Synthesis of graphene/polyaniline nanocomposite for supercapacitor electrodes

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Abstract. Graphene/polyaniline nanocomposite has been synthesized and applied as supercapacitor electrodes. Graphene was synthesized by oxidation of graphite followed by reduction of graphite oxide to form reduced graphene oxide then transformed into graphene by reduction with NaBH₄. The graphene/polyaniline nanocomposite was prepared by in situ polymerization of aniline in graphene suspension with a variation of the composition. Characterization of samples was conducted using FTIR spectrometer, XRD, and SEM. Specific capacitance was obtained from the cyclic voltammogram (CV) curve taken using the potentiostat/galvanostat. FTIR spectra show the presence of functional groups indicating the formation of a graphene/polyaniline composite. Results of XRD analysis indicated the presence of crystal phases of graphene and polyaniline. Morphology of graphene is looked like a rather thick sheet while graphene/polyaniline nanocomposites are looked like clumps which are an incorporation of graphene and polyaniline nanoparticles. The highest specific capacitance of the supercapacitor fabricated with graphene/polyaniline electrode was 128 F/g.

1. Introduction

Energy storage technology is an important issue today in relation to increasing energy use, particularly electrical energy [1]. On the other hand, the increasingly limited availability of energy, especially the hydrocarbon-based ones, encourages people to create energy efficient storage systems, particularly electrical energy. The energy storage device serves as a means of storing some forms of energy, including electrical energy, which can be taken for use when needed for various purposes [2]. In general, the storage of electrical energy can be done with storage media in the form of electrochemical devices such as batteries, capacitors and fuel cell [3].

A supercapacitor is a double layer capacitor in a common electrochemical system called an electrochemical double-layer capacitor [4]. The supercapacitor device consists of electrodes, separators, electrolytes, and charge collectors [5, 6]. In contrast to the conventional capacitors consisting only of two electrodes sandwiching a dielectric material. In the supercapacitor, energy is stored through charge transfer at the interface between the electrode and the electrolyte, this system forming a double layer on both sides of the electrode-electrolyte interface [7]. When a voltage is applied, charges accumulate on the surface of the electrode. The ions in the electrolyte flow through the separator into the pores of the electrode, therefore the electrode must be sufficiently porous. Meanwhile, electrons flow into the external circuit through the electron collector that produces electrical power.
An important characteristic of a supercapacitor device is indicated by a higher power density as well as a higher energy density when compared to other storage devices such as batteries and fuel cells. This is because the supercapacitor devices use an electrode that has super electrochemical properties as well as the double layer system (double-layer) it has. Surely the performance of a supercapacitor depends heavily on the properties of its electrode and electrolyte [8].

Electrodes are a central component in the development of supercapacitor devices, in addition to electrolytes and separators, due to their critical role in the charge transfer process. Various attempts have been made by the researchers to obtain electrodes that have excellent capacitive properties to produce supercapacitor device with high specific capacitances. Carbon-based materials are most often developed as supercapacitor electrodes, such as activated carbon, porous carbon, carbon nanotube, carbon dots and graphene [9-13]. These carbon-based materials have dominated the development of supercapacitor electrodes. In this research, we developed a graphene/polyaniline nanocomposite to be applied as supercapacitor electrodes. Previously, other researchers have been using graphene/polyaniline composite as supercapacitor electrode, but with different graphene sources [14-16]. The composition of the ratio of graphene and polyaniline that formed the electrode was studied to find optimal composition for supercapacitor electrodes.

2. Materials and Methods

2.1. Materials
The materials used in this study were graphite powder as graphene source, concentrated H\textsubscript{2}SO\textsubscript{4} solution, NaNO\textsubscript{3}, KMnO\textsubscript{4}, H\textsubscript{2}O\textsubscript{2}, NaBH\textsubscript{4}, distilled water, aniline, HCl, (NH\textsubscript{4})\textsubscript{2}S\textsubscript{2}O\textsubscript{8}, stainless steel, acetic acid, PVA, and chitosan.

2.2. Preparation of graphene oxide
A total of 5 g of graphite powder and 2.5 g of NaNO\textsubscript{3} were dissolved with 120 ml of concentrated H\textsubscript{2}SO\textsubscript{4} with strong stirring for four hours at a temperature below 20 °C in an ice bath. After stirring for two hours, 8 g of KMnO\textsubscript{4} was added gradually. It is then heated to 35 °C for a complete oxidation process while stirring for two hours. Then, 200 ml of distilled water gradually added and stirred for one hour. To remove the residual KMnO\textsubscript{4}, then into the solution is added 15 ml of 30% H\textsubscript{2}O\textsubscript{2} which produces air bubbles and the color change from brown to yellow. The solution is then centrifuged to obtain a precipitate of graphite oxide, then washed with distilled water repeatedly. The precipitate of graphite oxide was dried at 110 °C for 12 hours in a furnace.

2.3. Preparation of graphene (reduced graphene oxide)
A total of 40 mg of graphite oxide (GO) was dispersed into the distilled water with a concentration of 1 mg/ml then was sonicated for 120 minutes to transform graphite oxide to graphene oxide (GO) [16]. Reduction process of GO was carried out by adding 2.28 g of sodium borohydride (NaBH\textsubscript{4}) into a water dispersion of 200 mg of graphene oxide at a concentration of 1 mg/ml and then stirring for 12 hours. Graphene oxide will change color from brown to black which indicates a reduced graphene oxide (rGO) has formed. The reduced graphene oxide (rGO) is then neutralized its pH by washing using water six times with stirrer and dried at 110 °C.

2.4. Preparation of graphene/polyaniline nanocomposite
The graphene/polyaniline (GN/PANI) nanocomposite is prepared using reduced graphene oxide (graphene) and aniline monomer. The synthesis of GN/PANI nanocomposite was carried out by in situ polymerization of aniline in graphene suspension with a variation of graphene mass to aniline molarity with ratio each 1:1 for GN/PANI(1: 1) and 1:2 for GN/PANI(1:2). A total of 1 mg/ml of graphene was dissolved in 100 ml of distilled water and sonicated for one hour. Then, the aniline monomer is added slowly into the graphene solution while stirring strongly in the ice bath. The 20 ml of the mixture of ammonium peroxodisulphate (APS) ((NH\textsubscript{4})\textsubscript{2}S\textsubscript{2}O\textsubscript{8}) and HCl solution at a ratio of 1:1 was fed into the mixture of graphene/aniline to initiate polymerization of aniline monomer. The mixed solution will change color to green as an indication of the formation of polyaniline. The nanocomposite is then
washed with distilled water, then separated by centrifugation and dried. The nanocomposites were characterized by XRD, SEM and FTIR.

2.5. Assembly of supercapacitor
Two electrodes (anode and cathode) are prepared from the graphene/polyaniline nanocomposites. A total of 200 mg of nanocomposite can produce two supercapacitor electrodes in pellete form, each with a mass of 100 mg. Separators are made in the form of a membrane of a PVA/chitosan composite. A total of 3 g of chitosan was dissolved into 100 ml of 1% acetic acid solution. The mixed solution was stirred at room temperature until chitosan dissolves entirely in acetic acid. A total of 3 g of polyvinyl alcohol (PVA) was dissolved with 100 ml of distilled water in another container. Then, the PVA solution is heated at 120 °C while stirred until the PVA dissolves entirely. Both chitosan solution and PVA solution are mixed while stirring evenly using a stirrer, then casting on petri glass. After 2 days forming a solid film that will be used as a separator membrane on the supercapacitor device. The PVA/chitosan separator membrane was immersed in H$_2$SO$_4$ solution with concentration of 1 M. The separator membrane is sandwiched between two graphene/polyaniline nanocomposite electrodes, then pressed on the outer side with stainless steel which serves as the collector of charge. Area of the fabricated supercapacitor is 1 cm.

2.6. Super capacitor performance measurement
Supercapacitor devices are tested using the set up of the potentiostat equipment to obtain a cyclic voltammetric curve depicting the charging-discharging process. Cyclic voltammogram (CV) was recorded at a rate of 5 mV/s three times. The specific capacitance value (Csp) is determined from the CV curve using the following equation (1):

$$ C_{sp} = \frac{1}{\frac{dV}{dt} \times m} $$

Where $C_{sp}$ is the specific capacitance (F/g), $I$ is the constant charging or discharging current (A), $dV/dt$ is the potential sweeping rate (V/s) and $m$ is the effective electrode mass (g).

3. Results and Discussion

3.1. Crystal properties
The crystalline nature of the graphene/polyaniline (GN/PANI) nanocomposite sample was analyzed by X-ray diffraction. Samples are scanned with an angle of 20° ranging from 10° to 60°. The diffraction pattern of the three samples tested is shown in figure 1, respectively for the graphene, GN/PANI(1:1), and GN/PANI (1:2) nanocomposites. The diffraction pattern for graphene is the same as the graphite diffraction pattern according to JCPDS - International Center for Diffraction Data (ICDD) no. 41-1487, as shown in figure 1a. The graphene diffraction peak appears at 26.24° corresponding to the diffraction plane (002) with a diffraction plane spacing (d) is 3.4 Å, greater than the graphite having a diffraction plane spacing $d \sim 3.3$ Å. Graphene peak is seen to widen with low intensity indicating the value of the crystallite size is small. The crystallite size was calculated based on the diffraction pattern broadening on each peak by using the Debye-Scherrer equation relationship as follows

$$ \sigma = \frac{k \lambda}{\beta \cos \theta} $$

where $\sigma$ is the crystallite size, $k$ is a constant (0.9), $\lambda$ is the wavelength of the X-ray source of 1.54 Å, $\beta$ is the full width at half maximum (FWHM), and $\theta$ is the diffraction angle. The calculation result by using Debye-Scherrer relationship obtained an average crystallite size (ACS) of graphene is 43.26 nm.

The X-ray diffraction patterns of the graphene/polyaniline (GN/PANI) nanocomposite are also shown in figure 1, respectively for the GN/PANI(1:1) (figure 1b) and the GN/PANI(1:2) (figure 1c) nanocomposite. The diffraction pattern shown by the two samples of GN/PANI nanocomposite is more complex than the diffraction pattern of graphene alone. Many emerging peaks are coming from PANI structure, respectively at an angle of $20 = 17.79^\circ$, 20.31°, 23.92°, 28.54°, and 32.66°. Graphene peaks still appear in both nanocomposite samples at 26.20° but its intensity decreased as PANI fraction
increased. The intensity of the PANI diffraction peak greatly dominates in the GN/PANI nanocomposite sample, this is because polyaniline has a fairly strong crystalline property. The average crystallite size for the GN/PANI nanocomposite sample was smaller than the graphene alone, i.e 32.15 nm for the GN/PANI(1:1) nanocomposite and 31.97 nm for the GN/PANI(1:2) nanocomposite.

![Diffractogram of (a) graphene, (b) GN/PANI(1:1), and (c) GN/PANI(1:2) composites](image)

**Figure 1.** Diffractogram of (a) graphene, (b) GN/PANI(1:1), and (c) GN/PANI(1:2) composites

3.2. *Surface Morphology*

Surface morphology was taken using a scanning electron microscope (SEM). Figure 2 shows the SEM images of the four samples tested, respectively for graphene oxide and graphene with magnification 50000 times as shown in figure 1a and 1b, dan the GN/PANI(1:1) and GN/PANI(1:2) nanocomposites with magnification 200000 times were shown in figure 1c and 1d. Graphene oxide has a structure that is still thick and uneven on its surface. While graphene has a thin morphology and has a more evenly and uniform layer. This is due to the reduction process of graphene oxide. On the other hand, the surface morphology of GN/PANI nanocomposite has finer particle grains. The GN/PANI(1:1) nanocomposite has a particle size smaller than the GN/PANI(1:2) nanocomposite. It found that the greater the fraction of polyaniline in the composite the larger the particle size. The composite GN/PANI sample also appears to agglomerate (agglomeration).

3.3. *Functional groups*

The functional groups in the sample are tested using a FTIR spectrometer, for which scanning is performed in the range of wavenumbers from 500 to 4000 cm\(^{-1}\). Figure 3 shows infrared transmittance spectra for four samples tested, graphene oxide (GO), graphene, GN/PANI(1:1), and GN/PANI(1:2) nanocomposites, respectively. Graphene oxide spectra (figure 3a) is dominated by peaks of the constituent material at 3371 cm\(^{-1}\) identified as vibration of O-H stretching and at 1573 cm\(^{-1}\) belonging to the aromatic C=C bond. The oxidation result is identified at 1704 cm\(^{-1}\) due to vibration of C=O stretching and at 1033 cm\(^{-1}\) due to vibration of C-O stretching. The spectra of the graphene compound have a peak that is almost the same as the graphene oxide spectra.
FTIR spectra also indicate that the graphene oxide has been reduced well. This is indicated by the decrease in absorption at the peak of around 1033 cm$^{-1}$ (C-O stretching) and the absorption at 1704 cm$^{-1}$ which is the vibration of the C=O stretching. The increase of C=C aromatic bond absorption at 1573 cm$^{-1}$ is an indication of graphene formation. Increased absorption indicates that carbon content in the graphene is more than in the graphene oxide. This means that the reduction process results in changes in the amount of carbon and oxygen content in the compound. The emergence of the O-H stretching is due to the water content in the compound. The O-H stretching in the graphene oxide has a very wide shape compared to in the graphene. Graphene oxide and graphene spectra also show the appearance of C-OH stretching peaks which are vibrations in phenol (hydroxyl) functional groups at 1350 cm$^{-1}$ and C=O-C at 1218 cm$^{-1}$. The absorption by C-OH (phenol groups) is decreasing which indicates that the reduction of GO to graphene is complete. In the spectra there is no absorption around 2353 cm$^{-1}$ caused by O=C=O stretching. This group is a CO$_2$ gas that can block the reduction process.

FTIR spectra for both samples of GN/PANI nanocomposites are shown in figure 3c and 3d, each for GN/PANI(1:1) and GN/PANI(1:2) nanocomposites. The spectra of both the GN/PANI nanocomposites showed the emergence of an antisymmetric stretching group of NH$_3^+$ at 3147 cm$^{-1}$ and NH$_3^+$ deformation group at 1496 cm$^{-1}$. At 1558 cm$^{-1}$, the C=N stretching group appears and at 1118 cm$^{-1}$ also appears C=S stretching. The peak of NH$_3^+$ deformation group at 1496 cm$^{-1}$ is the polyaniline constituent group. This group is formed by the process of changing the compound from the aniline monomer to polyaniline. This shape change occurs due to an aniline reaction with an APS doped with HCl. The amino component (-NH) of the APS decomposes and forms a polyaniline compound.
Figure 3. FTIR spectra of (a) graphene oxide, (b) graphene, (c) GN/PANI(1:1), and (d) GN/PANI(1:2) nanocomposites

The appearance of C=N stretching groups and C=S stretching groups indicates the occurrence of a bond between the graphene and polyaniline. This bonding occurs due to the process of combining the two compounds into a composite. Meanwhile, the peak NH$_3$ antisymmetric stretching at wavenumber 3147 cm$^{-1}$ indicates that the group decomposes and does not bind to the main compound. The wavenumbers 740 cm$^{-1}$ and 686 cm$^{-1}$ respectively belong to the CH$_2$ and CH=CH deformation groups, the peaks appear due to the process of decomposition of hydrocarbon compounds from graphene to GN/PANI nanocomposite. In the GN/PANI(1:2) nanocomposite, there is a very wide stretching O-H group at wavenumbers 3386 cm$^{-1}$ and -OH deformation at wavenumber 617 cm$^{-1}$. This is because the amount of aniline solution reacted is enough high. In the GN/PANI(1:1) nanocomposite, no O-H peaks appear, this is possible because the water was released during the synthesis process.

3.4. Electrochemical performance

Testing of electrochemical performance of supercapacitor was performed using a potentiostat/galvanostat tool with a voltammetric mode to obtain a cyclic voltammetric (CV) curve. The voltammetric cyclic measurements were made by connecting the supercapacitor electrodes with the terminals at the computerized potentiostat/galvanostat, sweeping rate set at 5 mV/s. Three supercapacitor devices were tested for their electrochemical performance with their respective CV characteristics as shown in figure 4. The CV test results for the supercapacitor device with graphene electrodes and GN/PANI(1:1) had a CV curve with a rectangular shape. This shows that the charge and discharge process is perfect. This corresponds to the curve shape for the EDLC (Electric Double Layer Capacitor) supercapacitor. While the CV curve for the supercapacitor device with the GN/PANI nanocomposite electrode (1:2) still does not show the ideal curve of a supercapacitor. From the CV curve is determined the specific capacitance value ($C_{sp}$) of the supercapacitor based on equation (2). The $C_{sp}$ value of supercapacitor with graphene electrode is 102.5 F/g, while for supercapacitor with GN/PANI(1:2) electrode resulted in $C_{sp}$ value 108.5 F/g, and supercapacitor with GN/PANI(1:1) electrode had a specific capacitance of 128.3 F/g.
Figure 4. Cyclic voltammogram (CV) of three supercapacitor devices with different electrodes: (a) graphene, (b) GN/PANI(1:1) nanocomposite, and (d) GN/PANI(1:2) nanocomposite

The specific capacitances obtained in this study are still lower than those obtained by previous researchers, as obtained by Wang et al [14], Yu et al [15], and Zhang et al [16]. The low value of the specific capacitance obtained in the study is considered because the supercapacitor assembly process is not good so the interfacing between the electrode and the electrolyte does not occur well. In addition, the separation membranes used are not working properly and are unable to facilitate the charge transfer process perfectly. This results in the charge transfer process does not occur perfectly so that the charge-discharge process cannot take place properly.

4. Conclusion
The formation of graphene from the graphite powder was performed through three stages starting with formation of graphene oxide (GO), followed with reduction to reduced graphene oxide (rGO), then forming graphene. Synthesis of graphene/polyaniline (GN/PANI) for supercapacitor electrodes was performed by in situ polymerisation of aniline in the graphene suspension. The SEM image confirm the formation of graphene with a thin layer of morphology, in contrast to graphene oxide which still appears to have a stacked layer. GN/PANI nanocomposites have been well established as identified in the XRD analysis data. FTIR results showed that the process of reduction of graphene oxide to form reduced graphene oxide was well underway, as was graphene formation. It is characterized by the reduction of oxygen-based groups in graphene. Supercapacitor devices have been successfully fabricated using graphene alone and GN/PANI nanocomposite electrodes. Electrochemical test results show that the charge-discharge process in the supercapacitor device has occurred, this is characterized by the resulting cyclic voltammogram curve. The highest specific capacitance value (128.3 F/g) was found, for the supercapacitor device with the GN/PANI nanocomposite electrode with ratio GN/PANI is 1:1.
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