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# Biomass derived hierarchically porous and heteroatom-doped carbons for supercapacitors

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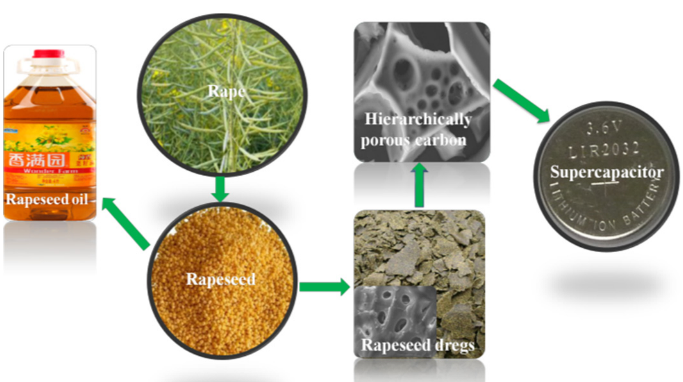
## GRAPHICAL ABSTRACT

The process of synthesis of RD-derived hierarchically porous and heteroatom-doped carbons and their applications for aqueous and organic supercapacitors.

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## ABSTRACT

In this research, Rapeseed dregs (RDs), as a byproduct of agriculture (derived from processing of rapeseed for oil production), were originally employed as a new carbonaceous precursor to synthesize hierarchically porous and heteroatom-doped activated carbons (ACs) with the activation of $ZnCl_2$ at various high temperatures. A variety of measurements have been adopted to systemically characterize the RD-derived ACs. The micro-morphology, pore structures and surface chemistry property were fully investigated by SEM, TEM, XRD, Raman, $N_2$ adsorption–desorption analysis, XPS and IR, respectively. The RD-derived ACs possess as large specific surface area as up to 1416.966 $m^2\ g^{-1}$ and the pore size distribution concentrates on 1–2, 2–5, 5–15 and 25–35 nm, indicating their hierarchically porous structures. Furthermore, electrochemical measurements including electrochemical impedance spectroscopy (EIS), galvanostatic

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charge/discharge (GCD) and cyclic voltammetry (CV) were conducted to estimate RDAC's supercapacitive performance and rate capability. The investigations illustrated that RD derived ACs reached as high specific capacitance as 170.5 and 153.2 F g$^{-1}$ at a scan rate of 5 mV s$^{-1}$ in 1 M $H_2SO_4$ and 1 M $Et_4NBF_4$/AN, respectively. In addition, the RD-derived ACs demonstrated good long-term cycling stability and more than 90% initial capacity have been retained after 6400 cycles at a large current density of 1 A g$^{-1}$.


## 1. Introduction

The high value-added reutilization of biomass has received extensive attention and gradually become a hot topic in the field of scientific research worldwide due to their merits of renewability, unique micro-structure, specific chemical composition [1,2]. Rapeseed dregs (RDs), as a byproduct of agriculture, are derived from processing of rapeseed for oil production. It is well known that China is as a leading producers of rapeseed over the world, tons of RDs are produced every year [3,4]. The main usage of RDs is employed as animal feed and fertilizer after de-toxicity, however, large percentages of original RDs are still discarded. Similar to beans, RDs are rich in protein, cellulose and lipid [4,5]. More interesting, RDs possess three-dimensional hierarchically porous structure [6,7]. Therefore, RDs are prone to be transformed into hierarchically porous and heteroatom-doped carbon materials with large surface area via heat treatment with the assistance of activating agents at inert atmosphere. More meaningful, the hierarchically porous and heteroatom-doped carbon materials are widely applied in various fields such as electrochemical energy storage and conversion [8,9], catalysis [10,11], biosensing and bioimaging [12–14]. As a result, transformation of RDs into carbons will bring about significant environmental, economic and social benefits.

Among these various applications, the new type of electrochemical energy storage device-supercapacitor is highly in demand for carbon materials which possess large specific surface area, well-developed hierarchical porous structure containing micro-, meso- and macro-pores and heteroatoms (introduction of N, S, P, B and O into the carbon framework) [15,16]. In general, three types of pores (macropores, mesopores and micropores) in hierarchical porous structure make different contributions to improving the overall performance of supercapacitor. Macropores function as the ion-buffering reservoirs to shorten the ionic diffusion distances at the internal surface of carbon materials, mesopores act as channels to facilitate the transportation of ions, while micropores provide the locations for charge accommodation. Hence, the large mesopores and macropores accelerate ion transfer, leading to high rate performance and high power density, the small mesopores and micropores offer large ion-accommodating surface area, promising a high specific capacitance and high energy density [17,18]. Furthermore, introducing heteroatom into carbon framework not only can improve the conductivity and wettability but also provide extra pseudo-capacitance caused by faradaic reactions from heteroatom in electrolytes, which can also enhance both specific capacitance and rate performance for carbon materials [17–19]. Traditionally, hierarchically porous and heteroatom-doped carbon materials are prepared by templates or carriers (to form hierarchically porous structure) followed by in situ doping or post-treatment in certain chemical environment (to incorporate into heteroatom) [20,21]. However, these general methods encounter some drawbacks such as complicated synthesis procedure, expensiveness of templates and precursors and difficulty to tune the porous structure, which seriously limit their large scale production and practical applications [15–19]. Consequently, researchers have started to pay progressive attention to utilizing environment friendly, renewable biomass or its byproducts to prepare hierarchically porous carbons and simultaneously to introduce heteroatom.

Till now, a wide variety of biomass materials have been widely adopted as the precursors to obtain hierarchically porous and heteroatom-doped carbon materials for supercapacitors including eggplant [22], bagasse wastes [17], broad bean shells [2], fungi [23], coffee beans [24], wheat straw [25], rice husk [26], tea leaves [27], watermelon [28], tobacco stems [29], Enteromorpha prolifera [30], dead leaves [31], various pollens [32], firewood [33], banana fibers[34], bamboo [35], glucose, lignin, cellulose, [36] chitosan [37], collagen [38], humic acid[39], biopolymer [40], cocoon [41], fish scale [42], tobacco rods [18], milk powder [43], animal's bones and feather [44,45], bacteria [9], human hair [46]. Most of above-mentioned biomass-based carbons possess satisfactory electrochemical capacitive performance, which is comparable to, even better than that of commercial activated carbons. However, from the viewpoint of cost-effectiveness, earth abundance of precursors and facile synthesis, some of them is difficult to realize large scale production as commercial activated carbons. Hence, more achievable, renewable, economical and high-quality biomass or its derivatives are badly in needed to meet the demand of widespread applications of carbons especially in the field of supercapacitors [47]. On the other hand, to pursue hierarchically porous structure, heteroatom-doping, large surface area, easy manipulation and facile procedure, the synthesis method is another key factor that influence the resultant carbon's physical-chemical properties.

Combing the RD speciality (Chemical composition: protein, cellulose and lipid. Texture: hierarchically porous structure.) as we described with the facile synthesis method, in this investigation, RDs mixed with excessive $ZnCl_2$ was experienced a thermal treatment in inert $N_2$ atmosphere (referred as high-temperature ionothermal reaction) to obtain hierarchically porous and heteroatom-doped carbons as shown in Fig. 1. The merits of this facile method consist in easy operation, desirable reproducibility, high output and scalable production. A variety of techniques including scanning electron microscopy (SEM), $N_2$ sorption isothermal analysis and transmission electron microscopy (TEM) were adopted to characterize carbon's porous structure and micro-morphology. Furthermore, Fourier Transform-Infrared (FT-IR) spectra, XRD, Raman spectra and X-ray Photoelectron Spectroscopy (XPS) were utilized to investigate the elements, surface groups and graphitic degree of RD-derived carbons. In addition, electrochemical measurements including cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) and electrochemical impedance spectroscopy (EIS) were carried out to estimate their capacitive behaviors in the electrolytes of aqueous (1 M $H_2SO_4$) and organic (1 M $Et_4NBF_4$/AN) solutions. The electrochemical analysis demonstrated that the resultant carbons possessed specific capacitance of 170.5 and 153.2 F g$^{-1}$ at a scan rate of 5 mV s$^{-1}$ in 1 M $H_2SO_4$ and 1 M $Et_4NBF_4$/AN, respectively. Moreover, supercapacitors based on these carbons manifested excellent rate performance and cycling life.