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Nontoxic Approach to Porous Carbon Activation from Cassava Peels Using Sodium Thiosulphate for Supercapacitor Applications

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Authors' contributions

This work was carried out in collaboration among all authors. Author TEA conceptualized the idea for the study and performed the data collection and analysis. He is the lead author and wrote the first draft of the manuscript. Authors JAA and OEA contributed materials, proof reading of manuscript and result analysis. All authors read and approved the final manuscript.

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ABSTRACT

Abundantly available cassava peels waste was used to prepare porous activated carbon using a nontoxic activating agent, sodium thiosulphate ($Na_2S_2O_3$). The activation was done under nitrogen flow at 800^0C. The resulting porous carbon showed good surface area of 306 m^2g^{-1}. The supercapacitor electrodes fabricated from the activated carbon exhibited excellent electrochemical characteristics; showing a specific capacitance of 93.4 Fg^{-1} while withstanding excellent performance even up to a voltage window of 1.1V.

Keywords: Supercapacitors; cassava peels; activated carbon; specific capacitance; charge storage; porous carbon.

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1. INTRODUCTION

Global energy demand is expected to increase by over eighty percent in a couple of decades [1], and this is not farfetched as the demand for energy consumption is on a steady rise. The role energy plays in economic development, quality of life and its impact on social wellbeing worldwide cannot be overemphasized. However, conventional sources of energy such as fossil fuels are no longer sustainable as continuous exploration has led to lasting damage to the ecosystem and extinction of wildlife and a left a negative change on the climate [2]. These challenges posed by existing energy sources opened the door for research into more sustainable and renewable sources of energy [3]. Renewable energy sources have been widely researched in literature; yet global adoption still poses challenges due to cost, availability of materials and storage. The advent of electric vehicles and new generation mobile electronic devices has led to the rise in demand for energy storage systems. Batteries have for a long time been the major source of energy storage but with a limitation of poor power density, its ability to keep with the trend of development is challenged and this has led to more interest in supercapacitors which provides high power density [4]. Supercapacitors (SCs) also offer long cycle life, and better chemical stability compared to commercially available batteries [5].

Supercapacitors, which are divided into two major categories; electrochemical double layer capacitor (EDLC) and pseudocapacitors, unlike the conventional capacitors, are able to store very large amounts of energy [6]. In EDLCs for instance, energy is stored in the electrode/electrolyte interface of the device and the storage capacity depends largely on the interfacing materials from the electrodes and the electrolyte [7]. Porous carbon materials are by far the most commonly used electrode material in EDLCs and this is as a result of its adequate pore size distribution and large surface area which are needed properties for effective charge storage [8]. These materials which can be easily utilized in the form of activated carbon, can be produced from biomass, petroleum by-products, organic compounds or even polymers. Activated carbon (AC) can be synthesized using two known methods; (1) physical activation, which involves a solid-gas interaction where a carbonized material interfaces with a steam, air or carbon dioxide (CO_2) and (2) chemical activation, involving a solid-solid interaction between a carbon precursor and an activating agent which could be an alkali carbonate/hydroxide, zinc chloride or phosphoric acid [9]. The porosity of carbon materials activated by physical method is almost exclusively made up of micropores which are less than 2 nm, but when chemical activation is used for synthesis, larger surface area and a porosity which is made up of micropores and mesopores is achieved which enhances energy storage [10].

Among several activating agents used in the synthesis of activated carbon, potassium hydroxide (KOH) has enjoyed a wider adoption as several researchers have reported in literature. Several carbon materials have been activated with KOH activation especially for EDLC applications; jute [11], distiller's grain [12], corncob [5], pomelo peel [13], rosewood [14], pine cone [15], banana fibre [16]. Despite the growing interest in utilization of KOH as a preferred choice of activating agent, its industrial and large scale adoption is still hampered due to economic and environmental concerns being raised due to its corrosive nature [8] and a result more environmentally friendly options are explored.

In this study, the synthesis procedure of achieving porous carbon based on the utilization of a non-corrosive and harmless inorganic salt, sodium thiosulphate ($Na_2SO_2O_3$) as an activating agent is presented. Also we present cassava peel as the starting material for production of activated carbon which leads to an all-round green route to AC production for application in the development of ELDC electrodes.

2. MATERIALS AND METHODS

2.1 Synthesis of Activated Carbon (AC) from Cassava Peels

Cassava peels was gotten from cassava harvested by indigenous farmers in the suburb of Abuja, Nigeria. The peels (samples) were washed repeatedly until all forms of dirt were removed. The washed samples were then dried in a thermofisher oven for 12 hours at 60^0C. A 3g measurement of the sample and 4g of $Na_2S_2O_3$ was poured into a laboratory mortar and stirred to form a uniform mixture. Using a carbolite tubular furnace, the mixture was carbonized at 750^0C under Nitrogen gas (N_2) flow at a 5^0C/min ramp rate. The carbonization process under N_2 flow was left to run for 1 hr., after which the

carbonized sample was allowed to cool off to room temperature. Distilled water was then used to consistently wash the carbonized material until a neutral pH was achieved. The washed samples were further oven-dried for 24hrs at 80^0C.

2.2 Electrode Fabrication

Graphite foil (GF) was used as current collectors in fabricating the device electrodes. In a procedure previously reported [4] a paste made of the synthesized carbon as the active material by adding carbon additive, and polyvinylidene fluoride binder in a ratio of 8:1:1 by mass with three (3) drops of 1-methyl-2-pyrolidinone (NMP) which was then coated on the GFs using Dr Blade's method [17]. The electrodes were then dried at 70^0C under vacuum.

2.3 Electrochemical Measurements

Setting up the device in a two-electrode test configuration, a BIO-LOGIC 805 potentiostat was used to perform electrochemical tests. The two-electrode setup was used since it offers a simpler setup and since the device is a symmetric device, a half cell measurement (which can be achieved in a three-electrode setup) will not be of much significance in measuring the device voltage [18]. Measurements carried out include cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) and electrochemical impedance spectroscopy (EIS).

3. RESULTS AND DISCUSSION

3.1 Physico-Chemical Analysis

XRD analysis is as presented in Fig. 1. Although in an ideal amorphous carbon, wide diffraction peaks are noticed at 2 theta around 25^0 and 44^0 [19], however, the sample showed only the first peak which is noticed around 30^0 while the peak expected around 43^0 to 52^0 is not visible and can be attributed to high ratio of impurities in the sample [20].

The Raman spectra representation is as presented in Fig. 2 for the activated sample. The material displayed obvious D and G bands at 1345cm^{-1} and 1590 cm^{-1} respectively. These peaks represent the vibrational modes of sp^2 carbon materials [21,22]. The G-band which represents the graphitic phase of carbon is as a result of the in-plane vibration of the C-C bond in the carbon material while the D-band peak arises due to resonance effect of the sp^2 rings and represents the diamond phase [23].

An interconnected and porous morphology of the carbon material is as seen in the SEM micrograph presented in Fig. 3. The irregular nature of the micrographs could be as a result of volatile organic materials within the sample [24].

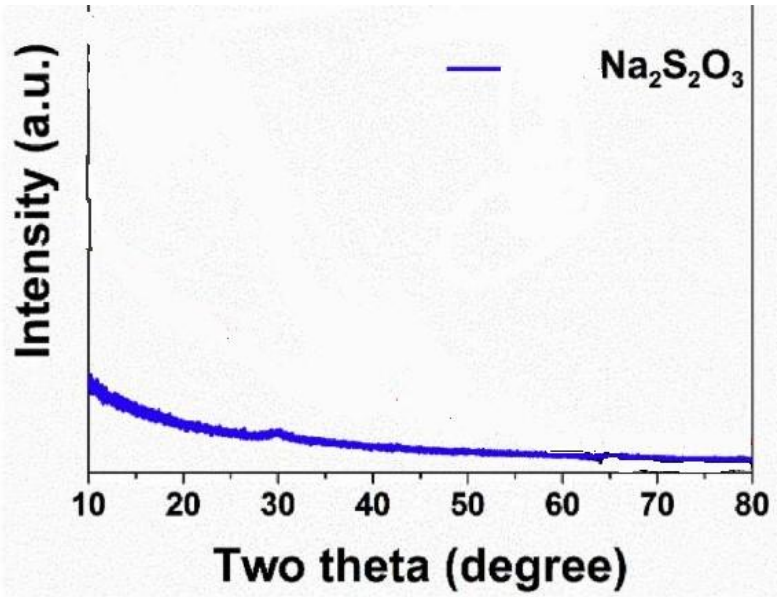

Fig. 1. XRD of activated carbon sample

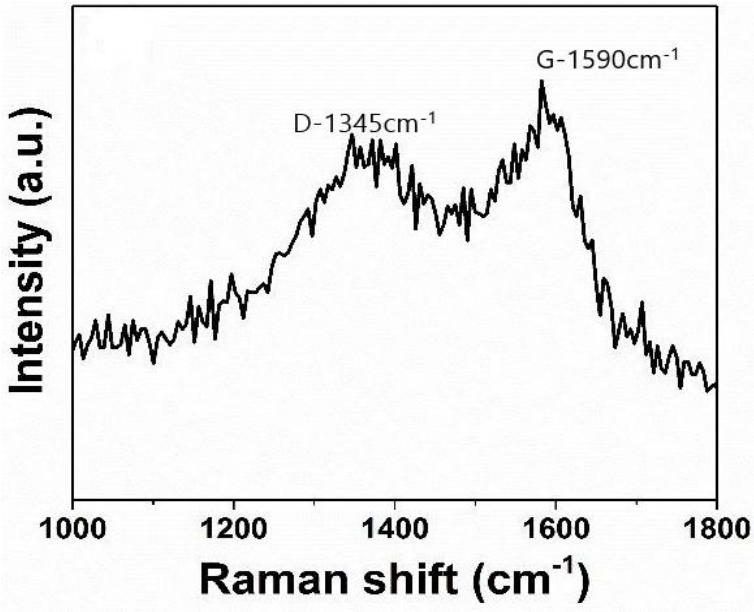

Fig. 2. Raman spectrum of the produced carbon material

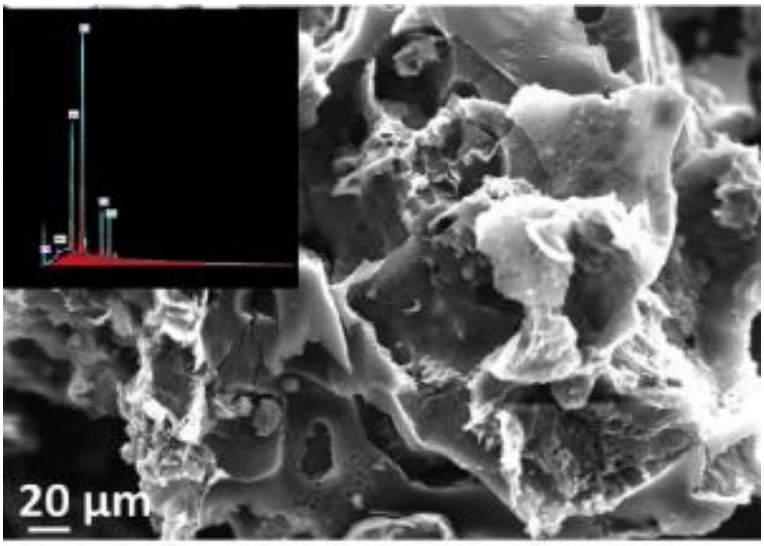

Fig. 3. SEM micrograph of the produced activated carbon with figure inset showing the EDX pattern of elemental composition

The porosity and surface area studies where carried out using nitrogen (N_2) adsorption-desorption analysis and the achieved result presented (Fig. 4.). The pore size distribution is as shown in the inset to the figure. The isotherms are shaped in a manner that suggests the presence of predominant micropores and good pore connectivity is reflected by the reversibility seen in the hysteris loop. The adsorption-desorption curve shows a sharp rise at low pressure with a hysteresis loop formation at P/P_0= 0.45.

The samples however, showed a small amount of absorbed gas which could be as a result of other competing constituents like sulphur [4] which might not have gotten complete combustion during activation.

The sample exhibits good pore characteristics which indicate the presence of micropores capable of adequate charge storage. Using the BET model [25], a specific surface area (SSA) of 306m^2g^{-1} was achieved. These results are as presented in Table 1. Results obtained were

compared to other biomass reported in literature (see Table 2).

3.2 Electrochemical Analysis

In other to ascertain the capability of the carbonized material to store charge, electrochemical analysis was done by characterizing the fabricated electrode in a 6M KOH electrolyte. The results thus obtained are presented in Figs. 5-7. An ideal near rectangular shape is maintained in Fig. 5 for the CV analysis at scan rates from $5mVs^{-1}$ to $100mVs^{-1}$. The fabricated cell could withstand upto 1.1V and shows a deviation from the near rectangular shape as the scan rate increases.

Constant current measurement (GCD) was done to confirm further electrochemical behavior of the electrode. The results show almost symmetric triangular curves (see Fig. 6.) at varying specific currents. The curves indicate good electrochemical reversibility of the device, which confirms an ELDC characteristic. From the GCD curves, specific capacitance of the electrodes is estimated using equation 1

$$C_{SP} = I\Delta t/m\Delta U \quad (1)$$

where ΔU is the voltage, I is the specific current (A), at specified sweep rates (mVs^{-1}), m is the mass of the material, Δt is the discharge time [26].

At $0.5Ag^{-1}$, the C_{sp} based on equation (1) was estimated to be $80Fg^{-1}$ which is a very competitive value with some reported carbon materials derived from biomass based materials which unlike $Na_2S_2O_3$ are even toxic to the environment. Table 2 is shows a summary of literature already reported in comparison with results obtained in this work. This excellent result can be attributed to extended potential window beyond 1.0V, high micropore volume, responsible for adequate ion-trapping from the electrolyte and a fair SSA of the material.

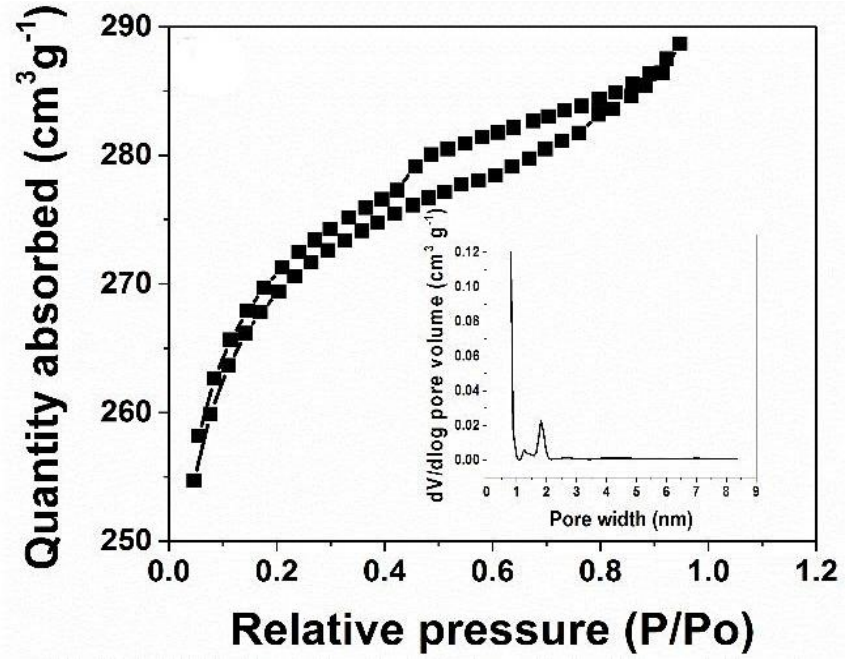

Fig. 4. Gas adsorption/desorption isotherms of $Na_2S_2O_3$ activated carbon. Inset to the figure shows the BJH pore size distribution

Table 1. Surface area (BET) and textural data obtained after activation at 800^0C

Sample	BET(m^2g^{-1})	Micropore volume (cm^3g^{-1})	Pore Diameter
$Na_2S_2O_3$ activated cassava peel	306	0.4017	2.64

Electrical conductivity of the electrode was further studied by the Electrochemical Impedance spectroscopy (EIS) analysis at a frequency range of 0.01Hz to 100kHz at a potential of 5mV amplitude. The semicircle as seen in the Nyquist plot (see Fig. 7) in the high frequency region indicates non-uniformity in the current distribution while the vertical line seen at the low-frequency region indicates an almost ideal capacitive characteristic exhibited by carbon-based materials previously reported [27,28].

Table 2. Comparison of obtained results with different materials

Source of electrode material	Activating agent	BET(m^2g^{-1})	Electrolyte used	Potential (V)	Specific capacitance (Fg^{-1})
Durian Shell	KOH	-	1M Na_2SO_4	1.00	93.1 [29]
Banana Fibres	$ZnCl_2$	1097	1M Na_2SO_4	1.00	74.0 [16]
Pomelo peel	KOH	2105	1M Na_2NO_3	1.70	43.5 [30]
Rubber seed-shell	KOH	620	6M KOH	-	63.2 [31]
Cassava peels	$Na_2S_2O_3$	306	6M KOH	1.1	94.3 – This work

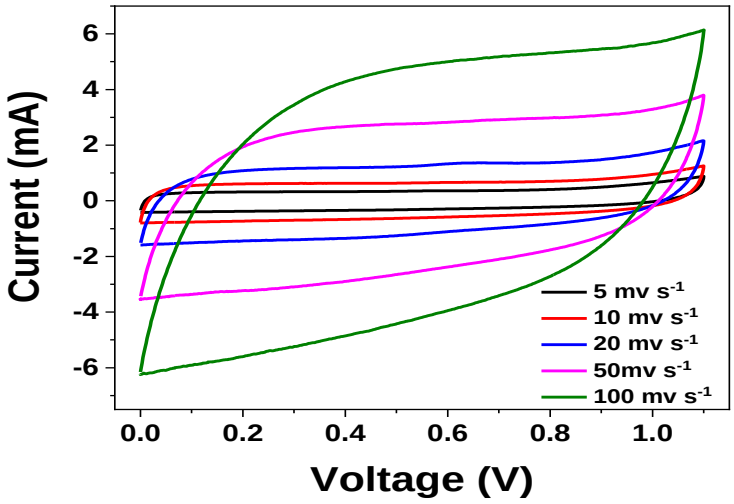

Fig. 5. Cyclic voltametry (CV) of $Na_2S_2O_3$ activated cassava peel with 5 mvs^{-1} to 100 mvs^{-1} scan rates

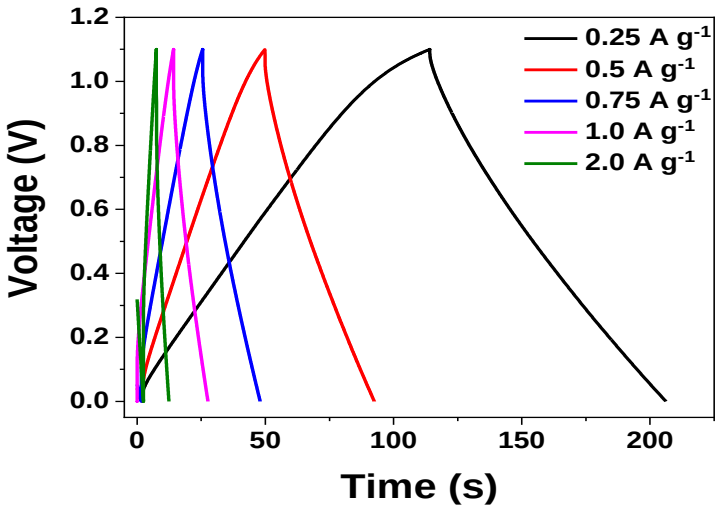

Fig. 6. Galvanostatic charge discharge (GCD) of $Na_2S_2O_3$ activated cassava peel at 0.5Ag^{-1} to 2.0Ag^{-1} specific current rates

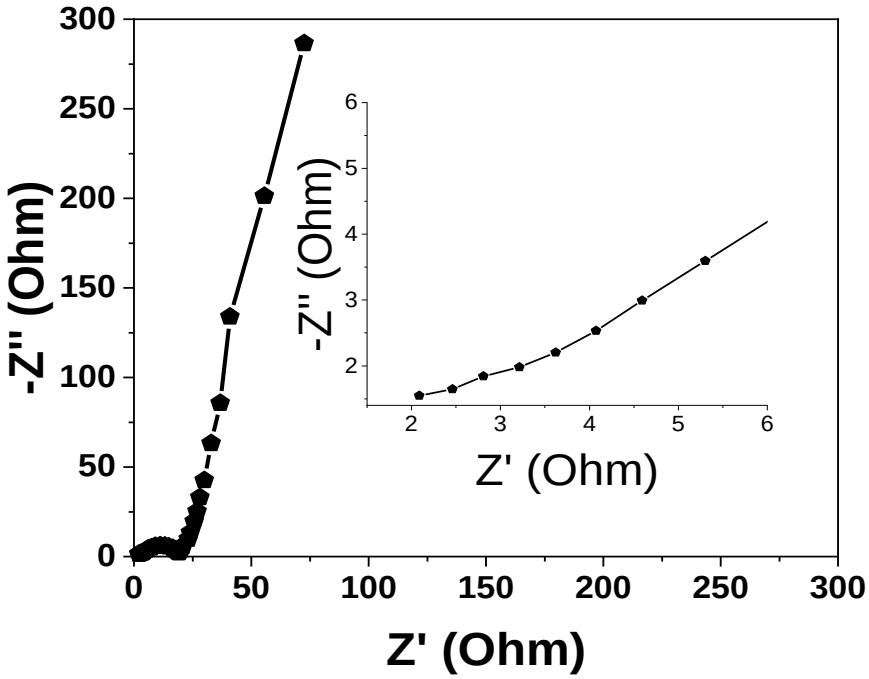

Fig. 7. Electrochemical Impedance spectroscopy (EIS) characteristics of the built cell

4. CONCLUSION

In this work, the production of porous carbon from cassava peels has been achieved using a nontoxic environmentally friendly activating agent, sodium thiosulphate. Moderate surface area (SSA) of $306m^2g^{-1}$ was achieved. Fabricated electrodes from the prepared carbon delivered specific capacitance (C_{SP}) of $94.3Fg^{-1}$. If fully explored, this could be a viable environmentally friendly process for the production of porous carbon for application in the supercapacitor industry.

DISCLAIMER

The products used for this research are commonly and predominantly use products in our area of research and country. There is absolutely no conflict of interest between the authors and producers of the products because we do not intend to use these products as an avenue for any litigation but for the advancement of knowledge. Also, the research was not funded by the producing company rather it was funded by personal efforts of the authors.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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