



# Facile synthesis of high-surface area mesoporous biochar for energy storage via *in-situ* template strategy

Yuan Gao\*, Yulin Zhang, Aimin Li, Lei Zhang

Key Laboratory of Industrial Ecology and Environmental Engineering (Ministry of Education), School of Environmental Science and Technology, Dalian University of Technology, Linggong Road 2, Dalian 116024, China



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## ABSTRACT

A novel synthetic strategy was successfully developed to fabricate mesoporous biochar with high-surface area from crab shell as carbon precursor and its natural  $\text{CaCO}_3$  as *in-situ* template. The influences of pyrolysis temperature on the pore structure were investigated via  $\text{N}_2$  adsorption-desorption isotherms and scanning/transmission electron microscope. The as-prepared biochar at pyrolysis temperature of 900 °C possessed high surface area of 634  $\text{m}^2/\text{g}$  and large mesopore percentage of 70.80%. The maximum specific capacitance of biochar electrode reached 220 F/g. The excellent supercapacitor performance of this supercapacitor was strongly attributed to the thermal decomposition of  $\text{CaCO}_3$ , producing high surface area and mesoporous structure for raw biochar.

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## 1. Introduction

Currently, tremendous attentions have been devoted to explore low-cost, environmentally friendly, and high-efficient carbon-based electrode materials for supercapacitors, such as activated carbon, carbon nanotube, carbon nanofiber and graphene [1]. As a newly arisen carbon material, biochar has attracted emerging research attentions in the recent decade, which has only been applied in soil amendment, adsorbent and catalysts. Unfortunately, biochar suffers from relatively low surface area, limiting its application in storage high-quantity energy. Besides, the performance of carbon-based electrode is not only related to its surface area but also affected by its pore size distribution. Microporous biochar-based electrodes always suffer from the disadvantageous of poor diffusivity of electrolytes into the pores due to the space confinement, leading to an unsatisfactory capacitive performance. Thus, synthesis of high-surface area and mesoporous biochar is an effective solution to address the above-mentioned issues.

On the one hand, considerable efforts have been devoted to post-treat biochar via pyrolysis or activation to improve surface area [2,3]. On the other hand, hard and soft template strategies have been used as two common approaches for synthesizing mesopore-enriched carbon materials [4,5]. In hard template method, mesoporous silica monolith as a template is required to

synthesize, then the removal of template after service has to use chemical etching with highly corrosive hydrofluoric acid. In soft template method, extra amphiphilic surfactants or block copolymers are served as additional template, while carcinogenic formaldehyde and phenol are inevitably used as precursors. Despite great efforts have been paid on these strategies, the processes are still somewhat fussy, time-consuming and costly. Herein, exploring an *in-situ* natural template from biomass waste would be more worthwhile. Niu et al. prepared porous carbons with high surface area using cattle bone as starting material and its own hydroxyapatite as natural defect mold [6]. The obtained carbon possessed high mesopore volume (1.829  $\text{cm}^3/\text{g}$ ) and excellent capacity performance (1488 mA h/g). Inspired by their work, this study aimed at using crab shell to synthesize mesoporous biochar owing to its natural high ingredient,  $\text{CaCO}_3$ .

Many researchers have proved that  $\text{CaCO}_3$  could be used as template to prepare hierarchical materials. For example, Gu et al. produced hierarchical porous carbon using micro- $\text{CaCO}_3$  as conformal template through chemical vapor deposition [7]. Yang et al. synthesized nitrogen-doped porous graphitic carbon by using melamine-formaldehyde resin as precursor and  $\text{CaCO}_3$  as template [8]. Zhao et al. prepared hierarchical disordered mesoporous carbon with formaldehyde resin as precursor and  $\text{CaCO}_3$  nanoparticle as template [9]. The shortcoming of additional  $\text{CaCO}_3$  is that they cannot fully react with precursors. Thus, the role of  $\text{CaCO}_3$  as template is not so strong as that of the natural ones in crab shell.

\* Corresponding author.

E-mail address: [gaoyuan1988@dlut.edu.cn](mailto:gaoyuan1988@dlut.edu.cn) (Y. Gao).

Crab shell (CR), a cheap and high quantity biomass waste, is composed of chitin, protein, lipid and  $\text{CaCO}_3$ . Additionally, the *in-situ* generated  $\text{CaCO}_3$  nanostructure is tightly bonded with the potential carbon precursors (i.e. chitin, protein, and lipid). Crab shell is natural reservoir of nanostructured  $\text{CaCO}_3$ , which provides a good *in-situ* sacrificial template for the formation of meso-porous structure via facile calcination and subsequent volatilization of  $\text{CO}_2$  and the removal of  $\text{CaO}$ . In this way, the mesopore-enriched biochar can be produced via direct carbonization of crab shell without any extra template or highly corrosive template-removal reagents. Benefiting from the removal of  $\text{CaCO}_3$ , many pore defects can be left, which could promote the capacitance of biochars. Thus, the motivations for this study were, one is to produce mesopore-enriched porous carbon by an *in-situ* strategy, and second is to improve the surface area of CR-derived biochar for promising electrode of supercapacitor.

## 2. Experimental section

Crab shell was collected from Bohai Beach, then washed, dried, and crushed into powder. Other reagents were purchased from DaMao, Tianjin Chemicals Ltd. In a typical synthesis procedure, 20 g of CR powder was directly heat-treated up to various temperatures from 300 to 900 °C under nitrogen. After carbonization, the samples were washed with 1 M HCl solution to remove the residues and dried at 105 °C overnight. The obtained samples were named as CSBC-300, CSBC-500, CSBC-700 and CSBC-900. To compare the effect of natural  $\text{CaCO}_3$  nanostructure on the porous property and prove the validity of *in-situ* template strategy, an acid-pretreatment process before carbonization was performed by soaking CR powder with 1 M HCl solution overnight. Afterwards, the acid-CR powder was washed several times with distilled water, and heat-treated at temperature of 900 °C. The obtained samples were designated as ACSBC-900. The procedure for biochar production is shown in Fig. 1.

The pyrolysis property was measured using a thermogravimetric analyzer (TG/DAT6300, Seiko Instruments Inc-SII). The porous carbon was characterized by scanning electron microscopy (S-4800, Hitachi), nitrogen adsorption-desorption apparatus (AS1, Quantachrome), and Fourier transform infrared spectra

(Nicolet-20DXB, Thermo Nicolet Nexus). The electrochemical measurements were performed in three-electrode system using Hg/HgO as reference electrode, platinum foil as counter electrode, and 6 M KOH aqueous solution as electrolyte on a CHI 760E electrochemical workstation. The working electrode was prepared by uniformly mixed CSBC-900 powder (80%), PTFE (10%) and 10% carbon black (10%). The cyclic voltammetry tests were conducted between  $-1.0$  and  $0$  V in the scan rate range from 10 to 100 mV/s. The galvanostatic charge/discharge tests were performed at current densities from 0.2 to 10 A/g. The cycling stability was investigated via galvanostatic charge/discharge tests at a current density of 5 A/g.

## 3. Results and discussion

$\text{N}_2$  adsorption-desorption curves of biochars are displayed in Fig. 2a. It can be seen that almost no mesopores were present in CSBC-300 and ACSBC-900. In contrast, CSBC-500, CSBC-700, and CSBC-900 exhibited type IV adsorption-desorption isotherms with remarkable hysteresis loops at the relative pressure above 0.4, indicating the presence of mesopores. As shown in Fig. 2b, the mesopore size distribution of CSBC-900 centered approximately 3 nm and 6 nm. The pore characteristics are summarized in Table 1. Increasing pyrolysis temperature was beneficial to increase the surface area, especially beyond 700 °C. The surface area and mesopore percentage of CSBC-900 were 634  $\text{m}^2/\text{g}$  and 70.80%. However, ACSBC-900 only possessed a surface area of 55  $\text{m}^2/\text{g}$ . TGA curve of crab shell displayed three decomposition stages (Fig. S1). The first stage occurred between room temperature to 300 °C, which was attributed to evaporation of water. The second stage presented in the temperature range of 300–700 °C due to the degradation of chitin. The third stage was observed within the range of 700–900 °C, which was derived from the decomposition of  $\text{CaCO}_3$  [10]. The chitin, protein, lipid molecules are interpenetrated with  $\text{CaCO}_3$  to form inter-connected organic network in crab shell. After carbonization at 900 °C, the volatilization of  $\text{CO}_2$  and removal of  $\text{CaO}$  by HCl-etching produced a lot of interconnected mesoporous carbon framework. Many previous investigations have proved that  $\text{CO}_2$  is an effective physical activating agent to produce mesoporous carbons [11]. In this study, one of the advantages is that

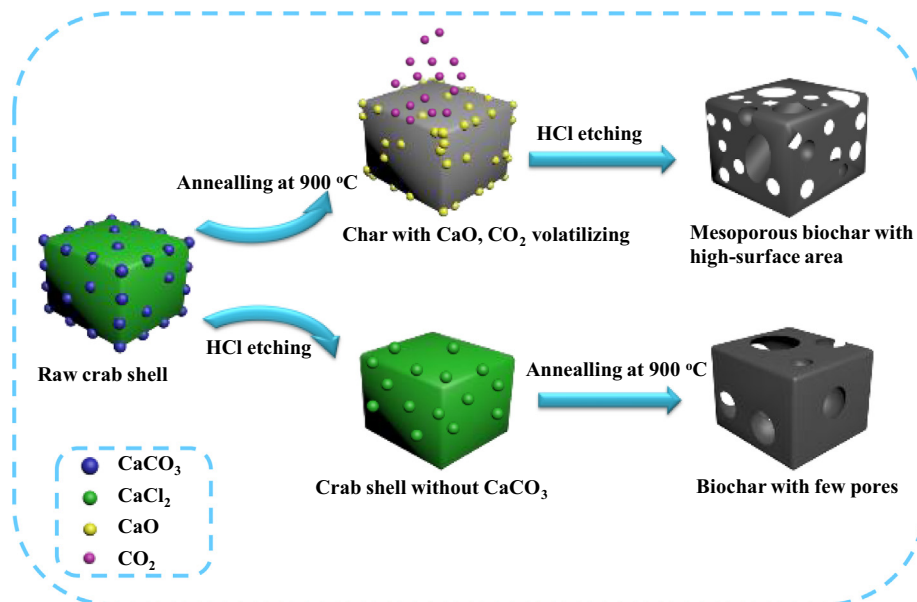


Fig. 1. Schematic illustration of production procedure for biochar from crab shell.

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