Characterization of polyaniline and graphene oxide as possible electrode materials for supercapacitor

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ABSTRACT – The aim of this study is to prepare the graphene oxide from exfoliation of natural graphite flakes by Hummer's method and polymerize an aniline by chemical polymerization technique. The preparation of those materials was done to establish the active material towards the development of supercapacitor cell. The conductive polymer; aniline/PANi was chosen due to its unique advantages in term of good conductivity, low cost, its flexibility and easy to synthesize. The structure and morphological study were performed by Fourier Transform Infra-red (FTIR) spectroscopy, Brunauer-Emmett-Teller (BET) and Scanning Electron Microscopy (SEM). The result demonstrate that polyaniline and graphene oxide are successfully polymerized and synthesized by modified Hummer's method.

1. INTRODUCTION

Graphene is a well-known two dimensional carbon one-atom/monolayer sheet of graphite which is made of sp^2 bonded carbon atoms arranged in a regular hexagonal/honeycomb lattice and can be prepared by several techniques[1]. Graphene possess an unusual high surface-to-volume ratio, high specific surface area of 2620m^2/g and high conductivity. However, due to some drawback of graphene sheets in term of tendency of irreversible agglomerate, reduction in electrolytes diffusion and lack of ion accessibility due to restacking of graphene layers, many researcher started to look at another alternative such as carbon composite, metal oxide and graphene derivative[2].

Graphene oxide (GO) is among the groups of graphene-graphite family and considered as derivative of graphene. They are readily made from graphite, exhibit the layered structure and surface related properties [3]. As the precursor of graphene, GO easily derived from oxidation of natural graphite at large scale in low cost.

Polyaniline (PANi) is a promising candidate among the other conductive polymer due to good environmental stability, high specific capacitance and excellent electro-activity. On the contrary, self-stand PANi unable to stand the swell and shrink during charge/discharge activity of supercapacitor. Therefore, the GO is needed as a scaffold composition to improve the mechanical and thermal stability[4].

In this work, the preparation of Polyaniline from Aniline and preparation of Graphene Oxide was done from natural graphite flakes as an active material for supercapacitor electrodes.

2. METHODOLOGY

2.1 Materials

Aniline ($C_6H_5NH_2$; ≥99.5%), potassium permanganate ($KMnO_4$; ≥97%, hydrogen peroxide (H_2O_2; 30%) and graphite fine extra powder were purchased from Merck, USA. Hydrochloric acid (HCl; 37% purity) and ammonium persulfate (APS-$NH_6S_2O_8$) were purchased from Sigma Aldrich, USA, whereas sulfuric acid (H_2SO_4) was purchased from Fischer Scientific, USA.

2.2 Synthesis of Graphene Oxide

The graphene oxide was synthesized using natural graphite. Hummer's method was used due to inexpensive and its convenience technique[5]. In this method, 3g of pure graphite powder was gradually added into solution of 70ml of sulfuric acid (H_2SO_4) and 7.78ml of H_3PO_4 protonated solvent with 9:1 ratio, in ice bath condition and mixed by magnetic stirrer for 30 min in 1000ml beaker.

Then, 9g of $KMnO_4$ was slowly added and vigorously stir for an hour in ice-bath condition. Then, the mixture was stirred for 60 min. at 40ºC in oil-bath followed by additional of 150ml deionized water for 15min. Finally 500ml of distilled water and 15ml of H_2O_2 were added and stirred for an hour or until yellow-brownish colour appeared[6].

2.3 Polymerization of Aniline

PANi was prepared by dissolving 2ml Aniline monomer into 50ml of 1M HCl. Another solution was prepared by mixing 2.5g APS into 50 ml of 1M HCl. Both solutions were rapidly stirred for 40 min. Then, the APS solution was added into Aniline solution in ice bath condition and stirred for another 5hrs until it became greenish in colour[7].

3. RESULTS AND DISCUSSION

3.1 FTIR Result of Graphene Oxide

The FTIR spectrum of graphene oxide (GO) in

Figure 1 depicted the presence of difference functionality of GO at 3405cm^{-1}, 1710cm^{-1}, 1584cm^{-1} and 1196cm^{-1} which correspond O-H, C=O, C=C and C-O-C stretching bands respectively. Another peak of 600cm^{-1} was due to the C-C out of plane (benzene ring). Based on FTIR spectrum, The O-H result was reduced and C=C aromatic stretch was assigned to absorbance of water molecules [6].

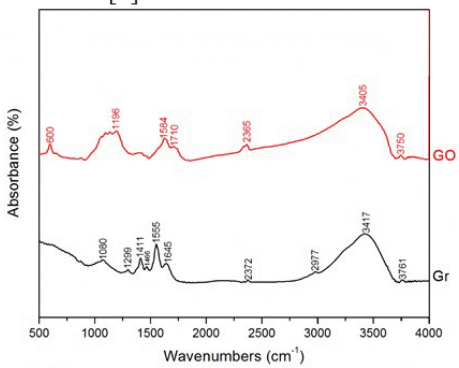


Figure 1 FTIR spectrum of natural graphite and synthesized graphene oxide

3.2 FTIR Result of Polyaniline

The FTIR spectrum in Figure 2 shows the characteristic band at 1569cm^{-1} and 1500cm^{-1} which correspond to C=C and C=N stretch quinoid and benzenoid structure of PANi on emeraldine salt (ES). Peak at 1299cm^{-1} assigned to C-N stretch band of benzenoid unit. Intense peak at 1110cm^{-1} is for the in-plane bending mode of C-H [8] .

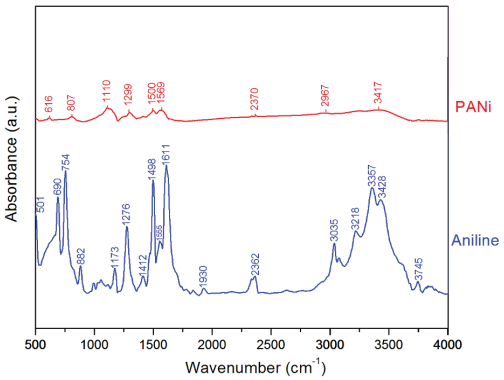
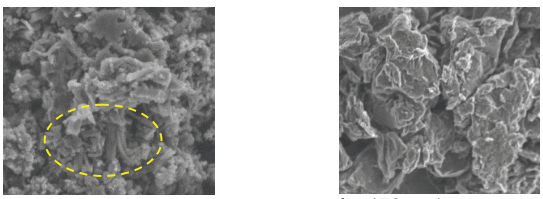


Figure 2 FTIR spectrum of aniline and polyaniline

3.3 Structure and Morphology

SEM image as obtained by Hitachi SU3500 show fibre-like structure of PANi (Fig.3a) and crumpled pattern of synthesized graphene oxide (Fig.3b).



a.(20µm) b. (50µm)

Figure 3 Morphology of a. Polyaniline and b. Graphene Oxide

3.4 Specific Surface Area (SSA)

The SSA result of PANi and GO were obtained by Micromeritics 3 Flex Surface Characterization. According to Table 1, the synthesized surface area of PANi and GO were expanded.

Table 1 BET Surface Area of PANI and GO

Properties	Data
Graphene Oxide	13.1268 m²/g
Polyaniline	1.0813m²/g
Natural Graphite	0.7045 m²/g

4. CONCLUSIONS

The FTIR spectrum shows the presence of various types of oxygen functional groups that confirmed the GO was successfully synthesized and followed by the improvement on the SSA. The PANI spectrum also confirmed the Emeraldine Salt (green colored) which indicates it was a conductive polymer. Thus, PANi/GO binary composite highly expected to be favorable materials for supercapacitor electrode.

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