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High electrochemical capacitor performance of oxygen and nitrogen enriched activated carbon derived from the pyrolysis and activation of squid gladius chitin

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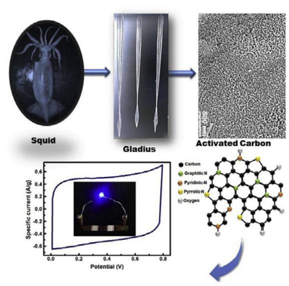
HIGHLIGHTS

- A novel O- and N- doped activated carbon is derived from squid gladius chitin.
- The microporous carbon is used for the fabrication of supercapacitor electrodes.
- The supercapacitors demonstrated remarkable electrochemical performances.
- The device shows long stability of ~100% after 25,000 charge/discharge cycles.

GRAPHICAL ABSTRACT



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ABSTRACT

Activated carbon containing nitrogen functionalities exhibits excellent electrochemical property which is more interesting for several renewable energy storage and catalytic applications. Here, we report the synthesis of microporous oxygen and nitrogen doped activated carbon utilizing chitin from the gladius of squid fish. The activated carbon has large surface area of 1129 $m^2 g^{-1}$ with microporous network and possess ~4.04% of nitrogen content in the form of pyridinic/pyrrolic-N, graphitic-N and N-oxide groups along with oxygen and carbon species. The microporous oxygen/nitrogen doped activated carbon is utilize for the fabrication of aqueous and flexible supercapacitor electrodes, which presents excellent electrochemical performance with maximum specific capacitance of 204 Fg^{-1} in 1 M H_2SO_4 electrolyte and 197 Fg^{-1} as a flexible supercapacitor. Moreover, the device displays 100% of specific capacitance retention after 25,000 subsequent charge/discharge cycles in 1 M H_2SO_4 electrolyte.

1. Introduction

Activated carbon derived from bio-resources such as plant and animal wastes has attracted the attention of both academic research and industries due to its potential applications in the field of catalysis and energy storage [1]. In past few decades, activated carbon from various bio-resources were effectively studied and utilized as electrode materials for energy storage systems; especially in supercapacitors (SC) [2].

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Since, the supercapacitor electrodes require a large surface area for charge storage by accumulating charge ions as an electric double layer between the electrode/electrolyte interfaces [3,4]. This can be effectively achieved through activated carbon owing to its large surface area with porous structure and additional properties like good conductivity, tunable structure, low cost and eco-friendly nature, affording more feasible for flexible or solid-state supercapacitor electrodes [5–7].

Generally, the porous activated carbon was obtained by pyrolysis of bio-waste and followed by a chemical or physical activation. The activated carbon from bio-wastes sources such as coconut shell [8], wood [9], corn [10], bamboo [11], soybean [12] etc., have been effectively used as the supercapacitor electrode materials. Even though the activated carbon shows good capacitance performance due to the origin of electric double layer capacitance, but it suffers from low energy density which hinders its wide applications [13]. Recently, efforts have been devoted to dope the carbonaceous materials with heteroatoms like O, N and S to enhance the capacitive performances by affording an additional pseudocapacitance and more wettability of the electrode materials in electrolyte [14]. Among these heteroatoms, porous nitrogen doped carbon is an interesting candidate for energy storage systems, especially in lithium ion batteries, fuel cells and supercapacitors [15–17]; since, the nitrogen dopant in carbon site enhances the conductivity and improves the charges transfer property of the material which tends to lead high charge/discharge rate and durability of the device. Moreover, the nitrogen doping can gain more active sites for effective ion adsorption and increases the capacitance of the electrodes [18,19].

In general, the incorporation of heteroatoms (O and N) into the carbon site requires an additional step like oxidation or ammoniation or pyrolysis with N rich polymers etc. [17,20–23] Recently, an alternative method has been adopted by direct pyrolysis of heteroatom rich renewable biomass into an activated carbon. Various bio-resources like clover biomass [24], egg shells [25], luffa sponge [26], silk cocoon [18], camellia oleifera shells [27] etc., have been used for the synthesis of heteroatom (O and N) containing activated carbons. Zhao et al., reported the synthesis of N-doped carbon through pyrolysis of nitrogen containing polysaccharide (chitosan a derivative of chitin) derived from biomass and demonstrated it as an efficient material for supercapacitor electrodes [28]. Chitin is a polysaccharide and naturally abundant bioresource mostly found in crustaceans, insects, annelids, molluscs, coelenterates, and zygomycetes fungi, which contain ~6.9 at. % of nitrogen from *N*-acetyl groups [29,30]. Thus, after pyrolysis of these biomasses, a considerable amount of nitrogen can be restored in the carbon network as a dopant, and leads to various possible applications. Recently, chitin based heteroatom doped activated carbon materials were derived from shrimp shells [31,32], crab shells [30] etc., and utilized as electrode materials for energy storage devices. The gladius of squid fish (squid pen) is another rich source of chitin which is treated as a bio-waste in the food processing industries. The squid gladius is an endoskeleton of the fish, so it has less impurities and requires short processing to convert into chitin than those derived from exoskeleton of shells like crab and shrimps [33]. This unexplored bio-waste (squid gladius) can be easily converted into heteroatom doped activated carbon and utilized as a potential electrode material for energy storage devices.

In this work, for the first time we carbonized squid gladius chitin into oxygen and nitrogen containing activated carbon by KOH activation process and demonstrated it as an excellent electrode material for supercapacitors. Interestingly, the squid gladius derived carbon (SGC) and KOH activated carbon (SGAC) consists 8.31 and 4.04 wt. % of nitrogen in the form of pyridinic/pyrrolic-N, graphitic-N and *N*-oxide and the SGAC have microporous large surface area of 1129 $m^2\,g^{-1}$. The symmetric supercapacitor designed using SGAC exhibited maximum specific capacitance values of 204 $F g^{-1}$ and 197 $F g^{-1}$ in 1 M H_2SO_4 electrolyte and PVA-H_2SO_4 gel polymer electrolyte respectively, with excellent electrochemical performances. The physicochemical and electrochemical properties of the SGC and SGAC have been comparatively analyzed and presented in the manuscript. In addition, the electrochemical performance of the SGC and SGAC supercapacitors in 6 M KOH electrolyte was studied and discussed in detail.

2. Materials and method

2.1. Materials

The raw material, squid gladius was collected from Noryangjin fish market, Seoul, Republic of Korea. The chemicals potassium hydroxide (KOH), sulfuric acid (H_2SO_4), hydrochloric acid (HCl) were purchased from Samchun Pure Chemicals Co. Ltd., (Korea) and Osaka Chemicals (Japan). Poly (vinyl alcohol) (PVA) molecular weight of 130,000 $g\,mol^{-1}$ was purchased from Sigma- Aldrich (USA). The stainless-steel substrate was purchased from Nilaco Ltd. (Japan). The carbon black, poly-(vinylidene fluoride) (PVDF) and *N*-methyl-2-pyrrolidone (NMP) were obtained from Alfa-Aesar (Korea).

2.2. Extraction of chitin from squid gladius

The squid gladius (length ~18.5 cm, width ~1.3 cm and thickness ~ 0.54 mm) was separated from the squid fish (*Todarodespacificus*), washed and dried at 60 °C. The dried squid gladius was ground into fine powder and used for the extraction of chitin. Initially, the protein present in the powdered gladius was removed by deproteinization using 1 M NaOH at 50 °C for 5 h. Then the light mineral contents in the sample was demineralization in 1 M HCl at room temperature for 2 h under constant stirring and the resultant chitin sample was dried at 60 °C in a hot air oven.

2.3. Pyrolysis of squid gladius chitin to SGC

The dried chitin derived from the squid gladius was directly precarbonized at 500 °C for 3 h in a tubular furnace at a heating rate of 10 °C min^{-1} under nitrogen flow (500 mL min^{-1}). Then the carbonized chitin was collected and washed with deionized water and dried overnight at 60 °C.

2.4. Preparation of SGAC from SGC

The activation process was performed by mixing the SGC sample with KOH in the ratio 1:1 and completely dried at 100 °C. Then the dried SGC: KOH sample was pyrolyzed at 750 °C for 1.5 h (optimized time and temperature) in a tubular furnace under nitrogen atmosphere (500 mL min^{-1}) at a heating rate of 10 °C min^{-1}. The resultant fine carbon powder was washed in 2 M HCl to remove K ions from the sample and washed several times in deionized water until reaches a neutral pH. Finally, the activated carbon sample was dried at 120 °C to remove the adsorbed water content.

2.5. Electrode and supercapacitor fabrications

The supercapacitor electrodes were fabricated by grounding the active materials (SGC and SGAC) (75 wt%), acetylene black (20 wt%) and polyvinylidene fluoride (5 wt%) with few drops of *N*-methyl-2-pyrrolidone solution. The obtained paste was coated over a stainless-steel (SS) substrate and gold coated polyethylene terephthalate (PET) substrate (150 nm thickness of gold was sputter coated using an Edwards Auto 306 Sputter Coater) of exposed geometric area 1 × 1 cm^2 and dried at 75 °C for 12 h. The mass of the active material present in a single electrode was ~2.5 mg. The supercapacitor (symmetric full-cell) was assembled utilizing the stainless-steel split test cell (EQ-STC) purchased from MTI Korea Ltd. The cell was assembled using a pair of sample coated SS electrodes of nearly similar weight were arranged face-to-face by sandwiching a filter paper as a separator (Whatman).