

Electronic supporting information

Sustainable carbon for energy storage applications: Investigation on chemical refinements of sorghum biomass for tuneability of carbon structure and supercapacitor performance

Rana Arslan Afzal,^a Pratheep K. Annamalai,^{b,c,d} Mike Tebyetekerwa,^a Paulomi (Polly) Burey,^{c,d} John Bell,^e Ashok Kumar Nanjundan,^{c,d*} Darren J. Martin^{a*}*

^a School of Chemical Engineering, The University of Queensland, St Lucia, Queensland 4072, Australia

^b School of Agriculture and Food Sustainability, The University of Queensland, St Lucia, Queensland 4072, Australia

^c Centre for Future Materials, University of Southern Queensland, Toowoomba, Queensland 4350, Australia

^d School of Agriculture and Environmental Sciences, University of Southern Queensland, Springfield, Queensland 4300, Australia

^e School of Engineering, University of Southern Queensland, Springfield, Queensland 4300, Australia

^f Deputy Vice-Chancellor's Office (Research & Innovation), University of Southern Queensland, Springfield, Queensland 4300, Australia

*** Corresponding authors**

Darren J. Martin – E-mail: darren.martin@uq.edu.au

Pratheep K. Annamalai – E-mail: pratheep.annamalai@unisq.edu.au

Ashok Kumar Nanjundan- E-mail: ashok.nanjundan@unisq.edu.au

Experimental

Materials

The seeds used to cultivate the SugargrazeTM variety of sorghum were supplied by the Queensland Department of Agriculture and Fisheries (DAF). Sodium hydroxide (NaOH, pellets, 98% purity) was acquired from Chem Supply. Sodium chlorite (NaClO₂, flakes, 80% purity) and acetic acid (CH₃COOH, glacial liquid, >99% purity) were obtained from Sigma-Aldrich Australia. The experiment used water filtered by reverse osmosis (RO). Commercial activated carbon was obtained from Activated Carbon Technologies Pty Ltd.

Precursor preparation

The sorghum (SugargrazeTM) biomass was harvested from the University of Queensland's research facility at the Gatton campus after 90 days of seeding. Manual screening and separation were conducted, and only the upper stem (greater than 1 metre above ground) was included in this study due to its unique features (30% plant section percentage and higher carbon content) [1]. The sample was water-washed, dried, and processed into a powder [1]. These water-washed dry powder sorghum samples were subjected to chemical treatments.

The alkaline treatments were performed as reported in our previous publication [2]. First, a slurry of sorghum biomass with a biomass-to-water ratio of 1:20 was created and continuously stirred overnight at 50 °C. Next, that slurry was treated with 2 or 10 wt./vol. Sodium hydroxide (NaOH) concentrations for 2 hours with continuous stirring while maintaining the temperature at 80 °C. After a 2-hour treatment, the alkali-treated pulp was moved to a 53-mesh screen (lab scale) and washed with hot water to remove dissolved material until the effluent became neutral. After 2 and 10% w/v NaOH treatments, the obtained pulp is presented as 2DL and 10DL, respectively.

Furthermore, the 2DL sample was bleached following a protocol reported earlier [3, 4]. The 2DL pulp was diluted with water to achieve a solids-to-liquids ratio of 1:30. One hour was spent bleaching with a 0.8% (w/v) NaClO₂ solution at 70°C and a pH of 4 (the pH was adjusted with glacial acetic acid). The material was rinsed with hot water on a 53-mesh screen after the dissolved material was removed, and the process was repeated until the effluent became neutral. This bleaching procedure was done twice to eliminate all dissolved and residual lignin. 2DL+BL denotes the sample produced according to this method. All these samples were freeze-dried using a laboratory freeze dryer (Alpha 1-2 LD plus freeze dryer). The chemically refined freeze-dried sorghum samples were carbonised under the conditions reported earlier to produce hard carbon with good porosity and surface area for energy storage applications [1, 5,

6]. Briefly, the biomass precursor samples were carbonised in a CARBOLITE[®] ceramic tube furnace at 1000°C in a nitrogen atmosphere. Carbonisation required an initial stabilisation by heating to 240°C at a rate of 5°C/min and holding for 2 h, followed by a step up to a carbonisation temperature of 1000°C at the same rate and growth time. The carbonised samples are referred to as 2DL-C and 10DL-C.

Carbon activation was performed as reported elsewhere [7]. 10DL-C was further activated by KOH. 2DL-C was mixed with KOH in a 1:1 ratio for 10h. The material was dried at 80°C and collected for pyrolysis. As-collected KOH adsorbed 10DL-C sample was pyrolysed at 800°C for 3 h at 2°C min⁻¹ heating rate to obtain 10DL-C activated carbon (10DL-AC). The obtained 10DL-AC sample was washed several times with 0.1 M HCl and deionised water and dried at 80°C.

Materials characterisation

The lignocellulosic composition of freeze-dried samples was analysed by a near-infrared spectroscopy (NIRS) method at Celignis Biomass Analysis Laboratories, Limerick (Ireland). Thermal analysis was performed using a thermogravimetric analyser (TGA STARe System, Mettler Toledo). Bruker D8 Advance X-ray diffractometer (Bruker, Germany) was used to perform X-ray diffraction (XRD) analysis. The samples were characterised using a scanning electron microscope (JEOL-7100F) and a high-resolution transmission electron microscope (Hitachi HT7700). ImageJ was used to analyse SEM and TEM images. The surface composition was evaluated using X-ray Photoelectron Spectrometry (XPS) using a Kratos Axis ULTRA X-ray Photoelectron Spectrometer equipped with a 165 mm hemispherical electron energy analyser. Atomic concentrations were calculated using the CasaXPS version 2.3.14 software and a Shirley baseline with Kratos library Relative Sensitivity Factors. Raman spectra were acquired using a Renishaw Raman microscope with a laser wavelength of 514 nm. The Micromeritics[®] Instrument Corporation TriStar II was used to measure carbon samples' porosity and specific surface area.

Electrochemical measurements

Nickel foam (Ni-F) was used as a substrate and current collector for electrochemical measurements. The electrode slurry was applied to the Ni-F substrate and dried in a vacuum overnight at 110°C. A three-electrode cell was used, with Ni foam coated with hard carbon as the working electrode, Hg/HgO as the reference electrode, and Pt wire as the counter electrode with 6 M KOH as the electrolyte. Electrochemical analysis was conducted on a CH Instruments electrochemical workstation. Cyclic voltammetry (CV) was measured at a potential window

between -1.0 and 0.0 V at various scan rates, and galvanostatic charge-discharge (GCD) was measured at different current densities. Electrical impedance spectroscopy (EIS) tests were done with frequencies from 100 kHz to 0.01 Hz and an amplitude of 10 mV. The cyclability was evaluated by doing 5,000 GCD cycles at 5 Ag⁻¹ consecutively. The specific capacitance (Fg⁻¹) values were calculated from the GCD by using the following expression:

$$C_s = \frac{I \times \Delta t}{m \times \Delta V}$$

where C_s is specific capacitance (F g⁻¹), I/m (A g⁻¹) is current density, Δt (s) is the discharging time, and ΔV (V) is the maximum potential window to discharge the cell.

Supporting Results

1. X-ray and Raman spectral analysis of carbonised samples

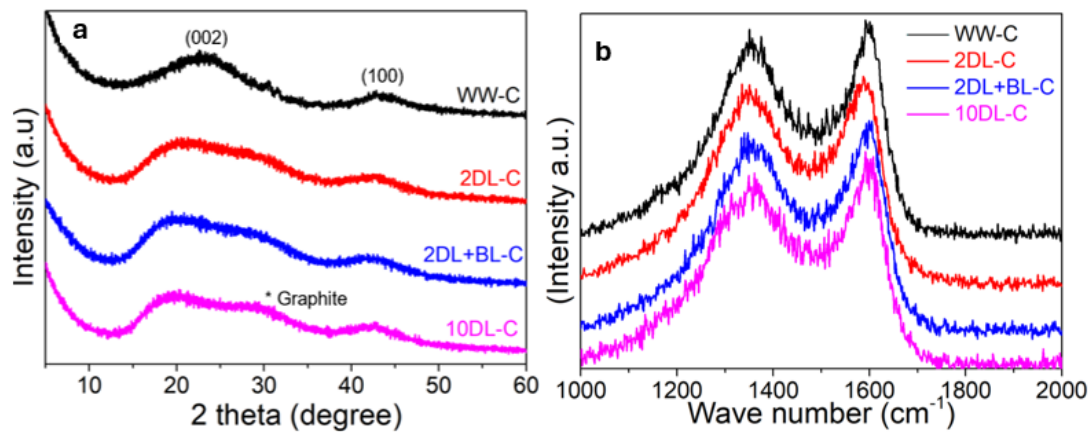


Figure S1: (a) XRD, and (b) Raman spectra of WW and chemically refined sorghum derived carbon samples

2. XPS analysis

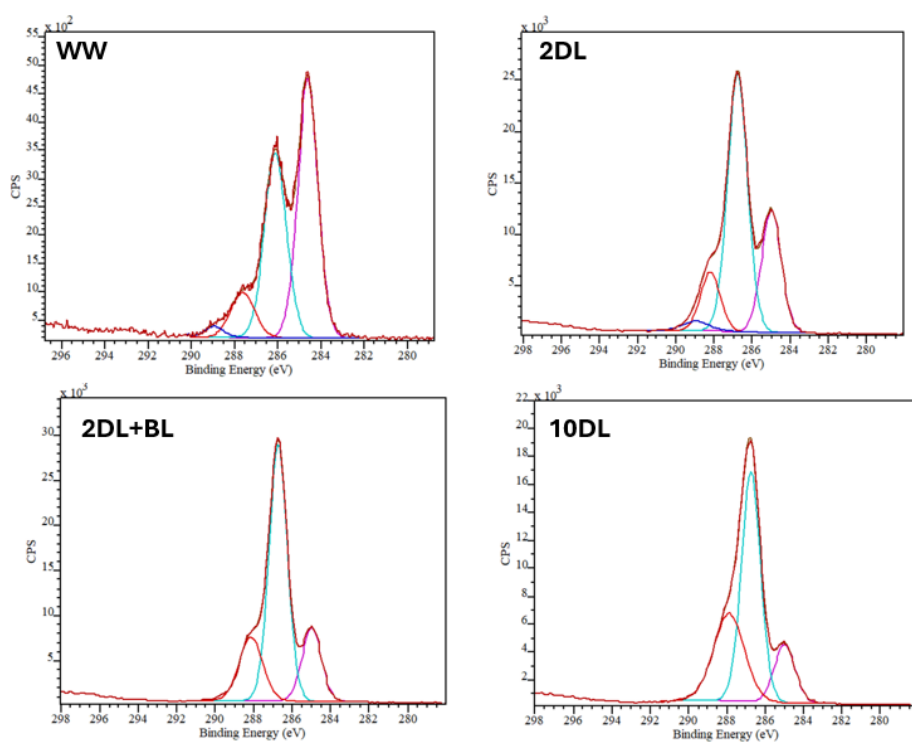


Figure S2: The deconvolution of the XPS peaks for different biomass samples

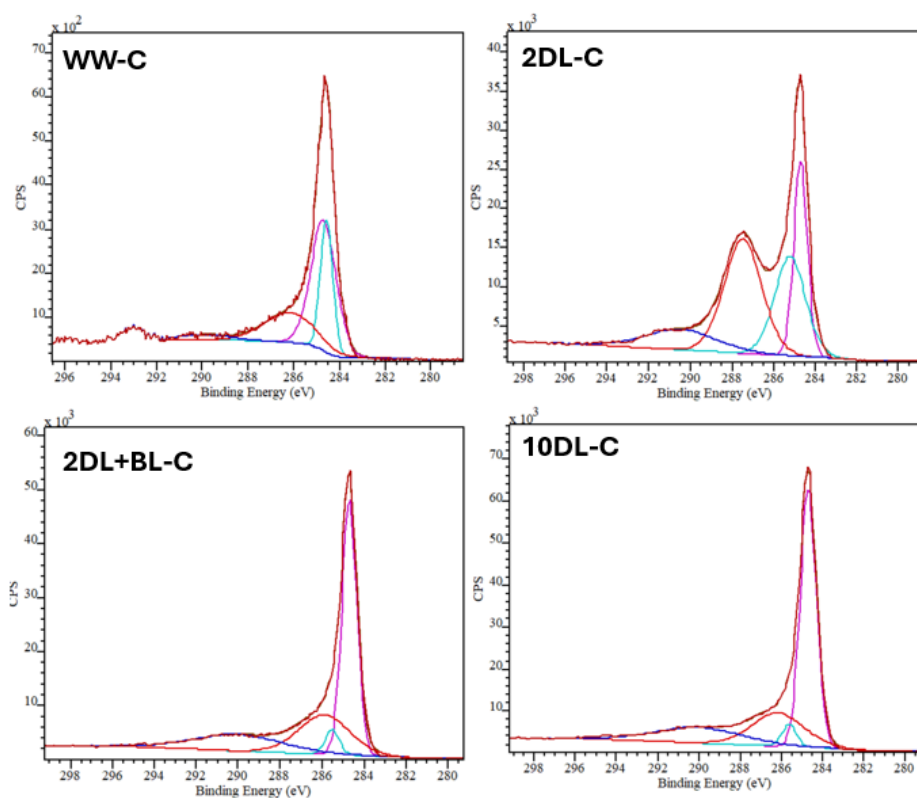


Figure S3: The deconvolution of the XPS peaks for different biomass derived carbon samples

3. Surface area and porosity analysis

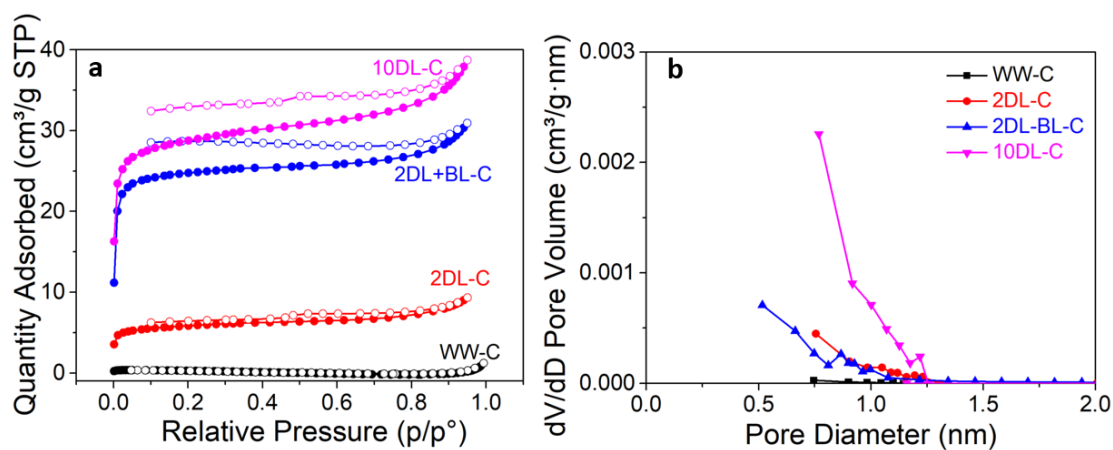


Figure S4: (a) N_2 adsorption/desorption isotherm and (a) Pore size distribution of carbonised samples.

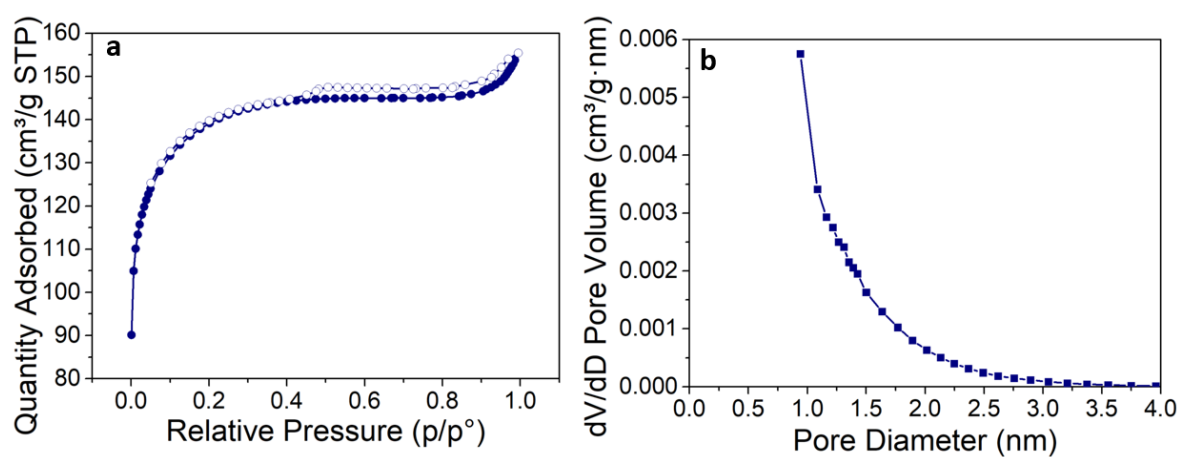


Figure S5: (a) N_2 adsorption/desorption and (a) Pore size distribution of 10DL-AC.

References:

1. Afzal, R.A., et al., *Lignocellulosic plant cell wall variation influences the structure and properties of hard carbon derived from sorghum biomass*. Carbon Trends, 2022. **7**: p. 100168.
2. Hosseinmardi, A., et al., *Facile Tuning of the Surface Energy of Cellulose Nanofibers for Nanocomposite Reinforcement*. ACS Omega, 2018. **3**(11): p. 15933-15942.
3. Hosseinmardi, A., et al., *Reinforcement of natural rubber latex using lignocellulosic nanofibers isolated from spinifex grass*. Nanoscale, 2017. **9**(27): p. 9510-9519.
4. Amiralian, N., et al., *Easily deconstructed, high aspect ratio cellulose nanofibres from Triodia pungens; an abundant grass of Australia's arid zone*. RSC Advances, 2015. **5**(41): p. 32124-32132.
5. Gaddam, R.R., et al., *Spinifex nanocellulose derived hard carbon anodes for high-performance sodium-ion batteries*. Sustainable Energy & Fuels, 2017. **1**(5): p. 1090-1097.
6. Nanjundan, A.K., et al., *Potassium-Ion Storage in Cellulose-Derived Hard Carbon: The Role of Functional Groups*. Batteries & Supercaps, 2020. **3**(9): p. 953-960.
7. Kim, M., et al., *Sorghum biomass-derived porous carbon electrodes for capacitive deionization and energy storage*. Microporous and Mesoporous Materials, 2021. **312**: p. 110757.