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Synthesis of Chemically Modified Activated Carbon for Supercapacitor Electrode Derived from Fibers of *Musa paradisiaca*

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ABSTRACT: For the growing energy demands, development of alternate energy sources is inevitable. This work mainly concentrates on developing a type of nitrogen doped carbon network derived from biomass waste (*Musa paradisiaca*) by carbonization and activation process. Different chemicals such as sulphuric acid, hydrochloric acid and phosphoric acid, are used to activate banana peel derived carbon, in order to achieve improved specific capacitance. The electrochemical performance of skin of *Muca paradisiaca* derived activated carbon for supercapacitor applications is evaluated using aqueous 0.5 M H_2SO_4 electrolyte solution at various current densities such as 0.025 $mA.g^{-1}$, 0.05 $mA.g^{-1}$, 0.1 $mA.g^{-1}$, 0.25 $mA.g^{-1}$ and scan rate of 30 mVs^{-1}. The advanced performance of chemically activated skin of *Musa paradisiaca* derived nanoporous carbon is ascribed to high surface area, with fast ionic diffusion of the electrolyte into and out of the pores. From CV analysis, the electrodes BPC, BPCH, BPCP and BPCS in 0.5 M H_2SO_4 electrolyte exhibited the specific capacitance of 148.7, 256.8, 9.52 and 306.2 Fg^{-1} respectively, with an excellent capacity retention ratio. From GCD analysis, 79.4, 182.1, 91.8 and 148.2 Fg^{-1} of specific capacitance is obtained for BPC, BPCH, BPCP and BPCS respectively at varying current density. When compared to all the prepared samples, BPCS exhibited small equivalent series resistance (0.1 Ω) and charge transfer resistance (16.6 Ω).

Keywords: *Musa paradisiaca*, Supercapacitor, Energy density, Power density.

I. INTRODUCTION

An electrode material should possess very good porous structure and electrochemical properties [1]. For the development of supercapacitor, activated carbon is the main choice [2]. Activated carbon derived from renewable biomaterials is socially and environmentally significant [3]. With controlled carbonization temperature [4] prepared carbon from banana peel with -OH, $-NH_2$ groups. Biomaterial can be very quickly carbonized and turned into solid carbon, when sudden heat is applied on it, which is almost similar to pyroclastic flow from volcano. This process takes place in three phases: such as drying, decomposition and cooling. Heating rate, peak temperature and feedstock are the major factors affecting the yield.

The banana peel pseudographite offers superb dual functionality for sodium ion and lithium ion battery anodes [5]. Carbonization of banana peels and activated it using KOH [6]. The porous structure and rich nitrogen-dopant facilitate penetration of electrolyte ions in fast manner [7]. Series of banana peels derived porous carbon materials were fabricated by pyrolysis carbonization [8]. Nitrogen doped banana peel [9] and Sulphur doped banana peel [10] exhibited mesoporous structure and good hydrophilicity [11]. Flexible graphene foam based supercapacitor exhibited 68% capacity retention ratio after 25000 cycles [12]. Yeast treated banana peel has enough pseudocapacitance sites which improve the specific capacitance [13]. By treating the banana fiber or waste cottonseed husk [14], rotten potato [15] with KOH, improve the surface area [16]. Biopolymers presented in the cell walls of banana peel absorb ionic compounds [17].

SnO_2 mixed biochar composite from banana peel which is developed as electrode material for supercapacitor using simple chemical co-precipitation method with high specific capacitance of 465 Fg^{-1} [18]. Nitrogen-doped banana peel–derived porous carbon foam from banana peels with high specific surface area of 1357.6 m^2/g which is used as a binder-free electrode for supercapacitors. Using corn starch biodegradable polymer electrolytes, solid state EDLC was fabricated with 90% of efficiency up to 500 cycles [19]. Solid state EDLC model for activated carbon electrode from the banana peel waste for supercapacitor application [20]. Supercapacitor device from Banana peels, exhibited hierarchical porous nano-architecture containing micropores, and mesopores with the specific surface area of 1362 m^2g^{-1} [21]. Flexible, interdigitated supercapacitor for emerging wearable/flexible electronic applications through banana peel impregnated with KOH.

The objective of this work is to synthesize low cost activated carbon composites derived from banana peel to measure its conductivity. Here Banana peels, a common fruit waste, which was adopted as a material that consists of highly porous activated carbon used as an electrode material for supercapacitor.

II. EXPERIMENTAL SECTION

A. Preparation of Activated Carbon from Musa paradisiaca

Initially, two kilograms of *Musa paradisiaca* were bought and only the peels were taken. This peel consists of thin outer skin and juicy inner skin which was dried at room temperature for 4 days. After the peels became arid, it was then completely washed with distilled water and the inner skin was ridded off using peelers and razors and

cut into small uniform square pieces. Then they were again dried at room temperature for 24 hours and kept in hot air oven for two days at 90°C for the moisture content removal. After the process, the weight of the peels was reduced by 78%.

Then the peel was grounded and kept in sigma high temperature furnace at 600°C for two hours. Finally, the extracted carbon from banana peel (BPC) was activated using sulphuric acid, phosphoric acid and hydrochloric acid and oven dried for about 8 hours and named as BPCS, BPCP and BPCH, respectively.

B. Sturctural and Electrochemical analysis of BPC, BPCS, BPCP and BPCH

Using copper radiation sources, XRD patterns were recorded between 10° and 90°. Molecular functional groups of the prepared BPC, BPCH, BPCS and BPCP were identified using FTIR measurement. The electrochemical analysis such as CV, GCD and EIS of the samples using three electrode method, were done by Origalys electrochemical work station at 25°C. To analyse the electrochemical performances of supercapacitor, the electrode was prepared as reported in previous work. Initially, the samples were taken and mixed with the rubber solution to make it as slury [22, 23]. Then the prepared slurry was coated on an ordinary graphite rod of 3 mm and it was act as a working electrode. For counter and reference electrodes, Pt wire and Ag/AgCl were used, respectively. At a scan raete of 30 mVs^{-1}, CV of all the prepared samples were recorded in 0.5 M H_2SO_4 aqueous solution. With varying current density, GCD of all the samples were measured. By using EIS, equivalent series resistance and charge transfer resistance of all the samples were measured.

III. RESULTS AND DISCUSSION

The pores are identified on the carbon surface because of the chemical activation. To identify the crystalline nature of BPC, BPCH, BPCS and BPCP samples, they were characterized by XRD method. The XRD patterns of the samples are shown in Fig. 1. From the diffraction pattern of the samples, a broad peak is observed at 19° for both BPC and BPCH, but BPCH exhibited higher intensity, broad peak than BPC, because of the chemical activation. Similarly, a broad peak is observed at 25° for both BPCS and BPCP. When compared to BPCP, BPCS exhibited peak intensity. The weak band is observed at 11° and 15° for BPCH and BPC respectively, and 80° for BPCS and BPCP. Highly amorphous carbon is identified from the presence of broad peak.

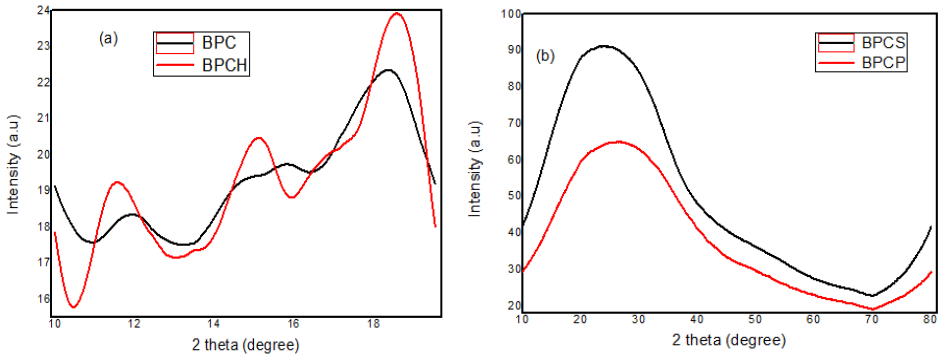

Fig. 1. XRD diffraction patterns of (a) BPC and BPCH (b) BPCS and BPCP.

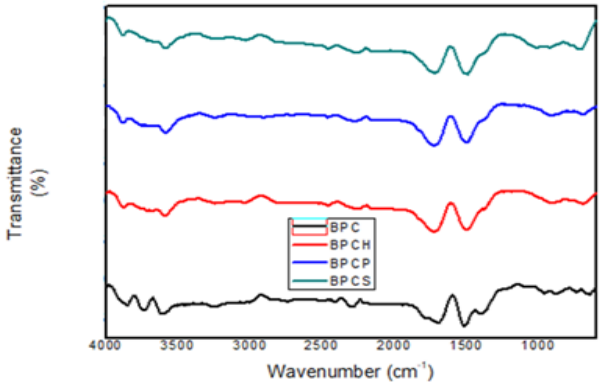

Fig. 2. Fourier Transform Infrared spectra of BPC, BPCH, BPCP and BPCS.

Fig. 2 shows the FTIR spectroscopy of BPC, BPCH, BPCS and BPCP using KBr method with the range of the spectrum is observed from 400 to 4000 cm^{-1}. Different chemical activation influenced the FTIR analysis of BPC. It showed a strong peak at 3970.47 cm^{-1} attributable to the hydroxyl stretching vibrations of the COH groups. The value of the peak at 1707.95 cm^{-1} is assigned to C=O stretching band, and band at 1519.92 cm^{-1} is assigned to C=O stretching. The band at about 1280 cm^{-1} is assigned to C-C stretching vibration. Peak at 1000 cm^{-1} are assigned to C-O stretching, and 600 cm^{-1} (weak) to (O-C=O).

The electrochemical analysis is performed using Origalys Electrochemical Workstation. 0.5 M aqueous H_2SO_4 is used as an electrolyte solution. To characterize the electrochemical capacitive behaviour and quantify the specific capacitance of the samples, CV is mostly used. Fig. shows the CVs for hot oven treated chemically activated banana peel derived activated carbon at scan rates of 30 mV s^{-1}. From the Table 1. highest specific capacitance is observed for sulphuric acid treated banana peels derived activate carbon.

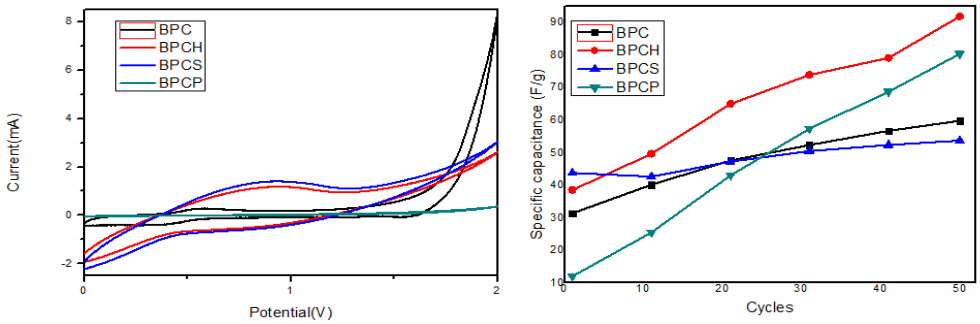

Fig. 3 (a) CV curves of BPC, BPCH, BPCS and BPCP a scan rate of 30 mVs^{-1}, (b) Cycle stability of BPC, BPCH, BPCP and BPCS.

Table 1: Specific capacitance obtained from CV analysis.

Materials	Specific Capacitance ($F.g^{-1}$)
BPC	148.73
BPCH	256.80
BPCS	306.18
BPCP	9.52

The charge discharge curve at current density of 0.025 $mA.g^{-1}$, 0.05 $mA.g^{-1}$, 0.1 $mA.g^{-1}$, 0.25 $mA.g^{-1}$ for BPC, BPCH, BPCS and BPCP is shown in Fig. 4 and the corresponding specific capacitance is tabulated in Table 2. GCD curves are usually taken to calculate the specific capacitance, energy density and power density. To understand the capacitive nature of chemically activated *Musa paradisiaca*, its electrochemical properties were analysed at different current densities using galvanostatic charge and discharge measurement. For BPC, the curves are approximately triangle with large amount of IR drop is observed. But for chemically activated samples, only a small amount of voltage drop is observed which further confirms the capacitive nature of chemically activated banana peels. At the same time, BPCP samples exhibited very lowest specific capacitance, even compared to BPC. The higher specific capacitance (182 Fg^{-1} at 0.25 mAg^{-1}) is observed for BPCH electrodes. From the obtained results, *Musa paradisiaca* can be used as low cost biomass based activated carbon for supercapacitors. Comparison with existing work is given in Table 3.

To further investigate the ion diffusion, EIS was employed. Fig. 5 shows the nyquist spectrum is recorded within the range of 100 kHz to 0.1 Hz. From the charge transfer resistance of the samples, the ion transport can be understood. All the samples exhibited the linear curve in the low frequency region, ascribed to excellent capacitive performance. Equivalent series resistance of BPC, BPCH, BPCS and BPCP, are 1.2 Ω, 0.2 Ω, 0.1 Ω and 1.3 Ω, respectively. All the samples exhibited very small ESR, suggested the high conductivity of the samples. Similarly, charge transfer resistance of the samples exhibited 69.6 Ω, 43.1 Ω, 16.6 Ω and 84.3 Ω for BPC, BPCH, BPCS and BPCP, respectively. When compared to all the prepared samples, BPCS exhibited lowest ESR and R_{ct}, which further confirm with the CV and GCD.

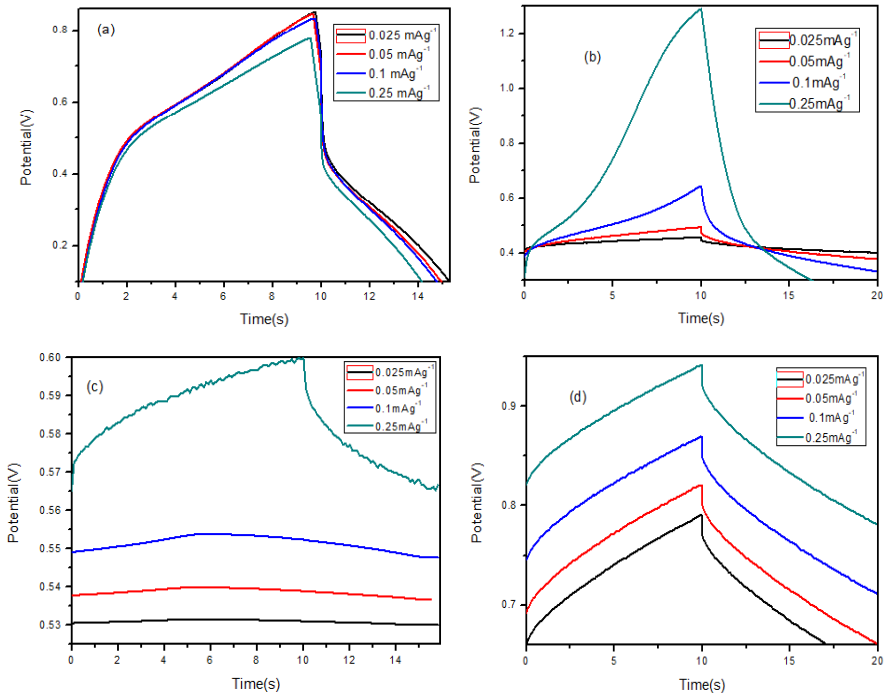

Fig. 4. Galvanostatic Charge and Discharge spectra of (a) BPC (b) BPCP (c) BPCS and (d) BPCH.

Table 2: Specific capacitance obtained from GCD analysis.

Materials	Specific Capacitance ($F.g^{-1}$) at 25 µA	Specific Capacitance ($F.g^{-1}$) at 50 µA	Specific Capacitance ($F.g^{-1}$) at 100 µA	Specific Capacitance ($F.g^{-1}$) at 250 µA
BPC	67.13	66.40	70.61	79.42
BPCH	182.09	75.50	65.56	53.02
BPCS	55.99	148.18	60.22	57.59
BPCP	15.38	91.75	23.32	12.77

Table 3: Comparison with existing work.

Electrode material	Specific capacitance	Ref.
Banana peels/PVAC	72.93 $F.g^{-1}$	[6]
Nitrogen-doped banana peel–derived porous carbon foam	173 $F.g^{-1}$ at 0.5 $A.g^{-1}$	[9]
Hierarchical porous carbon foams	206 $F.g^{-1}$ at 0.1 $A.g^{-1}$	[16]
Banana peel based carbon	68 $F.g^{-1}$	[20]
Porous carbon	328 $F.g^{-1}$	[21]
Banana peel / HNO_3	125 $F.g^{-1}$	[24]
SnO_2 mixed biochar derived from banana peel	465 $F.g^{-1}$ at 10 mV s^{-1}	[25]
Porogen /banana peel	173 $F.g^{-1}$ at 0.1 $A.g^{-1}$	[26]
Mn_3O_4 bio-synthesized from banana peel	216 $F.g^{-1}$ at 0.3 $A.g^{-1}$	[27]
BPCS	306.2 $F.g^{-1}$ at 30 mVs^{-1}	This work

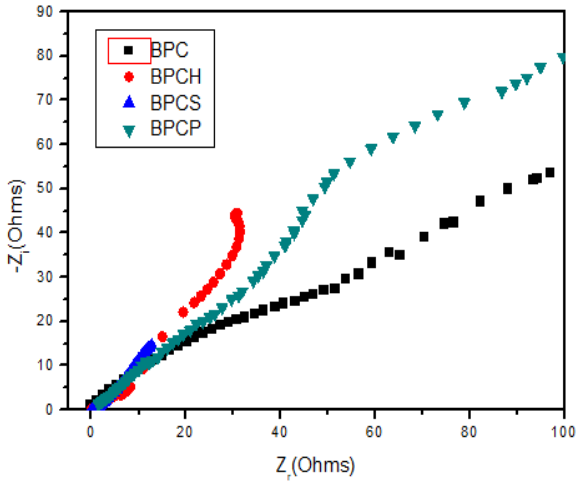

Fig. 5. Nyquist plots of BPC, BPCH, BPCS and BPCP.

IV. CONCLUSION

Banana peel-derived biomass carbons have been successfully prepared by carbonization and chemically activated using hydrochloric acid, sulphuric acid and phosphoric acid. Among the activated samples, BPC activated using sulphuric acid exhibited better electrochemical performance. The specific capacitance of BPC activated using sulphuric acid is 306 F g^{-1} at 30 mV s^{-1}, which is greater than that of the commercial AC. The well-developed structure of sulphuric acid activated BPC, is promising choice for the low-cost design of high-performance coin cell supercapacitor. As the prepared organic carbon from banana peel showed a good performance, usage of these carbons as alternative will result in great advantage. In future it is possible to infuse any inorganic chemicals with this banana peel derived carbon to enhance its electrochemical conductivity.

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Conflict of Interest. The Authors declare that there is no conflict of interest.

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