

Gelam Tree-Derived Carbon Nanosheets as Thick and Free-Standing Electrode for Supercapacitor

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Most electrodes for supercapacitors are prepared as thick layer electrodes. Compact, thick and free-standing electrodes are needed for supercapacitor with high volumetric capacitance and energy density. Carbon nanosheets were obtained from treating the bark of the Gelam tree (*Melaleuca cajuput Powell*) via hydrothermal and microwave processes. The XRD results showed the presence of graphitic carbon in the Gelam tree-derived carbon nanosheet. The carbon nanosheet (the thickness of 0.01 cm) was mixed with graphite and poly(aniline) as conducting binder to fabricate a supercapacitor electrode. Conductivity as high as $3.67 \times 10^{-2} \text{ S cm}^{-1}$ were obtained from the electrode using the carbon nanosheet to graphite the ratio of 3:7. The electrode with this composition had a porous structure. The electrode with a carbon nanosheet to graphite the ratio of 7:3 had a granular morphology with a low conductivity of $0.8 \times 10^{-3} \text{ S cm}^{-1}$. Cyclic voltammetry tests were conducted in lithium chloride and ammonium cyanate-based electrolytes. Both types of electrodes (ratio 3:7 and 7:3) had the same trend of capacitance and voltage window in lithium chloride and ammonium cyanate-based electrolytes. Capacitance as high as 0.0618 F was obtained from the electrode using the 7:3 ratios nanosheet in 10 % ammonium cyanate electrolyte. A novel supercapacitor with high capacitance designed using a thick layer electrode can readily be prepared from the carbon nanosheets derived from the agricultural wood waste.

1. Introduction

The supercapacitor is a type of electrochemical energy storage device that can store higher energy density than conventional supercapacitors. It can deliver higher power density than batteries. Supercapacitor has attracted considerable attention in various applications such as electric vehicles, back-up power, camera flash, and many more (Sumboja et al., 2012). Among different classes of materials for supercapacitor, a lot of attention has been focused on carbon-based materials due to their exceptional conductivity (Syarif et al., 2018), tuneable morphology (Taha and Alsharif, 2018) and stability. Various types of carbons which store the charge via electrical double layer capacitance have been developed, such as graphene and carbon nanotubes (Yan et al., 2014). Despite the promising performance of the supercapacitor based on carbon nanotubes or graphene electrode, the use of such materials is limited by their high production cost, the complicated synthesis process as well as low synthesis yield (Sumboja et al., 2013).

Nature has offered a wide range of biomass which can be used as the green, inexpensive, and renewable source of carbon precursors. Biomass-derived carbon could be used as electrodes in batteries and supercapacitors (Syarif et al., 2018). Eggplant-derived microporous carbon sheets were produced in mass production through the efficient bifunctional oxygen electrocatalysts at low cost; it was used as rechargeable

Zn-air batteries. A large amount of biomass from plants (phytomass) is generated including the shells from coffee, coconut, rice, and corncob, which all have been explored as the source of biomass-derived carbon. Carbon can also be derived from the bark of Gelam trees (*melaleuca cajuput* Powell) (Syarif, 2014). These trees overgrow in a short time, with the composition of the stem bark reaching 10 % of the overall volume. Gelam wood has rough whitish stem skin can be peeled by itself, generating biomass surrounding the trees. The bark cannot be used for woodworking, carpentry, or further processing. Their conversion to carbon will help to reduce the amount of waste generated by the Gelam tree. The nanosheet morphology suits the charge storage requirement of the electrical double layer capacitance of supercapacitors (Syarif and Prasagi, 2016), such as the high surface area and good electrical conductivity (Syarif et al., 2014). The nanosheet morphology also promotes rapid charging and discharging process as well as large charge storage capability (Niu et al., 2017). The carbon nanosheet electrode can store relatively large amounts of energy (Peng et al., 2016). Despite the promising characteristics, the pellet electrode prepared from the carbon nanosheets has low capacitance (Yong et al., 2012). Carbon nanosheet-based electrodes require conducting substrates as a current collector. They are often fabricated as a thick-layered electrode with low loading mass which leads to forming supercapacitors with low capacitance and energy density. The electrode layer composition/thickness and electrolyte affected to both parameters. The electrode was prepared from the carbon nanosheets, but it has drawbacks, namely low capacitance. The carbon nanosheet-based electrodes require conducting support as a current collector.

The volume and weight ratio between the active material, such as carbon nanosheet, and the components in the supercapacitor (i.e. electrolyte, current collector, and packaging), are large. The capacitance normalized to the total volume, and weight of the supercapacitor became very small. In this work, a novel carbon nanosheets were fabricated from the bark of Gelam wood via hydrothermal and microwave treatment. The carbon nanosheets were then mixed with graphite and poly(aniline) to produce thick electrodes as a novel supercapacitor. Poly(aniline) acts as a conducting binder to replace the existing non-conducting binder to maintain the low resistance of the electrodes (Yong et al., 2012). A capacitance of 0.0618 F and conductivity of $3.67 \times 10^{-2} \text{ S cm}^{-1}$ have been achieved from the electrode having the carbon nanosheet to graphite ratio of 7:3.

2. Materials and methods

2.1 Synthesis and preparation of the electrode

Carbon nanosheets were prepared from the bark of the Gelam tree as described by Syarif (2014). The barks were soaked in water for 12 h and dried under sunlight for 24 h. They were then cut and crushed into a powder form. 40 g of the bark powder was mixed with 0.1 L of 0.014 M KOH and transferred into the hydrothermal reactor to undergo the hydrothermal treatment for 16 h at 200 °C to produce torrefaction materials. To obtain carbon nanosheets, the powder was then subjected to microwave pyrolysis at 1,500 W of microwave power to make 800 °C inside the microwave furnace chamber. The furnace was removed from the oven after 20 min of contact and cooled to room temperature. The carbon nanosheets would be formed.

The electrodes were prepared by mixing the carbon nanosheet and graphite with a weight ratio of 3:7 or 7:3 in the addition of 10 % of binder polyaniline. Polyaniline was added to enhance the conductivity of the electrode. The mixture was homogenized in ultrasonicator to form a brown paste. The paste was coated on a glass plate with an average thickness of 0.01 cm to form a thick and free-standing electrode

2.2 Material and electrochemical characterizations

Morphology of the electrode was characterized by scanning electron microscope (SEM) JEOL JED-2300. The sample was placed onto the SEM sample holder without coating. The crystallography of the electrodes was characterized by Shimadzu X-ray diffractometer XRD 7000. The electrode was pinned on a sample holder and operated within the 2θ range of 25-90 ° at 40 kV and 30 mA. The thickness of the electrodes was measured using digital Vernier calipers. Conductivities of the electrodes were determined by resistance measurement using Eq(1) and Eq(2).

$$\rho = \frac{R.A}{t} \quad (1)$$

$$K = \frac{1}{\rho} \quad (2)$$

where ρ is resistivity ($\Omega \text{ cm}$), R is electrical resistance (Ω), A is the surface area of the electrode (cm^2), t is the thickness of the electrode (cm), and K is conductivity ($\Omega^{-1} \text{ cm}^{-1}$).

Electrochemical characterization of the electrodes was studied in a three-electrode set up which is connected to a potentiostat (Cheapstat). Pt and Ag/AgCl rod were used as a counter and a reference electrode. The measurement was conducted in lithium chloride and ammonium cyanate-based electrolytes without using the support of the current collector. The cyclic voltammetry method was conducted at various scan rates (5, 10, 20, 50, and 100 mV s^{-1}) to investigate the charge storage mechanism of the electrodes and to calculate their specific capacitance. The specific capacitance was calculated by Eq(3) (Kim et al., 2005).

$$C_{avg} = \frac{\Delta Q}{(s \times \Delta V)} = \frac{(\int I dV)}{(s \times \Delta V \times w)} \quad (3)$$

where ΔQ is the total charges within the measured potential window (ΔV) which can be obtained by integrating the area under the cyclic voltammetry curve ($\int I dV$), w is the weight of carbon nanosheets on the electrode (g), I is the measured current (A), s is scan rate (mV s^{-1}).

3. Result and discussion

3.1 Material characterization

Two types of carbon nanosheet -based electrodes were prepared in this study by varying the weight ratio of carbon nanosheet to graphite in the electrode (ratio 3:7 and 7:3). The same amount of polyaniline conductive binder was used in all electrodes. The conductivity of the electrodes was first measured to determine the effect of carbon nanosheet content in the electrode. The electrode with a high amount of carbon nanosheet (ratio 7:3) has a conductivity of $0.8 \times 10^{-3} \text{ S cm}^{-1}$. The electrode with a low amount of carbon nanosheet (ratio 3:7) has an improved conductivity ($3.67 \times 10^{-2} \text{ S cm}^{-1}$). The functional groups of biomass-derived carbon nanosheet may result in the low conductivity of the electrode with high carbon nanosheet content (Xiao et al., 2017). The wrinkled morphology of carbon nanosheet may scatter the electron transport, leading to the high resistance of the electrode with high carbon nanosheet content (Gomez-Martin et al., 2019). The conductivity of the electrode with graphite: carbon nanosheet of ratio 7:3 is comparable to other carbon-based electrodes which were derived from pyrolysis of biomass ($0.001 - 1.5 \text{ S cm}^{-1}$) (Pollak et al., 2006) and within the conductivity of semiconductor materials ($10^{-8} - 10^3 \text{ S cm}^{-1}$) (Hu et al., 2013). Both electrodes exhibit similar morphology of porous structure. The graphite has a rigid structure, distributed uniformly below scattered carbon nanosheet structures. The electrode with large content of graphite shows a more granular structure (Figure 1a) as compared to its counterpart with the small content of graphite (Figure 1b). The rigid morphology of the graphite engulfed the nanosheet structure of the carbon nanosheet, resulting in a more rigid structure of the electrode with large content of graphite. The robust nature of the electrode suggests the effectiveness of polyaniline as a conductive binder used in this work. The utilization of conductive binders has the potential to replace the non-conductive binders (i.e., PVDF and PTFE) which are more commonly used as a binder in the supercapacitor electrode (Sumboja et al., 2012). This is particularly useful in thick and free-standing electrodes where the conductivity can be a bottleneck on improving the capacitance of the electrode.

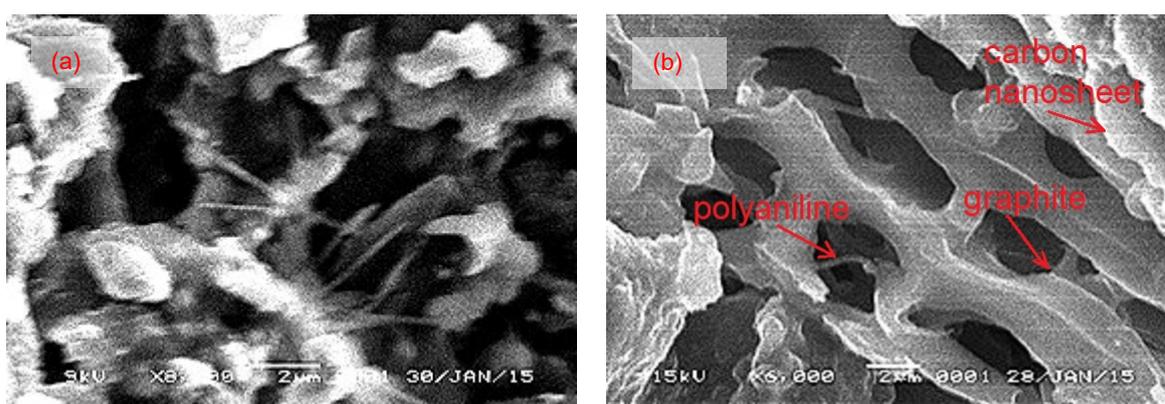


Figure 1: SEM image of electrode carbon nanosheet – graphite ratio of (a) 3:7 and (b) 7:3

The crystal structure of both electrodes was investigated with X-ray diffraction (XRD). The XRD patterns of both electrodes are given in Figure 2a and 2b. Both patterns show the existence of graphitic carbon at 2θ of 26.60 degrees which are in agreement with the presence of 002 planes of crystalline or graphitic carbon in JCPDS database no 75-1621. The sharp peak of XRD indicates the presence of large crystals, whereas the

high intensity of the sharp peak confirms the presence of a large amount of graphitic carbon (Ray and Salehiyan, 2020) in the electrode with carbon nanosheet: graphite ratio of 3:7. Carbon nanosheet consists of carboxylic and hydroxyl functional groups could act as active sites that promote higher ionic adsorption on electrodes (Syarif and Prasagi, 2016).

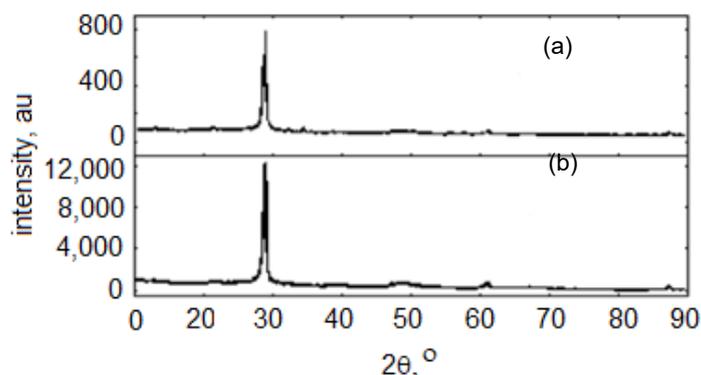


Figure 2: The diffractogram of the electrode with carbon nanosheet – graphite ratio of (a) 3:7 and (b) 7:3

3.2 Electrochemical characterization

Carbon provides a wide range of capacity that able to increase its active sites on adsorbing ions (Zhang et al., 2017). Besides the inherent nature of carbon as the active material for electrical double layer capacitance, the carboxylic and hydroxyl functional groups of carbon nanosheet provide active sites that can promote high ionic adsorption and enhance the capacitance of the electrode. Cyclic voltammetry was used to study the electrochemical properties of the electrodes in lithium chloride and ammonium cyanate. Figure 3a and 3b show the voltammograms of the electrode with high graphite content (carbon nanosheet: graphite ratio of 3:7) in the electrolyte containing 10 and 20 wt% lithium chloride.

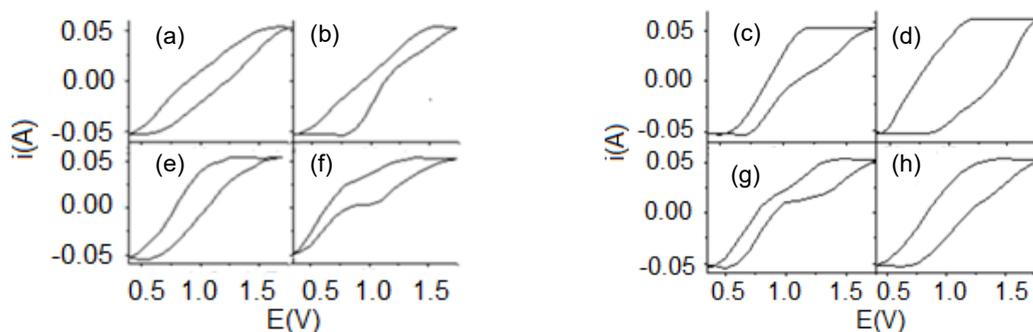


Figure 3: Voltammograms of the electrodes with carbon nanosheet:graphite ratio of 3:7 at various concentration of electrolytes measured at scan rate 20 mV s^{-1} : (a) 10 % lithium chloride (b) 20 % lithium chloride (e) 10 % ammonium cyanate (f) 20 % ammonium cyanate; with carbon nanosheet:graphite ratio of 7:3 at various concentration of electrolytes measured at scan rate 20 mV s^{-1} : (c) 10 % lithium chloride (d) 20 % lithium chloride (g) 10 % ammonium cyanate (h) 20 % ammonium cyanate

The electrode has a rectangular capacitive behaviour indicating the characteristic of the electrical double layer capacitance of the electrode (Sumboja et al., 2013). It can be seen in Figure 1a, the double-layer capacitance of the electrode is observed within a relatively small voltage window (0.35 V) in the electrolyte containing 10 % of lithium chloride. The voltage window can be slightly enlarged to 0.5 V in an electrolyte containing 20 % of lithium chloride. In Figure 1b, a much-enhanced voltage window can be obtained when ammonium cyanate is used as the electrolyte. The electrodes can exhibit a rectangular-shape voltammogram within a voltage window of 1 V in the electrolyte with 10 and 20 % of ammonium cyanate. A similar trend of voltage window was observed when the electrodes with carbon nanosheet and graphite ratios of 7:3 were tested in lithium chloride and ammonium cyanate electrolytes. The voltage window of the electrodes in the electrolyte with 10 % lithium chloride was the smallest among the samples. A stable voltage window of 1 V with rectangular-

shape voltammograms can be obtained when the electrodes were tested in ammonium cyanate-based electrolytes.

Due to an enlarged voltage window in ammonium cyanate-based electrolyte, both electrodes with carbon nanosheet and graphite ratio of 3:7 and 7:3 exhibits an improved capacitance in ammonium cyanate-based electrolyte as compared to their counterparts tested in lithium chloride-based electrolyte.

As summarised in Tables 1 and 2, almost all electrodes exhibited a higher capacitance when they were tested in ammonium cyanate-based electrolytes. The highest capacitance (0.062 F) was obtained from the electrode with carbon nanosheet: graphite ratio of 3:7, which was measured at a scan rate of 5 mV s⁻¹ in ammonium cyanate-based electrolyte. The effect of carbon nanosheet: graphite ratio to the capacitance of the electrodes is more pronounced at slow scan rates as compared to the measured capacitance at fast scan rates.

The electrodes with high graphite content 3:7 have higher capacitance than the electrodes with low graphite content of 7:3, specifically at slow scan rates. The high conductivity of the electrodes with large graphite content attributes to their large capacitance, specifically at slow scan rates (Fic et al., 2012). At fast scan rates in 100 mV s⁻¹, the capacitance of the electrode is limited by the slow diffusion of the electrolyte's ion in the carbon-based electrode.

Table 1: Capacitance of electrodes with carbon nanosheet: graphite ratio of 3:7

Scan rate (mVs ⁻¹)	Capacitance (F) at various electrolyte concentration			
	LiCl 10 %	LiCl 20 %	NH ₄ SCN 10 %	NH ₄ SCN 20 %
5	0.024	0.006	0.062	0.015
10	0.018	0.002	0.029	0.006
20	0.011	0.001	0.012	0.003
50	0.003	0.001	0.001	0.002
100	0.001	0.001	0.001	0.001

Table 2: Capacitance of electrodes with carbon nanosheet: graphite ratio of 7:3

Scan rate (mVs ⁻¹)	Capacitance (F) at various electrolyte concentration			
	LiCl 10 %	LiCl 20 %	NH ₄ SCN 10 %	NH ₄ SCN 20 %
5	0.007	0.006	0.025	0.040
10	0.003	0.003	0.016	0.019
20	0.001	0.003	0.010	0.005
50	0.001	0.001	0.002	0.018
100	0.001	0.001	0.001	0.001

All electrodes had similar capacitance at fast scan rates since ionic mobility tends to be low in a high concentration of electrolytes. The capacitance of the electrodes tends to be low in concentrated electrolytes.

4. Conclusions

The carbon nanosheets have been explored as the thick electrode without the need for conducting support (current collector) for supercapacitor applications. The electrode with carbon nanosheets: graphite ratio of 3:7 has achieved a conductivity of 0.0367 S cm⁻¹ and capacitance of 0.0618 F in ammonium cyanate-based electrolyte. The amounts of graphite in the electrodes affect the conductivity and capacitance of the electrodes at slow scan rates.

The voltage windows of the electrodes show the dependence on the type and concentration of the electrolytes. The barks of the Gelam tree have been used as the green, inexpensive, and renewable/sustainable source of electrode carbon. A simple, safe and scalable synthesis method was developed to obtain carbon nanosheets from the barks of the Gelam tree. This work contributes to the development of compact, thick and free-standing electrodes for supercapacitor with high volumetric capacitance and energy density

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