Jusami Jurnal Sains Materi Indonesia
Homepage: http://jusami.batan.go.id
Akreditation No : 21/E/KPT/2018
Date 9 July 2018
ISSN 1411-1098
E-ISSN 2614-087X

SYNTHESIS AND CHARACTERIZATION OF GRAPHENE FROM COCONUT FIBER (COCOS NUCIFERA) AS ANODE MATERIALS FOR Li-ION BATTERY

Indra Gunawan[1], Wagiyo H[2], Bambang Sugeng[3] and Sudaryanto[4]
Pusat Sains dan Teknologi Bahan Maju (PSTBM) - BATAN
Kawasan Puspiptek, Serpong 15314, Tangerang Selatan
E-mail: irgun.ig@gmail.com

Received: 14 Desember 2018 *Revised: 28 February 2019* *Accepted: 6 March 2019*

ABSTRACT

SYNTHESIS AND CHARACTERIZATION OF GRAPHENE FROM COCONUT FIBER (COCOS NUCIFERA) AS ANODA MATERIAL FOR LI-ION BATTERIES. Synthesis of graphene from coconut fiber conducted in two stages. The first stage is heating the powder of coconut fiber that passes 325 meshes by hydrothermal method at 200 °C for 4 hours. Furthermore, the pyrolysis then treated at temperature of 1000 °C for 2 hours. The grain size and surface morphology from graphene observed using SEM in the 1000X magnification. From the SEM image of graphene, it shows the pattern of several thick layers build mutual three-dimensional, forming a flake structure. Observations also show stacks of graphene structure with more big flakes forming a thick pallet. Another characterization was performed by using X-ray diffractometer (XRD), Raman Spectrometer and LCR meter. From XRD observation there is an amorphous pattern at the first stage of synthesis, after pyrolysis at 1000 °C for 2 hour a peak near $2\theta = 24^{o}$, 42^{o} and 52^{o} which corresponds to crystal indexes (002), (400) and (511) became visible. The peak at around 1350 cm^{-1} in the Raman is the D band. The D band is represented defects, like disruption in the sp^2 bonding because of heptagon and pentagon rings, vacancies, edge effect, and etc. DC conductivity or bulk electrical conductivity of about 4.6×10^{-3} Scm^{-1}.

Key words : *Hydrothermal, Pyrolysis, Coconut fiber, Anode, Battery, Li-ion*

ABSTRAK

SINTESIS DAN KARAKTERISASI GRAPHENE DARI SERAT KELAPA (COCOS NUCIFERA) SEBAGAI BAHAN ANODA UNTUK BATERAI LI-ION. Sintesis graphene dari serat kelapa dilakukan dalam dua tahap. Tahap pertama pemanasan serbuk sabut kelapa yang melewati 325 mesh dengan metode hidrotermal pada 200 °C selama 4 jam. Selanjutnya, pirolisis kemudian dirawat pada suhu 1000 °C selama 2 jam. Ukuran butir dan morfologi permukaan dari graphene diamati menggunakan SEM dalam perbesaran 1000X. Dari citra SEM graphene, itu menunjukkan pola beberapa lapisan tebal membangun saling tiga dimensi, membentuk struktur serpihan. Pengamatan juga menunjukkan tumpukan struktur graphene dengan serpih lebih besar membentuk palet tebal. Karakterisasi lain dilakukan dengan menggunakan X-ray diffractometer (XRD), Raman Spectrometer dan LCR meter. Dari pengamatan XRD ada pola amorf pada tahap pertama sintesis, setelah pirolisis pada 1000 °C selama 2 jam puncak dekat $2\theta = 24^{o}$, 42^{o} dan 52^{o} yang sesuai dengan indeks kristal (002), (400) dan (511) menjadi terlihat. Puncaknya sekitar 1350 cm^{-1} di Raman adalah D band. D band direpresentasikan sebagai cacat, seperti gangguan pada ikatan sp2 karena cincin segi tujuh dan segi lima, kekosongan, efek tepi, dan lain-lain. Konduktivitas DC atau konduktivitas listrik massal sekitar $4,6 \times 10^{-3}$ Scm^{-1}.

Kata kunci: *Hidrotermal, Pirolisis, Sabut kelapa, Anoda, Baterai, Li-ion*

INTRODUCTION

Although graphene structure has been known since the 1960s, it was not possible to isolate such a monolayer until a few years ago. The feat was first achieved in 2004 by Andre Geim and Konstantin Novoselov, who used adhesive tape to peel thin layers off a graphite crystal [1]. Since then, this new nanomaterial has been the object of a large interest due to its peculiar and intriguing properties. Large-scale graphene sheet is applicable to electronic devices, whereas small-scale graphene can be used for optical applications such as the saturable absorbers and intensity/phase modulators for lasers [2]. Graphene is a single atomic plane of graphite, which is sufficiently isolated from its environment to be considered free-standing. Atomic planes are of course familiar to everyone as constituents of bulk crystals but one-atom-thick materials such as graphene remained unknown. The basic reason for this is that nature strictly forbids the growth of low-dimensional (D) crystals. Crystal growth implies high temperatures (T) and, therefore, thermal fluctuations that are detrimental for the stability of macroscopic 1D and 2D objects. One can grow flat molecules and nm-sized crystallites, but as their lateral size increases, the phonon density integrated over the 3D space available for thermal vibrations rapidly grows, diverging on a macroscopic scale. This forces 2D crystallites to morph into a variety of stable 3D structures. The impossibility to grow 2D crystals does not actually mean that they cannot be made artificially. With hindsight, this seems trivial. Indeed, one can grow a monolayer inside or on top of another crystal (as an inherent part of a 3D system) and then remove the bulk at sufficiently low T such that thermal fluctuations are unable to break atomic bonds even in macroscopic 2D crystals and mold them into 3D shapes [3]. It has attracted great interest because of its advantageous material properties, including high charge mobility, transparency, mechanical strength and flexibility. Low crystalline quality graphene is already used for several applications, such as composite materials and electrodes for batteries. An ideal graphene sheet consists entirely of sp^2-hybridized carbon atoms [4,5].

There are four main methods to synthesize Graphene. First method is the chemical vapor deposition and epitaxial growth and second method is micromechanical exfoliation of graphite, this is also known as the "Scotch Tape method" or the peel off method, third method is epitaxial growth on electrically insulating surfaces, fourth method is based on creation of colloidal suspensions [6]. However, chemical reduction of graphite oxide colloidal suspensions has been considered as an effective route to synthesize graphene sheets due to its simplicity, reliability, ability for large-scale production and exceptionally low price [7,8].

There is increasing strong interest in new energy storage technologies to meet the future challenges of high-efficiency energy storage systems. Among the energy storage systems, electrochemical capacitors (ECs) and lithium-ion batteries (LIBs) are currently considered to be the most promising energy storage devices [9]. Of many different kinds of ECs, electric double-layer capacitors (EDLCs) using carbon-based active materials, are the most common devices at present. Graphene, with extraordinary properties such as high surface area, ultrahigh electrical conductivity and superior mechanical flexibility, has become one of the most appealing conductive carbon matrices for nanostructured hybrids as electrodes [10,11].

Its large surface to mass ratio (SSA) of graphene exceeding 2600 m^2g^{-1}, high electrical conductivity (σ), high mechanical strength, with the added value of mass production, is a promising material for electrodes in Li-ion batteries. While single layer graphene (SLG), grown *via* chemical vapor deposition (CVD), has a limited capability of up taking Li ions (5% surface coverage) due to repulsion forces between Li^+ at both sides of the graphene layer, large efforts have been devoted to the exploitation of chemically modified graphene (CMG) such as graphene oxide (GO) and reduced GO (RGO), both at the anode and cathode [12,13]. However, although CMG can be produced in large quantities, they suffer from limited σ and diffusion of Li ions. To date, the best anodes with CMG have reached specific capacity of ~1200 $mAhg^{-1}$ at 100 mAg^{-1} current rate in half cell and ~100 $mAhg^{-1}$ at 29 mAg^{-1} current rate when assembled in full battery [14-16].

Numerous studies have been found in litterateurs to use graphene as filler in the $LiFePO_4$ as cathode material to increase its conductivity. In this paper we report graphene synthesis that can be made as anode materials for Li-ion battery system.

EXPERIMENTAL METHODS

Materials

The experiment was carried out by using materials of Coconut fiber ash, other materials and solvents were of analytical grade, commercially available and used without further purification.

Methodology

Synthesis of graphene from coconut fibers was conducted in two stages. The first stage is the heating of the powder of coconut fiber passes in 325 meshes at a temperature of 200 °C for 4 hours. Further, pyrolysis was carried out at 1000 ° C for 2 hours with a nitrogen atmosphere. Grain size and surface morphology of graphene observed using SEM with 1000X magnification. The crystal structure of graphene characterized by means of X-ray diffraction. The presence of graphene was investigated using Raman Spectrometer. The conductivity of graphene measured using LCR meter.

RESULT AND DISCUSSION

Graphene, a two-dimensional honeycomb lattice formed by a flat monolayer of hexagonally arrayed sp^2-bonded carbon atoms, is the basal building block in all graphitic materials [17]. A scanning electron microscope (SEM) image of resulting product of the first stage synthesis shows flakes like structures in Figure 1.

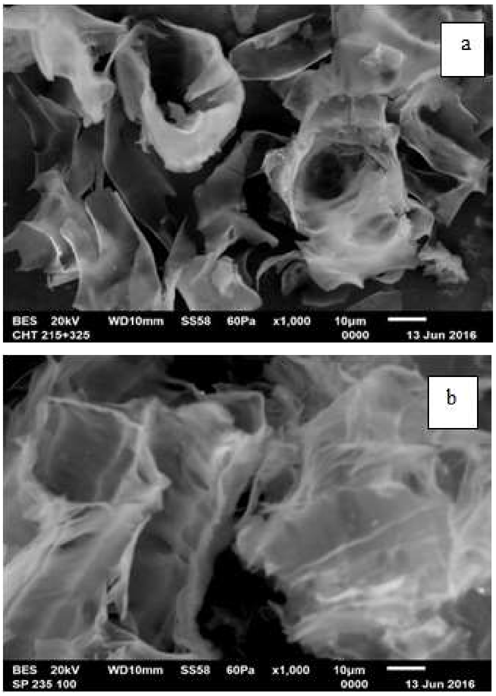

Figure 1. The morphologies of resulting product of the first stage graphene synthesis (a) and second stage graphene synthesis (b) investigated using SEM in the magnification of 1000X.

The SEM images displays a flakes as the materials was well-exfoliated (Figure 1). The majority of the flakes were only a few layers thick and several tens of micrometers in diameter. Figure 1(a) shows an individual flake, elongated in the C axis which is 20 µm in diameter. After further treatment graphite flakes were became worm-like and twisted (Figure 1b), but also formed lot of porous structure. The largest flake in Figure 1(b) is 60 µm in diameter. The appearance of bright edges and smooth stages across the area arises from the presence of oxygenated functional groups [1]. The SEM image shows the pattern of several thick layers build mutual three-dimensional, form a flake structure.

Observations also showing stacks of graphene structure with more big flakes forming a thick pallet. Also, its layers are transparent and very thin. It could be confirmed that mild oxidants and a hydrothermal treatment contributed to the expansion of the graphite flakes and helped to peel them into the thin graphene-like nanosheets. The SEM images of the sample display a wrinkled paper-like structure of the ultrathin graphene sheets and stacking of sheets. The partial overlapping or coalescing of flexible graphene sheets resulted in the formation of physical cross-linking sites of the framework of the graphene. Thus, the inherent flexibility of graphene sheets is a crucial property for constructing the 3D macrostructures.

In Figure 2 there is an amorphous pattern at the first stage of synthesis, after pyrolysis at 1000^{o} C for 2 hour a peak near $2\theta = 24^{o}$, 42^{o} and 52^{o} which corresponds to crystal indexes (002), (400) and (511) became visible. This indicates the presence of oxygen functionalities. According to the XRD patterns, mainly hexagonal structure (2H) existed in graphite with a little rhombohedral structure (3R) and did not change after expansion. At the base of XRD analysis the 002 distance was enlarged slightly due to intercalate reaction but still kept the planar stacking structure. The pattern of the sample contains very broad reflections at 24° (corresponding to d spacings of 0.37), indicating restacking to form an ordered graphite-like material. These results suggest the existence of π-π stacking between graphene sheets and also the presence of residual oxygenated functional groups on reduced GO sheets [18].

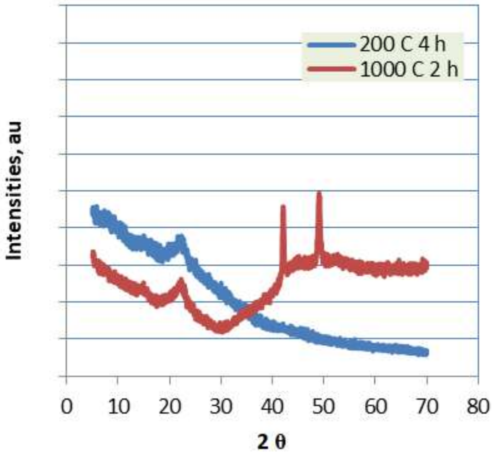

Figure 2. XRD pattern from graphene result of synthesis route.

Raman spectroscopy is a powerful non destructive tool to characterize carbon materials, particularly for distinguishing ordered and disordered crystal structures of carbon. The oxidation leads to a huge reduction in the size of graphite nanosheets in GO, compared to the size of the na- tural graphite flakes [1]. As the preparation of graphene involves hydrothermal reactions in a solution, it is very likely some redox active sites or defects are activated and remained on it, where the sharp Raman disorder-induced phonon mode (D-band), in Fig. 3 is perhaps the good indication for the presence of defects. Raman spectroscopy was employed to analyze the structural changes during chemical processing from graphene oxide to graphene. After chemical reduction of graphene oxide, the conjugated graphene network (sp^2 carbon) will be reestablished [1].

The D band which has been associated with defects in graphene is rather uniform, except for regions where wrinkles are present and close to few-layer

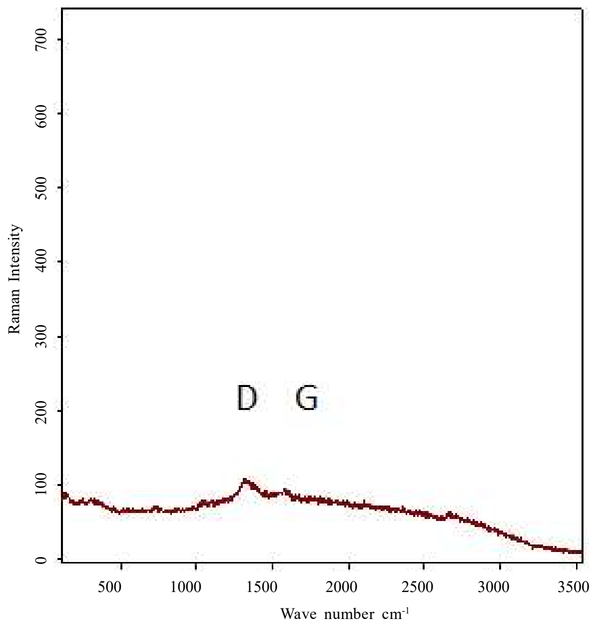

Figure 3. Raman spectra from the marked spots with corresponding the presence of graphene.

regions. The G band is near the background level and the D band clearly show the presence of more than one layer in the flakes. In the wrinkled regions, there are peak height variations in both the G and D bands, and there is a broadening of the D band. From the result, it clearly seen at the Fig. 3 that the sample consists of two dominant peaks at 1350 cm^{-1} and 1590 cm^{-1}. The peak at around 1350 cm^{-1} is the D band. The D band is represented defects, like disruption in the sp^2 bonding because of heptagon and pentagon rings, vacancies, edge effect, and etc. The defect also caused by wrinkle formation and the presence of functional groups [19]. 2D peaks didn't appear in this work. Furthermore, Raman spectroscopy was performed to indicate the structures of graphene by the resulting characteristic G and D bands sensitive to defects and disorder, respectively. An analysis of the intensity showed that the area with the lightest is more than 90 %, and all Raman spectra randomly collected from this area show monolayer graphene.

The log-log scale of conductivity measurement on graphene is shown in Fig. 4. The electrical conductivity of the electrolyte was calculated by equation, $\sigma = \lambda/(RbXA)$ where Rb is the bulk resistance from AC impedance, λ the film thickness and A the surface area of electrode. The DC phenomenon of this conductivity found in low frequency to the high frequency of this measurement. Meanwhile in highest range frequency the conductivity followed AC conductivity phenomenon. In addition to the excellent apparent mechanical strength, the G is electrically conductive with a DC conductivity or bulk electrical conductivity of about 4.6 x 10^{-3} Scm^{-1}, which is also an attractive property for many practical applications [18].

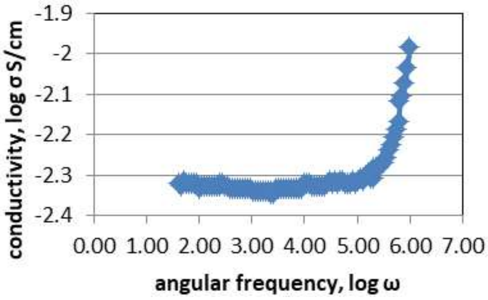

Figure 4. The log-log scale of conductivity measurement on graphene.

This is mainly due to the recovery of conjugated system from GO sheets upon hydrothermal reduction, as confirmed by the X-ray diffraction (XRD) patterns. The complex conductivity follows Jonscher's power law and is varied with angular frequency [20]:

$$\sigma_{ac}(\omega) = \sigma_{dc} + A\omega^{n} \qquad \text{................} \quad (1)$$

where:

σ_{dc} = DC conductivity
A, = The AC conductivity parameter
n = Power law exponent

The conductivity plots were fitted to Jonscher's law equation using a non-linear least squares fitting procedure to extract the conductivity parameters. Fitted values are A=10E-11.062 and n = 1.4555.

CONCLUSION

Synthesis of graphene from coconut fibers conducted in two stages produce large area graphene. This method was carried out with the conversion level of graphite flakes to graphene and shows that graphene is formed. XRD conform its graphene to hexagonal structure. SEM images show an individual flake, elongated in the C axis which is 20 µm in diameter. After further treatment graphite flakes were became worm-like and twisted, but also formed lot of porous structure. The largest flake is 60 µm in diameter. The D band which has been associated with defects in graphene is rather uniform except for regions where wrinkles are present and close to few-layer regions. 2D peaks didn't appear in this work. Furthermore, Raman spectroscopy was performed to indicate the structures of graphene by the resulting characteristic G and D bands sensitive to defects and disorder, respectively. The measurement of DC conductivity was 4.6 x 10^{-3} Scm^{-1}.

ACKNOWLEDGEMENTS

We would like to thanks to Dr. Abu Khalid Rivai, as Lead of BSBM and Prof. DR. Ridwan as Lead of PSTBM BATAN to support the research and writing of this scientific paper.

REFFERENCES

[1]. S. Sheshmani and M. A. Fashapoyeh, "Suitable Chemical Methods for Preparation of Graphene Oxide, Graphene and Surface Functionalized Graphene Nanosheets," pp. 813-825, 2013.

[2]. B. D. Ossonon and D. Bélanger, "Functionalization of graphene sheets by the diazonium chemistry during electrochemical exfoliation of graphite," *Carbon N. Y.*, vol. 111, pp. 83-93, 2017.

[3]. A. K. Geim, " Graphene: Status And Prospects," *Prospects*, vol. 324, pp. 1-8, 2009.

[4]. B. Ankamwar and F. Surti, "Water Soluble Graphene Synthesis," *Chem. Sci. Trans.*, vol. 1, no. 3, pp. 500-507, 2012.

[5]. K. Dissanayake, W. R. de Silva, A. Kumarasingha, and K. N. de Silva, "Synthesis of Graphene and Graphene Oxide Based Nanocomposites," in *SAITM Research Symposium on Engineering Advancements 2014*, 2014, vol. 2014, pp. 75-78.

[6]. C. Xiu-Yun, "Graphene-like nanosheets synthesized by natural flaky graphite in Shandong, China," *Int. Nano Lett.*, vol. 3, pp. 6-10, 2013.

[7]. B. Huang *et al.*, "A free-standing electrochemical sensor based on graphene foam-carbon nanotube composite coupled with gold nanoparticles and its sensing application for electrochemical determination of dopamine and uric acid," *J. Electroanal. Chem.*, vol. 801, no. May, pp. 129-134, 2017.

[8]. J. Zhu, R. Duan, S. Zhang, N. Jiang, Y. Zhang, and J. Zhu, "The application of graphene in lithium ion battery electrode materials.," *Springerplus*, vol. 3, no. 1, p. 585, 2014.

[9]. K. Leng *et al.*, "Graphene-based Li-ion hybrid supercapacitors with ultrahigh performance," *Nano Res.*, vol. 6, no. 8, pp. 581-592, 2013.

[10] B. Lung-Hao Hu, F.-Y. Wu, C.-T. Lin, A. N. Khlobystov, and L.-J. Li, "Graphene-modified LiFePO4 cathode for lithium ion battery beyond theoretical capacity," *Nat. Commun.*, vol. 4, 2013.

[11] X. Li *et al.*, "Large-Area Synthesis of High-Quality and Uniform Graphene Films on Copper Foils," *Science (80-.).*, vol. 324, no. 5932, pp. 1312–1314, Jun. 2009.

[12] Y. Long, Y. Shu, X. Ma, and M. Ye, "In-situ synthesizing superior high-rate LiFePO4/C nanorods embedded in graphene matrix," *Electrochim. Acta*, vol. 117, pp. 105–112, 2014.

[13] Y. Zhang, W. Wang, P. Li, Y. Fu, and X. Ma, "A simple solvothermal route to synthesize graphene-modified LiFePO 4 cathode for high power lithium ion batteries," *J. Power Sources*, 2012.

[14]. J. Hassoun *et al.*, "A lithium-ion battery based on a graphene nanoflakes ink anode and a lithium iron phosphate cathode," Rome.

[15]. H. Xu, J. Chang, J. Sun, and L. Gao, "Graphene-encapsulated LiFePO4 nanoparticles with high electrochemical performance for lithium ion batteries," *Mater. Lett.*, vol. 83, pp. 27–30, 2012.

[16]. J. Mun, H. W. Ha, and W. Choi, "Nano LiFePO4 in reduced graphene oxide framework for efficient high-rate lithium storage," *J. Power Sources*, vol. 251, pp. 386–392, 2014.

[17]. N. Li *et al.*, "Preparation of magnetic CoFe2O4-functionalized graphene sheets via a facile hydrothermal method and their adsorption properties," *J. Solid State Chem.*, vol. 184, no. 4, pp. 953-958, 2011.

[18]. C. L. Yuxi Xu, Kaixuan Sheng and G. Shi, "Self-Assembled Graphene Hydrogel," *ACS Nano*, vol. 4, no. 7, pp. 4324-4330, 2010.

[19]. D. N. Jayanti *et al.*, "Defect and Magnetic Properties of Reduced Graphene Oxide Prepared from Old Coconut Shell Defect and Magnetic Properties of Reduced Graphene Oxide Prepared from Old Coconut Shell," *IOP Conf. Ser. Mater. Sci. Eng.*, vol. 196, 2017.

[20]. H. Jodi, A. Zulfia, Deswita, and E. Kartini, "A Study of The Structural and Electrochemical Properties of Li_3PO_4-MMT-PVDFComposites for Solid Electrolytes," *IJTech*, pp. 1291-1300, 2016.