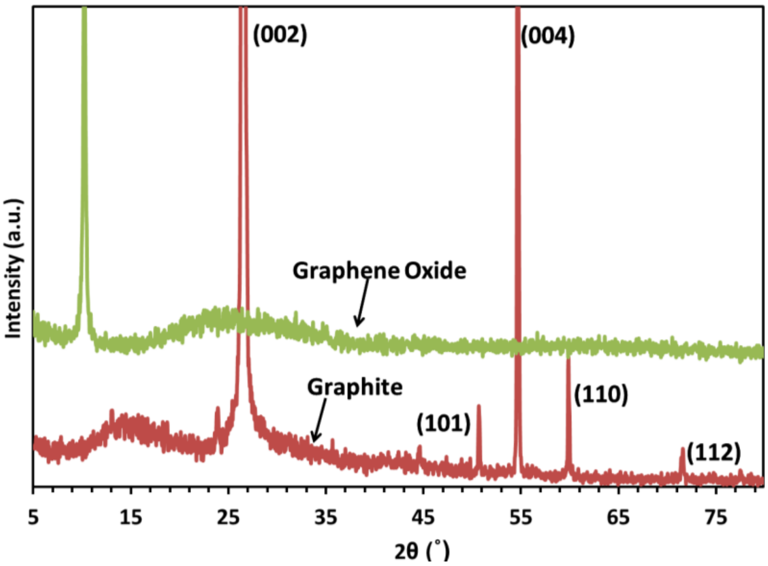

Figure 3. XRD patterns of graphite and graphene oxide.

FTIR measurement was employed to investigate the bonding interactions in graphene before and after the oxidation process. Fig. 4 shows that GO has a peak at 1081 cm^{-1} which is attributed to the C-O bond, confirming the presence of oxide functional groups after the oxidation process. The peaks in the range of 1630 cm^{-1}to 1650 cm^{-1} show that the C=C bond still remained before and after the oxidation process. The absorbed water in GO is shown by a broad peak at 2885 cm^{-1} to 3715 cm^{-1}, contributed by the O-H stretch of H_2O molecules [8]. This supports the fact that GO is a highly absorptive material, as verified by its ability to become a gel-like solution.

The cyclic voltammetry for Al foil and GO-Al are shown in Fig. 5. The scan rate was fixed at 100 mV/s in the range of -0.1 V to +1.0 V. A filtrate paper, which was soaked in 1.0 M of sodium sulphate solution, was used as a separator because of the porous structure of the filtrate paper and the good capacitive behavior of sodium sulphate [7]. The electrochemical performances of GO-Al are far superior to that of Al foil, which was used as a control, as it displays a much larger value of current response and CV area (Fig. 5a). The *quasi*-rectangular area suggests high double layer capacitance [9] and the capacitance could be calculated by integrating the curve area of the CV curve [10]. The capacitance of GO-Al is 2.03 mF while the capacitance of the Al foil is 0.0105 mF. The capacitance of GO-Al foil is two orders higher than the capacitance of Al, therefore GO enhanced the capacitance performance significantly. GO-Al has high electrochemical stability as the shape of the CV diagram was maintained even after 5 cycles, as shown in Fig. 5b.

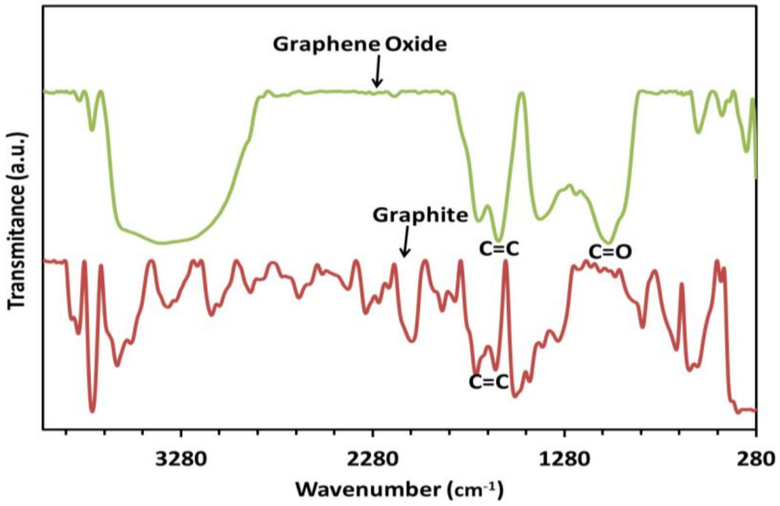

Figure 4. FTIR spectra of graphite and graphene oxide.

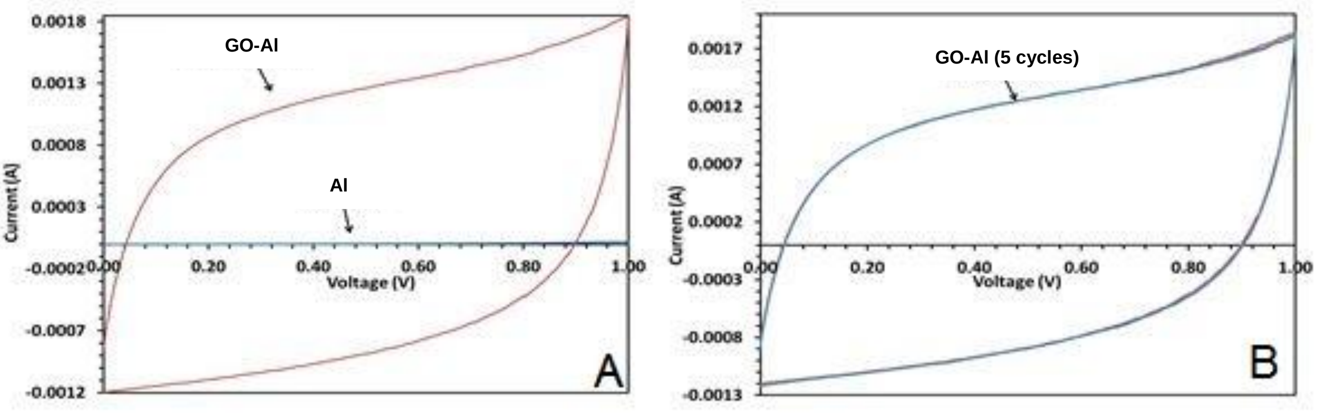

Figure 5. (A) Cyclic voltammetry of GO-Al and Al, and (B) cyclic voltammetry of GO-Al (5 cycles).

The electron impedance spectroscopy (EIS) data was analyzed using a Nyquist plot and is a profile of the imaginary component (Z”) of the impedance against the real component (Z’) in the frequency range of 50 Hz - 5MHz . The missing Warburg curve as in Figs. 6a and 6b indicate that the electrodes have short ion diffusion path, which facilitate the efficient access of electrolyte ions to the surfaces of the electrodes [11]. The equivalent series resistance (ESR) is represented by the intersection of the plots at the x-axis [12]. The ESR for Al foil and GO-Al are 0.196 Ω and 0.503 Ω, respectively. The small difference in the ESR values between the Al foil and GO-Al suggests that GO does not behave as an insulator to the Al foil.

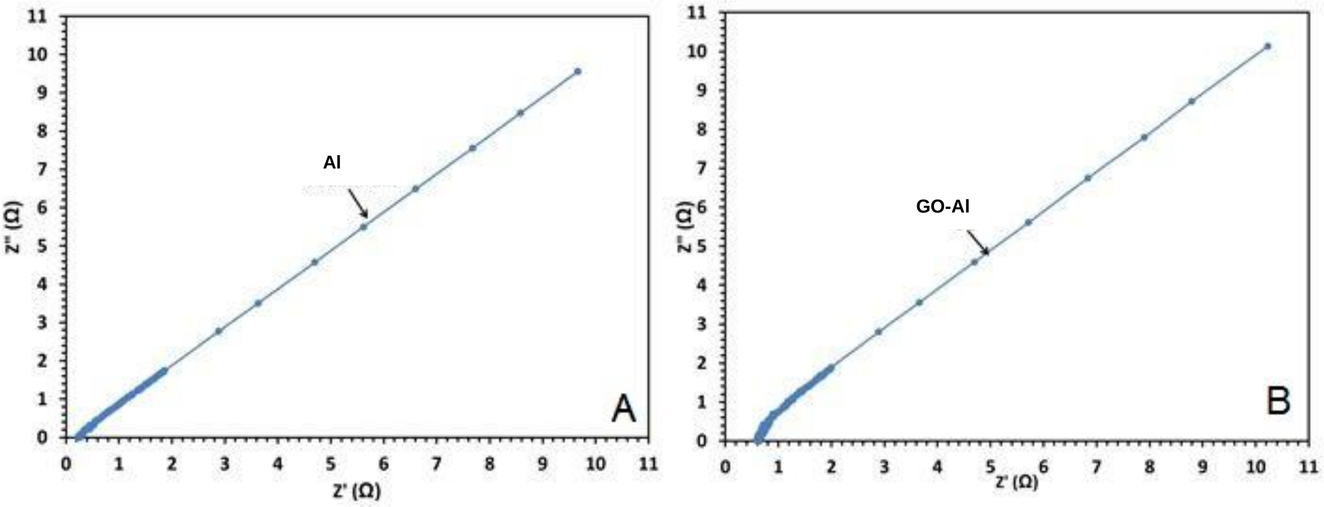

Figure 6. Nyquist plots for (A) Al and (B) GO-Al.

4. CONCLUSION

We had successfully synthesized large area graphene oxide using the simplified Hummer’s method. Graphene oxide was found to enhance the electrochemical behaviors of the supercapacitor set-up.

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