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Biopolymer phytigel-derived porous nanocarbon as efficient electrode material for high-performance symmetric solid-state supercapacitors

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Abstract

In the present work, a porous nano-carbon (PNC) based electrode materials were successfully derived from the natural biopolymer phytigel via a facile hydrothermal and combustion process. The carbon phase structure of the PNC electrode was confirmed using different spectroscopy, microscopy and N₂ adsorption-desorption analyses. The surface morphology investigation showed a distinct shape and size for the PNC that demonstrated its porous nature. The electrochemical performance of PNC was completely reliant on the calcination temperature (800 °C) and it delivered the maximum capacitance of 122 F g⁻¹ at 0.25 Ag⁻¹. An AC impedance and cyclic voltammetry analyses proved the intrinsic electrochemical behavior by their cycling. Besides, the fabricated symmetric solid-state supercapacitor displayed an outstanding cycle durability with a stable capacitance retention of 85.8% over 8,000 cycles, suggesting favorable prospects for its use as an active candidate for symmetric solid-state supercapacitor applications.

Keywords: *biopolymer, hydrothermal, porous carbon, electrochemical properties.*

1. Introduction

Supercapacitors (SCs) are alternative energy storage systems that can offer long life times ($>10^5$), fast charge-discharge process, outstanding safety, and high power densities (10 kW kg^{-1}) and have played a decisive protagonist in several areas such as in the evolution of hybrid electric vehicles, automobiles and memory back-up *etc.* [1-5]. Nevertheless, their forthcoming usage has been restricted through their low energy density [6, 7]. To resolve this dispute, several efforts have been made to build high-performance SCs with high energy densities using various materials include transition metal oxides, porous carbon, and conducting polymers [8-10]. In general, carbon based material are being used as alternative electrode materials for supercapacitor applications owing to their low cost, high surface areas, and excellent thermo-electrical conductivity [11-13]. Moreover, carbon derivatives such as graphene, carbon fibers, carbon nanotubes, and activated carbon have also been considered as active electrode materials for high-performance SCs. Among them, porous carbon offers better intrinsic electrochemical properties than those of other carbon allotropes [14-20].

Nowadays, numerous researches have been keen to improve the energy density of carbon compounds by combining them with conducting polymers and oxides of transition metal ions and the resulting materials have been employed as anode materials of solid-state battery-type asymmetric SCs (ASCs) [21-23]. However, unfortunately, the cycling and electrochemical performances of such devices were very poor, which did not allow the carbon SCs to grow in popularity. The major drawback that limits the development of carbon-based SCs are the capital cost and limited resources because most carbon materials are obtained from petroleum-based hydrocarbons [24, 25]. In this context, biomass-derived carbon materials are receiving growing demand from the scientific community for the construction of high-performance carbon based

SCs due to their abundance in earth and because they are ecofriendly and cheap [7, 26]. So far, many biomass materials such as banana peel waste [26, 27], celery stem [28], lignin [29], onion tissue [30], lentinus edoes [31], chicken feathers [32], and chitosan [33] have been converted to carbon for use in supercapacitors and their performances have been investigated. In addition, a general route to improve the surface area is through activation, which has shown to lead to excellent charge discharge rates [34]. For example, KOH-activated bamboo sticks and NaOH-activated *Eichhornia crassipes* demonstrated improved performance in terms of cycling stability, energy density, and specific capacitance [35, 36]. Herein, we aimed to prepare a porous nanocarbon (PNC) from biopolymer phytigel using a simple hydrothermal strategy. The reason for choosing phytigel as a potential candidate for carbon source may attributed to the following facts: (a) It is one of the naturally occurring carbohydrate biopolymer with admirable assets for instance cost effective, eco-friendly nature, nonhazardous, thermal resistance, and easy chemical modification (b) further, it comprises of chemically reactive -OH and -COOH moieties, which deliver easily available sites for functionalization [37, 38]. The phase and morphology of the PNC derived from phytigel and its electrochemical features such as specific capacitance and charge discharge behavior were investigated and have been discussed herein in detail.

2. Experimental

The raw phytigel (1000 kg/mol; low acylation degree), orthophosphoric acid (85 wt%, M_w : 98.0), and potassium hydroxide (M_w : 56.11) were purchased from Sigma Aldrich. The PNC was derived from the biopolymer phytigel powder according to a procedure reported elsewhere [39, 40]. Prior to the purification step, the phytigel was kept in vacuum for 12 h at 50 °C.

0.5 g of the dried phytigel powder was hydrolyzed using 40 mL of a dilute orthophosphoric acid solution (H_3PO_4) under mild stirring and gently heating at 50 °C for one

day. The possible activation process of phytigel with H_3PO_4 is displayed in Figure 1. Then, the tacky pasty solution was reassigned into a 40 mL Teflon-sealed autoclave and subjected to hydrothermal treatment at 160 °C for 16 h in an oven. Subsequently, the autoclave was endorsed to chill naturally. The colloidal product obtained subsequently was rinsed with double DI water and dried at 60 °C overnight.

Figure 1: Schematic mechanism of activation process of phytigel using orthophosphoric acid

Dried samples were then treated with KOH in the stoichiometric ratio of 1:1.5 and the mixed powders was moved to a porcelain crucible that was then kept in a high temperature tube furnace. The furnace temperature was raised into 800 °C at 10 °C min⁻¹ heating rate in an argon

atmosphere and seized at 800 °C for 2 h. Then, the furnace was naturally allowed to settle down to ambient temperature. The solid product gotten was treated with the mixtures of HCl/water and water/ethanol solutions several times. In order to avoid impurities the washed PNC powders were dried at 80 °C for 12 h in an oven to obtain a fine pure powder. The synthesis is schematically exemplified in Figure 2.

Figure 2: Schematic synthesis of PNC powder using hydrothermal and combustion methods

The working-cum-counter active electrodes were prepared in this following fashion: A mixture with 80% of synthesized PNC, 10% of Super P, and 10% PVdF (poly vinylidene fluoride) content were dispersed in an N-methyl pyrrolidone solvent and allowed to form a coagulated paste, which was used to coat a current collector Ni Foam that was then, placed beneath vacuum at 120 °C for overnight and used as the positive and negative electrodes. A hybrid symmetric cell was fabricated using the abovementioned fabricated electrodes and a

Whatman filter paper separator (soaked in 6 M KOH). The active masses of the electrodes were 0.055 g and 0.049 g.

The structural behaviors of the synthesized PNC were examined through Raman spectroscopy (FT-Raman), X-ray diffraction analysis (XRD), transmission electron microscopy (HR-TEM), thermogravimetric analysis (TGA), and field-emission scanning electron microscopy (FE-SEM). The XRD analysis was conducted through Rigaku X-ray diffractometer (D-Max 2500) at 40 kV and 30 mA reflux at $2^\circ/\text{min}$ via Cu-K α ($\lambda=1.540 \text{ \AA}$) with $2\theta = 10\text{--}80^\circ$. Raman analysis was performed utilizing a Renishaw Micro-Raman spectrometer analyzer by means of a He-Ne source in the range $2000\text{--}1000 \text{ cm}^{-1}$. TGA measurements were performed via a thermobalance (Thermo Plus2/TG-DTA, Rigaku Co) that were recorded by a computer from the temperature range from 35 to 800°C at $10^\circ\text{C}/\text{min}$. The surface morphology of the PNC powder was perceived using FE-SEM (JSM-6700F) and HR-TEM (JEM-2010F). Brunauer–Emmett–Teller measurements of the PNC were carried out in a liquid nitrogen atmosphere using ASAP 2010 analyzer (Micromeritics, USA). Electrochemical measurements were performed via cyclic voltammetry (CV), charge–discharge (GCD), and electrochemical impedance spectral (EIS) analyses. Electrochemical analyses were conducted by means of the VersaSTAT3 electrochemical workstation (Princeton, USA). The CV curves were analyzed in the potential range -1 to 0 V at diverse scan rates ($5\text{--}50 \text{ mVs}^{-1}$). Impedance analysis was carried out in the frequency range from 0.1Hz to 1MHz with a signal amplitude of 10 mV. GCD curves were recorded at various current rates ($0.25\text{--}8 \text{ Ag}^{-1}$).

3. Results and Discussions

3.1. Physicochemical analyses

The crystallinity and phase purity of the PNC derived from the phytagel biopolymer was estimated through the X-ray diffraction pattern obtained, displayed in Figure 3(a). The figure shows two predominant broad peaks at $2\theta = 21.5^\circ$ and 43.2° , which are related to the (002) and (100) reflection planes of carbon, respectively. Both peaks showed a shift to lower 2θ values compared to those noted for graphitic carbon derived from other bio-resources [41, 42], owing to the introduction of C-O bonds initiating slackening and distortions in the sp^2 carbon and increase in the interlayer distance between adjacent graphitic layers within the structure. The broadness of the diffraction peaks further clearly confirmed the amorphous nature of the prepared sample, which was in agreement with results reported earlier [36]. The Raman analysis was performed from 2000 to 800 cm^{-1} , as shown in Figure 3(b). Two dominant peaks were observed at 1320 cm^{-1} and 1590 cm^{-1} , owing to the A_{1g} and E_{2g} modes of D and G bands, respectively. The perfection and tangled structure of graphitic carbon was evaluated through the Raman intensity ratio I_D/I_G , and it was found to be 1.11. The obtained high I_D/I_G value undoubtedly indicated that the synthesized graphitic carbon contained of a scarce layers of graphitic sheets with minor flaws include empty sites, topological imperfections and, dangling bonds which ought to be the presence of O-atoms in the carbon lattice structure.

The TGA thermogram of graphitic nanocarbon is shown in Figure 3(c). The prepared sample exhibited two thermal degradation events: an initial water loss up to 220°C and thermal decomposition (T_m) at temperatures of $340\text{--}380^\circ\text{C}$. The second thermal event, which occurred at around 360°C , might be mostly ascribed to the decomposition of C-H, O-H, C-C, C=O, and C-O bonds during the dilapidation of the biopolymer phytagel polysaccharide chain. A greater amount of graphitic carbon residue observed at 440°C (28.0%) might represent the percentage of carbon particles. The observed phenomenon is in accordance with earlier reports and also

confirmed the formation of carbon particles at elevated temperatures. Figure 3(d) shows the N₂ adsorption–desorption isotherm acquired for the synthesized nanocarbon. It is evident from the isotherm that the synthesized carbon consisted of both mesopores and macropores, *i.e.* both type II and type IV curves were present at low and high vapor pressures. Further, two different insulated capillary condensation of hysteresis ladders observed in the isotherm curve at $p/p_0 < 0.92$ and > 0.92 confirmed the meso–macroporous structure of the synthesized samples. The surface area and pore volume were recognized to be $0.08021 \text{ cm}^3\text{g}^{-1}$ and $930 \text{ m}^2\text{g}^{-1}$, which confirmed the high porosity of the synthesized PNC.

Figure 3: (a) XRD pattern, (b) Raman spectrum, (c) TGA thermogram and (d) N₂ adsorption-desorption isotherm obtained for PNC.

The morphology and particle size of the synthesized PNC were perceived through FE-SEM and HR-TEM analyses and the ensuing images are depicted in Figure 4(a-d). The PNC particles consisted of a three-dimensional interconnected polyhedron network with a distinctly smooth morphology, as shown in Figure 4(a). The size distribution of the PNC particles encompassed the range 65–75 nm. Figure 4(b) shows a high-magnification image that exhibits more opaque and larger pores over the microporous network structure. To confirm the results acquired by SEM analysis, HR-TEM analysis was employed, as displayed in Figure 4(c, d). Cautious inspection of the images clearly indicates homogeneous distribution of the PNC particles and an ordered polyhedral shape. The average size of each polyhedron was found in the range of 75– 85 nm, which is in close agreement with results derived by SEM analysis.

Figure 4: (a, b) FE-SEM of PNC powder at high and low magnifications, (c,d) HR-TEM images of PNC at different magnifications.

3.2. Supercapacitive performance

To validate the electrochemical behavior along with the feasibility of using PNC electrodes in SCs, a symmetric cell was assembled using the synthesized PNC as symmetric electrodes *i.e.*, working-cum-counter electrodes, and a KOH-soaked Whatman filter paper as separator electrolyte. The capacitive performance of the symmetric cell was assessed using cyclic voltammetry and the ensuing curve is provided in Figure 5(a) for the fixed potential window of -1 to 0 V. The shape of the CV profile was almost quasi-rectangular without any redox peak, which implied that the capacitance is stored by non-faradaic reactions on the

electrode–electrolyte interfaces, which is recognized as double layer capacitance. It is recognized that carbon-based electrodes exhibit electric double layer behavior, and so it is genuine to accept that the double layer capacitive effect arose from the PNC working electrode [43]. In general, the specific capacitance is assessed by integral part of area under the curve; in the present investigation, an increasing trend was noted for the capacitance with increase in cycles, as displayed in Figure 5(b). The CV curves obtained for the PNC cell at various scan rates are depicted in Figure 5(c). No significant changes were found in the voltammograms even at high scan rates, demonstrating the firm charge–discharge behavior. Furthermore, the intercalating and de-intercalating current enhanced with increase in the scan rate and did not follow an undeviating fashion, as depicted in Figure 5(d). Therefore, the electrochemical charge–discharge process was facile over the electrolyte–electrode interfaces and was further strengthened by galvanostatic charge–discharge processes, as discussed later.

In order to utilize the synthesized PNC electrodes for practical SC applications, the solid-state symmetric SC cells were subjected to galvanostatic charge–discharge processes as displayed in Figure 6(a). The specific capacitance C_{sp} of the cells were evaluated using the following expression:

$$C_{sp} = 2 \times \frac{\Delta t \times I}{\Delta V \times m} \quad (1)$$

where Δt and ΔV represent the discharge time and potential window range respectively; m indicates the mass of the active electrode sample, and I is the discharge current. As depicted in Figure 6(b), the calculated C_{sp} of the symmetric cell based on the above equation was 122 Fg^{-1} at 0.25 A g^{-1} , which was knowingly greater than recently reported for biopolymer-derived carbon-based SC devices [44-48]. The previously reported porous carbon capacitance values are displayed in Table 1 which were extracted from bio-waste materials.

Furthermore, the energy density (ED) and power density (PD) of the PNC-based symmetric device was also determined through the resulting two equations given below:

$$ED = (\Delta V^2 \times C_{sp} / 2) / 3.6. \quad (2)$$

$$PD = (ED * 3600 / \Delta t) \quad (3)$$

The calculated ED and PD values were plotted in a Ragone plot exposed in Figure 6(c). The SC symmetric cell offered of a high ED value of 14.38 and 5.62 Wh kg⁻¹ at a PD of 360 and 980 Wkg⁻¹ respectively. The measured ED and PD values of the present system was superior compared to other recently reported biopolymer-derived carbon-based SC cells. As represented in Figure 6(d), the outstanding long-term stability of the PNC-based symmetric SC device was verified and the device maintained 85.8% of the C_{sp} even after the 8000 cycles, which suggests that the prepared PNC can be a promising candidate for practical solid-state energy storage devices.

Table 1: Electrochemical performance of carbon electrodes resulting from biomaterials

Electrode	Electrolyte	Specific capacitance	Capacitance retention (%) for minimum 1000 cycles	Ref
Porous nanocarbon derived from Phytigel	6M KOH	122 Fg⁻¹	85.8 (8000 cycles)	This work
PAN based carbon nanofiber paper	Et ₄ NBF ₄ in acetonitrile	108 Fg ⁻¹	64.8	[49]
Sodium alginate based carbon	1 M H ₂ SO ₄	198 Fg ⁻¹	89.98	[50]
Seaweed carbon	1 M H ₂ SO ₄	180 Fg ⁻¹	--	[51]
Activated carbon	Li ₂ SO ₄	102 Fg ⁻¹	89	[52]

porous carbon nanofiber derived from polymethylhydrosiloxane (PMHS)/polyacrylonitrile (PAN)	6M KOH	126 Fg ⁻¹	---	[53]
Cellular CNT films	10 wt% H ₃ PO ₄ /polyvinyl alcohol (PVA) gel electrolyte	72.9 Fg ⁻¹	82.85	[54]
CNT	1-M Na ₂ SO ₄ solution	120 Fg ⁻¹ for CNT	---	[55]
Carbon black+ reduced graphene oxide	PVA+H ₃ PO ₄	115 Fg ⁻¹	88	[56]
CNT growth on stainless steel	poly-ethylene glycol diglycidal ether (PEDGE) – ionic liquid (IL)	120 mFcm ⁻³	---	[57]
Graphene oxide	6M KOH	94.4 Fg ⁻¹	51.3	[58]
Porous carbon nanoparticles	5M KOH	343 Fg ⁻¹	95	[59]
Heteroatom doped carbon derived from human waste	6M KOH	166 Fg ⁻¹	98.3	[60]
Mesoporous activated carbon	6M KOH	222 Fg ⁻¹	94	[61]
Hemp derived activated carbon	1.8 M TEMABF ₄ /PC	160 Fg ⁻¹	83.9	[62]
Activated carbon	PVA+H ₃ PO ₄	188 Fg ⁻¹	99	[63]
Soybean derived carbon	1 mol L ⁻¹ H ₂ SO ₄	150 Fcm ⁻³	>60	[64]
N-containing chitosan doped carbon	1 M H ₂ SO ₄	19.5 μFcm ⁻²	83	[65]
Hierarchically porous carbon microspheres-PANI (chitin)	1M H ₂ SO ₄	76 Fg ⁻¹	90.6	[66]
Microporous activated carbon synthesized from waste compact discs	EMImBF ₄	51 Fg ⁻¹	80	[16]
graphene-like carbon nanosheets derived from cucumber	6M KOH	143 Fg ⁻¹	97	[15]
hierarchical porous activated carbon derived from waste cumin plant	1M H ₂ SO ₄	155 Fg ⁻¹	96.9	[17]
Waste-derived Microporous carbon-based materials	6M KOH	512 Fg ⁻¹	>90	[18]
Nanoporous	6M KOH	330 Fg ⁻¹	85.6	[19]

pyropolymer nanosheets derived from citreae peels				
Hierarchical porous carbons derived from waste plastic bags	EMImBF ₄	100 Fg ⁻¹	97.1	[20]

Figure 5: (a) CV curves for PNC, (b) CV curves for PNC recorded at different cycles, (c) CV curves recorded for PNC at different scan rates, and (d) peak current observed for PNC as a function of scan rate.

To evaluate the capacitive and charge transfer behaviors of the synthesized PNC, electrochemical impedance spectral analysis was performed; the registered complex impedance data are shown in Figure 6(f). The corresponding magnified region of the Nyquist plot for high frequencies is shown in the inset. Both of the Nyquist plots obtained for PNC before and after

cycling consisted of two important regions: it behaved like a resistor in the maximum frequency (f) region and like a pristine capacitor in the lower f region, *i.e.*, the presence of a compressed semi-circle in the former region might be ascribed to the charge transfer resistance (R_{CT}) over the electrode electrolyte interface whereas the inclined spiky line in the latter corresponded to capacitor behavior. This phenomenon was further evaluated by an equivalent circuit fitting model using the *Z-man* software. Based on the fitted equivalent circuit model, it can be decided that the high f non-zero intersection of the real Z' axis was related to the series resistance (ESR), which was a combination of the internal, ohmic, and interfacial resistances of the active electrode, the electrolyte, and interactions between the particles, respectively [67, 68]. The calculated ESR values for the fresh and post-cycling PNC-based cells were 1.34 and 1.91 Ω , respectively, which clearly indicated that there was no crucial change in the ESR value and therefore the prepared PNC was highly stable. Furthermore, the intermediate f region of the plot exhibited a solitary compressed semicircle that may be accredited to the charge transfer resistance (R_{CT}) over the electrolyte electrode interface. The minor enhancement in the value of the R_{CT} after cycling (fresh cell: 2.7 Ω ; after cycling: 3.7 Ω) may be due to lower ion transport, which in turn disturbed the conducting environment at the electrode–electrolyte interface. Additionally, the presence of an inclined spike line in the low f range exhibited Warburg (W_R) resistance at angles of 45–90°, possibly on account of the electrolyte ions diffusion over the electrode–electrolyte interface. Lastly, a constant phase element, namely, the electric double layer capacitance (CPE_{dl}), was included in the electric circuit to represent non-ideal performance. The values obtained for the parameter demonstrated the superior electrochemical behavior of the PNC electrode in combination with the electrolyte solution used.

Figure 6: (a) GCD curves of PNC at different current rates of 0.25–8 Ag^{-1} , (b) C_{sp} vs current density rate, (c) PD vs ED, (d) evolution of specific capacitance of PNC over 8000 cycles, (e)

GCD curves of PNC at initial and final cycles and (f) EIS of PNC (inset: enlarged image for the high-frequency region).

4. Conclusions

In summary, a porous nano-carbon (PNC) electrode was synthesized hydrothermally using a biopolymer phytagel and electrochemically evaluated for its application in solid-state supercapacitors. CV analyses of the PNC electrode showed a stability window of 1 V and demonstrated that it was electrochemically robust in the scanned potential range. Further, the PNC electrode exhibited 122 Fg^{-1} as its highest specific capacitance at 0.25 Ag^{-1} with outstanding capacity retention. The Ragone plot of the synthesized PNC electrode indicated energy densities 14.38 and 5.62 Wh kg^{-1} at power densities of 360 and 980 Wkg^{-1} , respectively. The facile synthesis and improved capacitance behavior of the PNC electrode could lead to the progress of high-performance solid-state supercapacitor devices in the near future.

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