



## Research paper

# Interconnected open-channel carbon nanosheets derived from pineapple leaf fiber as a sustainable active material for supercapacitors



Jedsada Sodtipinta<sup>a,1</sup>, Chanoknan Ieosakulrat<sup>b,1</sup>, Natchapol Poonyayant<sup>b</sup>, Pinit Kidkhunthod<sup>c</sup>, Narong Chanlek<sup>c</sup>, Taweechai Amornsakchai<sup>b,d</sup>, Pasit Pakawatpanurut<sup>b,d,\*</sup>

<sup>a</sup> Faculty of Applied Science and Engineering and Indo-China Country International Trade and Economic Research Sector, Khon Kaen University, Nong Khai Campus, 112 Chalermprakiet Road, Muang District, Nong Khai 43000, Thailand

<sup>b</sup> Department of Chemistry and Center of Sustainable Energy and Green Materials, Faculty of Science, Mahidol University, 272 Rama 6 Road, Ratchathewi, Bangkok 10400, Thailand

<sup>c</sup> Synchrotron Light Research Institute (Public Organization), 111 University Avenue, Muang, Nakhon Ratchasima 30000, Thailand

<sup>d</sup> Center of Excellence for Innovation in Chemistry, Faculty of Science, Mahidol University, 272 Rama 6 Road, Ratchathewi, Bangkok 10400, Thailand

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## ABSTRACT

The interconnected open-channel carbon nanosheets were prepared from the agro-waste pineapple leaf fiber using a simple hydrothermal technique and KOH chemical activation under heat treatment in Ar atmosphere. The obtained activated carbon showed amorphous structure with porous graphitized carbon nanosheets and a high specific surface area of  $1681 \text{ m}^2 \text{ g}^{-1}$ . When used as an active material for supercapacitor, such natural fiber-derived carbon nanosheets revealed a high electrochemical performance (the specific capacitance was as high as  $202 \text{ F g}^{-1}$  at  $5 \text{ mV s}^{-1}$  in  $1 \text{ M H}_2\text{SO}_4$ ) and a superb cycling stability even after 10,000 cycles of operation. The carbon nanosheets reported herein, therefore, represent a green energy material that combine the benefit of sustainability of an active component and the promise of high-performance energy storage device.

## 1. Introduction

Supercapacitor or electrochemical capacitor is a promising high-power electrochemical energy storage device. The underlying mechanisms for the high-power characteristic include an efficient charge accumulation that takes place via either Faradaic or non-Faradaic process (Conway, 1999; Simon and Gogotsi, 2008; Zhang and Zhao, 2009). The charge transfer-based supercapacitor, so called pseudocapacitor, relies on redox reactions of the active materials, such as metal oxides and conducting polymers. On the other hand, the charge accumulation-driven supercapacitor, called electrical double layer capacitor (EDLC), stores energy through the electrostatic adsorption of electrolyte ions on the surface of porous carbon materials. The EDLC has recently gained increasing interest because of its high power density and cycling stability (Zhang and Zhao, 2009). In addition to its advantageous electrochemical properties, the use of carbon materials in EDLC also offers great flexibility in material design; the porous carbon materials (e.g., activated carbon (Balducci et al., 2007), carbon nanotube (Sodtipinta et al., 2013), reduced graphene oxide (Stoller et al., 2008), carbon nanofiber (Chen et al., 2012), templated carbon

(Liu et al., 2008), and starbon materials (White et al., 2009)) have been demonstrated as a favorable active component for supercapacitors due to their low cost, high natural abundance, large surface area, good conductivity, long-term stability, and environmental benignity (Simon and Gogotsi, 2008; Zhang and Zhao, 2009). Among all porous carbon materials, the activated carbon is arguably the most studied and can be prepared from various renewable sources (Zhu et al., 2011). Partly driven by the costly production of graphene, many researchers produced activated carbons and graphene-like materials from biomass or agricultural wastes using hydrothermal or pyrolysis process. For example, Wang and coworkers prepared the supercapacitor electrode from the interconnected carbon nanosheets derived from hemp bast fiber (Wang et al., 2013). They found that the interconnected two-dimensional structure of the carbon nanosheets showed an excellent EDLC behavior with a specific capacitance of  $106 \text{ F g}^{-1}$  at  $10 \text{ A g}^{-1}$  ( $0^\circ \text{C}$ ) in an ionic liquid electrolyte. At different temperatures (20, 60, and  $100^\circ \text{C}$ ) and a current density of  $100 \text{ A g}^{-1}$ , the material showed specific capacitances of 113, 144, and  $142 \text{ F g}^{-1}$ , respectively, with capacitance retention of 72–92% (Wang et al., 2013). Biswal and colleagues also prepared a high-conductivity microporous carbon

\* Corresponding author at: Department of Chemistry, Center of Sustainable Energy and Green Materials, and Center of Excellence for Innovation in Chemistry, Faculty of Science, Mahidol University, 272 Rama 6 Road, Ratchathewi, Bangkok 10400, Thailand.

E-mail addresses: [pasit.pk@gmail.com](mailto:pasit.pk@gmail.com), [pasit.pak@mahidol.ac.th](mailto:pasit.pak@mahidol.ac.th) (P. Pakawatpanurut).

<sup>1</sup> Equal contribution as first authors.

material from neem dead leaves with a specific capacitance of  $400 \text{ F g}^{-1}$  in  $1 \text{ M H}_2\text{SO}_4$  electrolyte solution at a current density of  $0.5 \text{ A g}^{-1}$  (Biswal et al., 2013). Similarly, the ultrahigh carbon content and highly-ordered macroporous carbon material from a small chunk of red cedar wood was reported with a specific capacitance of  $115 \text{ F g}^{-1}$  in dilute nitric acid electrolyte solution (Jiang et al., 2013).

Agro-waste-based material primarily containing cellulose, hemicellulose, and lignin is an attractive bio-feedstock for carbon material production. The natural feedstock not only yields favorable capacitive properties (Biswal et al., 2013; Jiang et al., 2013; Wang et al., 2013), but it also provides a sustainable solution for the production of carbon-based energy devices. Unlike a number of agricultural wastes that have been investigated to date for carbon synthesis, pineapple leaves offer a promising, novel alternative because of their high abundance and sustainable availability; for example, in Thailand, one of the world's largest producers and exporters of pineapples, about 240,000 acres are used for the cultivation of pineapples, which annually leave behind a total of 20,000–25,000 tons per acre of pineapple leaves (Holt, 2011; TPIA, 2014), all of which go unused.

In an attempt of turning an abundantly produced agro-waste into high-value energy devices, we studied the conversion of the pineapple leaves into the activated carbon. The method reported herein involves the preparation of the pineapple leaf fiber (PALF) from the raw material and the subsequent production of the activated carbon via the hydrothermal technique and the chemical activation, along with the heat treatment under argon atmosphere. The chemical and electrochemical characterizations of the obtained activated carbon were conducted in order to investigate the capacitive performance for supercapacitor application.

## 2. Experimental

### 2.1. Preparation of PALF

The harvest of pineapple leaves was performed in Phitsanulok, Thailand, and the preparation method for PALF was explained in detail elsewhere (Kengkhetkit and Amornsakchai, 2012; Kengkhetkit and Amornsakchai, 2014). Briefly, after cleaning the leaves, the fresh pineapple leaves (containing ~85% of water) were cut to 5 mm in length and were then milled with a disc mill that consisted of two 150-mm-diameter circular plates (one rolling and one fixed). The rotating speed was set at ~7700 rpm. The projecting teeth separated the circular plates, and the samples were ground in between the plates. The chopped pineapple leaf was continually milled for about 10 s by feeding it into the hopper of the machine. The dried scrap was ground with a high speed grinder. The rotating grinder (Hao Peng, China) was operated at a speed of 25,000 rpm for 30 s. The resulting product was whole ground leaf that consisted of fibrous and non-fibrous materials. The fibrous component was the PALF, which was separated from the non-fibrous part by using a steel wire mesh number 60.

### 2.2. Preparation of activated carbon from PALF

Carbon materials were prepared from the PALF via hydrothermal and carbonization processes. Briefly, 1.5 g of PALF was immersed in 10% w/v NaOH for 30 min to remove lignin and hemicellulose and was then washed several times in DI water until pH 5.5–6.0. The sample was dried overnight in an oven at 50 °C. The dried PALF was put in 50 mL of 0.5 M  $\text{H}_2\text{SO}_4$  and was then transferred to a 70-mL Teflon-lined stainless steel reactor, which was heated at 180 °C for 24 h. The reactor was later allowed to slowly cool down to room temperature. The obtained product was washed in DI water until pH 5.5–6.0 and was dried overnight at 50 °C. The obtained carbonaceous product, termed “biochar,” was chemically activated by grinding it with potassium hydroxide pellet at 1:3 (biochar:KOH) ratio by mass. Then the mixed sample was carbonized in a tube furnace under argon atmosphere using

a heating rate of  $3 \text{ }^\circ\text{C min}^{-1}$  to achieve the temperature of 800 °C, at which it was maintained for 1 h and was later cooled down gradually to room temperature. After that, the carbon product was immersed in 0.5 M HCl overnight with continuous stirring, after which it was washed in DI water until pH 5.5–6.0. Finally, the carbon product was dried overnight in an oven at 100 °C. The final product, porous carbon nanosheet (CNS), was generated. The obtained black powder product using the activation ratio of 1:3 was called 1–3 CNS. To study the relationship between the degree of KOH activation and other properties (morphology, surface area, and specific capacitance), we also performed an activation at 1:1 ratio of biochar:KOH using the same procedure described above. The obtained product was named 1-1CNS (see the Supplementary Content).

### 2.3. Material characterizations

The crystal structure of activated carbon was investigated using powder X-ray diffractometer (XRD; Bruker) from  $2\theta = 5^\circ$  to  $80^\circ$  using the  $\text{CuK}\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) at 40 kV and 40 mA current. The morphology of activated carbon was studied via field emission scanning electron microscope (FE-SEM; JSM-7001F) equipped with energy dispersive X-ray spectrometry (EDS) and high-resolution transmission electron microscope (HR-TEM; TECHNAI G2 20). Raman spectra of activated carbon were obtained by using Fourier-transform Raman spectrophotometer (FT-Raman; NTEGRA spectra). Elemental analysis was performed on an elemental analyzer (2400 Series II CHNS/O System, PerkinElmer). The porous texture, the Barrett-Joyner-Halenda (BJH) pore size distribution, and the specific surface area according to Brunauer-Emmett-Teller theory ( $S_{\text{BET}}$ ) were carried out at 77 K using  $\text{N}_2$  adsorption analyzer (Autosorp-c1, Quantachrome). The chemical states and compositions were analyzed using X-ray photoelectron spectroscopy (XPS; PHI5000 Versaprobe II, ULVAC-PHI, Japan) at the SUT-NANOTEC-SLRI joint research facility. The spectra were collected using monochromatic Al  $\text{K}\alpha$  radiation source at 1486.6 eV. X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectra of the S K-edge were recorded in the fluorescence mode using 4-element Si-drift detector at the SUT-NANOTEC-SLRI XAS beamline (BL5.2) (electron energy of 1.2 GeV; bending magnet; beam current 80–150 mA;  $1.1\text{--}1.7 \times 10^{11} \text{ photon s}^{-1}$ ) at the Synchrotron Light Research Institute (SLRI), Nakhon Ratchasima, Thailand. For the acquisition of all spectra, a InSb (111) double crystal monochromator with an energy resolution ( $\Delta E/E$ ) of  $2 \times 10^{-4}$  was used. The normalized XANES and EXAFS data were processed and analyzed after background subtraction in the pre-edge and post-edge region using software ATHENA and the EXAFS analysis was performed using software ARTEMIS, both of which are included in an IFEFFIT package (Newville, 2001; Ravel and Newville, 2005).

### 2.4. Electrochemical tests

Working electrodes were fabricated using a sol-gel coating method. Each working electrode consisted of a mixture of 80 wt% activated carbon, 10 wt% carbon black, and 10 wt% polyvinylidene fluoride (PVDF) dissolved in *N*-methylpyrrolidone as a binder. The slurry mixture was coated on a titanium foil (99.7%; Sigma-Aldrich), and the coated foil was then dried at 90 °C for 24 h. The working electrode with a  $1 \times 1 \text{ cm}^2$  active area contained ~1–2 mg of dried slurry. Electrochemical properties of the working electrode were investigated in a 1 M  $\text{H}_2\text{SO}_4$  aqueous solution at room temperature using a three-electrode electrochemical cell, with platinum rod and Ag/AgCl as a counter and a reference electrodes, respectively. The charge-discharge tests and the cyclic voltammetry were performed using a potentiostat/galvanostat at different scan rates (5, 10, 20, 50, and  $100 \text{ mV s}^{-1}$ ) and different current densities (0.2, 0.5, 1, 2, and  $5 \text{ A g}^{-1}$ ). Additionally, the cyclic voltammetry (CV) and the galvanostatic charge-discharge curves were recorded after CV aging of 200 cycles at a scan rate of

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