Hierarchical nanoporous activated carbon as potential electrode materials for high performance electrochemical supercapacitor

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ABSTRACT

Recently, biomass-derived activated carbon nanomaterials represent a potential candidate in achieving sustainable and low-cost energy storage devices. Herein, we report a facile synthesis of hierarchical nanoporous activated carbon (NAC) by template-free and cost effective approach using bio-derived food waste namely "Indian Cake Rusk" (ICR) and its application in high performance supercapacitors for the first time. The influence of carbon activation process over the physicochemical properties, morphological structure, as well as supercapacitive performance was systematically studied. When used as an electrode in a supercapacitor, the as-synthesized NAC material offered a high specific capacitance of $381.0 \, F \, g^{-1}$ at a current density of $1.7 \, A \, g^{-1}$ with an impressive 95% capacity retention even after 6000 cycles using $1.0 \, M \, H_2SO_4$ electrolyte. The NAC material also furnished a maximum energy density of $47.1 \, Wh \, kg^{-1}$ and power density of $22644.0 \, W \, kg^{-1}$ which is higher than the existing carbon based electrode using $1.0 \, M \, LiPF_6$ electrolyte in symmetric supercapacitor. The superior electrochemical performance of NAC material is ascribed to huge BET surface area ($1413.0 \, m^2 \, g^{-1}$), hierarchical micro/nanoporosity, and good electrical conductivity which could serve as a promising carbon material for advanced applications in energy, environmental, and biomedical fields.

1. Introduction

Owing to the ever growing energy demand, electrochemical energy storage systems with higher energy and power densities such as lithium-ion batteries (LIBs), supercapacitors (SCs), etc. have attracted tremendous attention [1,2]. In recent years, electrochemical supercapacitors have received a great interest as a renowned power sources because of their advantages of high power density coupled with extended cycle life, simple configuration, and easy mode of operation [3–7]. Although, electrochemical supercapacitors are widely used for numerous portable applications in the field of electronics, power backup, memory systems, etc. and they face tough challenges for producing high energy density supercapacitors in comparison to batteries [8,9]. In an effort to improve the energy density, nanostructured carbon based electrodes have played a major role among various electrode materials due to its low-cost, high electrical conductivity, and good durability. Generally, carbonaceous materials with high porosity and large surface area ($1000–1500 \, m^2/g$) deliver the energy density of $\sim 5.0 \, Wh \, kg^{-1}$ and gravimetric capacitance of $\sim 120.0 \, F \, g^{-1}$. In this context, several carbon nanostructures such as graphene [10,11], carbon nanotubes [12,13] and carbon nanofibers [14,15] having a high

surface area of $\geq 1500.0 \, m^2 g^{-1}$ were investigated for supercapacitor applications. However, the forbidden production cost and attaining high pure material still remain a challenging task towards commercialization. Thus, the recent research efforts were widely focussed on the carbon based/derived materials having advantageous attributes like tuneable pore size, high surface area, low cost, and environmental benignity [16–18].

In search for better carbonaceous materials, activated carbons derived from various natural sources, food waste, bio wastes, etc. have been investigated extensively to find suitable carbon materials [19]. Impressed with low cost factor, high surface area, and environmental sustainability, biomass derived activated carbon materials are exceptionally attractive for energy storage applications [20]. While chemical etching approach is often used to prepare porous activated carbon through etching of metal or silica present in the metal organic framework (MOF) [21,22] the method generally involves multistep synthesis and unfriendly etching process. In this context, synthesis of biomass derived activated carbon is considered as a cost effective strategy where the presence of biomolecules create numerous pores on the carbon surface during high temperature activation [19,23]. Natural raw materials, including banana peel [24], human hair [25], corncobs [26],

teakwood sawdust [27], coir pith [28], rice husks [23], etc. [29–33] have been used to obtain the porous activated carbons materials using various chemical activation agents [34–40]. Therefore, developing a simple synthetic strategy using abundance low-cost precursors for the production of porous structured carbon nanomaterials with high surface area still remains a mainstream research.

Herein, we demonstrate for the first time a facile, cost-effective, and template-free large scale synthetic strategy for novel hierarchical CN material from food waste of Indian Cake Rusk (ICR) for application in high performance supercapacitor. The prime advantages of this study includes (i) a facile and effective synthetic strategy; (ii) high surface to volume ratio, economic and inexpensive sustainable resource of food waste as the precursor; (iii) high porosity with an average pore diameter of ~ 3 nm without using any template agents; (iv) can be integrated either as three-electrode or two-electrode configurations towards super capacitance application and (v) exhibits the best maximum energy density of 47.1 Wh kg^{-1} and power density of 22644.0 W kg^{-1} due to synergistic effect arising from large surface area and hierarchical nanoporous structure. The present investigation will endow with new opportunity for the large-scale production of highly mesoporous NAC from biomass for stimulating environmental and energy applications.

2. Experimental section

2.1. Synthesis of CN materials

In a typical synthesis of carbon material, the collected Indian Cake Rusk (ICR) food waste from Bakery was ground well using mortar and pestle to obtain a fine powder. The powder was then annealed in an alumina crucible at 450 °C for 4.0 h using a tubular furnace (Carbolite furnace, UK) under N$_2$ atmosphere at a ramp rate of 5 °C min^{-1} and the resultant carbon powder was collected after cooling down the furnace to room temperature. In order to activate the obtained carbon, it was mixed well with KOH (Alfa Aesar) in a stoichiometric ratio of 1:3. Finally, the mixed powder was transferred to an alumina crucible and again annealed at 750 °C for 3 h in an inert atmosphere. After cooling the furnace, the carbon material was collected, washed thoroughly with pure water till the combined washings attain pH ~ 7.0. Finally, the activated carbon material was collected by centrifugation and dried at 60 °C for overnight in a hot air oven.

2.2. Physiochemical characterization

Powder X-ray diffraction (XRD) pattern was recorded with a Philips XRD 'X'PERT PRO diffractometer with Cu K$_\alpha$ rays ($\lambda = 1.5418$ Å). FT-IR spectrum was carried out with a BRUKER OPTIK spectrometer, GMBH, Germany (Model No. TENSOR 27) using KBr pellet technique. Raman measurements were performed using Renishaw (UK) spectrometer with a incident wavelength laser light of 632.8 nm. Surface area measurements were performed with autosorb IQ series (Quantachrome Instruments). Field emission scanning electron microscopic (FESEM) measurement was accomplished using of FEI Quanta FEG 200 HR-SEM after coating desired carbon samples on sample stub and transmission electron microscopic (TEM) images were recorded with a JEOL (JEM-2100 Plus) operating at 200 kV by coating test carbon sample on a copper grid.

2.3. Electrochemical characterization

High-pure stainless steel foil with a thickness of 0.04 mm (SS 304, Alfa Aesar) was thoroughly polished with a emery paper followed by washing with pure water and acetone, and subsequently dried up in an oven at 60 °C for 3 h. The working electrodes were constructed by modifying the foil (geometrical surface area of ~ 1.0 cm^2) with slurry containing 85 wt% of as-synthesized porous activated carbon, 10 wt% of Super P carbon (Alfa Aesar) and 5 wt% of polyvinylidene difluoride

(PVDF) (Alfa Aesar) in N-methyl-2-pyrrolidone solvent (NMP) (Alfa Aesar) and then dried at 120 °C under vacuum for 12 h. The mass of the active electrode materials was calculated to be ~ 1.2 mg/cm^2. The electrochemical properties were evaluated in a three-electrode configuration by using platinum (Pt) as a counter electrode, saturated calomel electrode (SCE) as a reference electrode and 1 M H$_2$SO$_4$ as an electrolyte in the potential window of $-0.3 - 0.9$ V. Whereas coin type symmetrical supercapacitor was assembled in an argon-filled glove box (M'BRAUN, Germany) with < 1.0 ppm of oxygen and moisture content. LiPF$_6$ salt dissolved in EC:DMC solvents (1:1 vol%) was used as an electrolyte and polypropylene was used as a separator in symmetrical supercapacitors. Electrochemical measurements were performed in the potential window of 0.0–2.5 V using a Biologic workstation (VSP-300). The electrochemical impedance spectroscopic (EIS) measurement was performed in the frequency range of 10 mHz–100 kHz. Discharge specific capacitance (SC) of the activated porous carbon material was estimated by means of the following equation for three electrode system:

$$SC = I \, t \, / \, (m \, \Delta V) \tag{1}$$

And the specific energy (SE) and specific power (SP) of a supercapacitor were estimated using the following equations [41,42].

$$SE = (It\Delta V/m)/2 \tag{2}$$

$$SP = (I\Delta V/m)/2 \tag{3}$$

Where, "I" refers the current in ampere used for charge/discharge cycling, "t" presents the time required for discharge, "m" means the mass in grams of the active carbon material and "ΔV" is the operating potential window in 'volt' for the charge or discharge. Discharge specific capacitance (SC) value of the porous activated carbon electrode for two electrode system was measured using the following equation [43]:

$$SC = 4 \, I \, t/m\Delta V \tag{4}$$

The values of energy density and power density for the as-developed activated porous carbon (NAC) material were estimated using the following equation [44,45],

$$\text{Energy density} = 1/2C * \Delta V^2 * 1/3.6 \tag{5}$$

$$\text{Power density} = E/\Delta t * 3600 \tag{6}$$

Where, "C" represents the specific capacitance, "ΔV" refers the potential window, "E" presents the energy density and "t" the discharge time in seconds.

3. Results and discussion

As a class of biomass, ICR mainly contains wheat flour which has high surface area, large surface to volume ratio, and huge porosity. Schematic representation for the synthesis NAC material from food waste of ICR is presented in Scheme 1. The hierarchical nanoporous activated carbon material was produced without using any sacrificial templates simply by thermal annealing (carbonization) and followed by chemical activation process at 750 °C. Fig. 1a shows the X-ray diffraction patterns of the NAC materials obtained prior to- and after KOH activation process, indicating a low degree of crystallinity. The characteristic diffraction peaks observed at 25.0 and 43.0 2θ corresponding to (002) and (100) planes indicate a typical layered structure with short-range order. As shown in Fig. 1a, the crystallinity of the NAC

Scheme 1. Schematic illustration of the synthesis of the NAC materials.