



# Porous graphitic carbon materials prepared from cornstarch with the assistance of microwave irradiation



Hong Lei <sup>a,\*</sup>, Yuhao Wang <sup>b</sup>, Jichuan Huo <sup>c</sup>

<sup>a</sup> Engineering Research Center of Biomass Materials, Ministry of Education, Southwest University of Science and Technology, Mianyang 621010, PR China

<sup>b</sup> School of Material Science and Engineering, Southwest University of Science and Technology, Mianyang 621010, PR China

<sup>c</sup> Analytical and Testing Center, Southwest University of Science and Technology, Mianyang 621010, PR China

## ARTICLE INFO

### Article history:

Received 30 June 2013

Received in revised form

29 January 2015

Accepted 6 February 2015

Available online 17 February 2015

### Keywords:

Porous carbon

Graphitization

Microwave

Biomaterials

Starch

## ABSTRACT

Porous graphitic carbon materials (PGCs) have attracted great interest because of their properties shown in fields such as catalyst supports, electrochemical double layer capacitors, Li-ion batteries, etc. Biomass is a promising resource to produce PGCs, as it is cheap, eco-friendly and renewable. Using cornstarch as raw material, two PGCs (PGC-1 and PGC-2) were prepared by combining microwave-assisted catalytic graphitization and chemical activation. PGC-1 was made from new gelatinized starch and the other (PGC-2) from retrograded starch. The former was mainly composed of graphitic nanocoils. The latter, on the other hand, was more likely to be a product of activated loose packing carbonaceous sheets. Narrowly distributed hierarchical pores were observed in the PGCs. Both of the PGCs were partly graphitized and had large surface areas (353 m<sup>2</sup>/g for PGC-1 and 686 m<sup>2</sup>/g for PGC-2). Cyclic voltammetry and electrochemical impedance spectroscopy test showed that they had good capacitive property.

© 2015 Elsevier Inc. All rights reserved.

## 1. Introduction

Porous carbon materials have long been researched all over the world, because of their chemical and mechanical stabilities, electronic and thermal conductivities, and adsorption capability. They have potential to be applied in gas storage, gas separation, catalyst supports, specific adsorbents, and electrochemical double layer capacitors or Li-ion batteries, etc [1,2]. As combining good electronic conductivity with a large and accessible surface area, porous carbons with graphitic structure are superior to amorphous carbons in certain emergent applications, e.g. as electrodes in double-layer electrical capacitors or as catalyst supports in low-temperature fuel cell systems [3]. Thus, porous graphitic carbon materials (PGCs) have recently attracted great interest.

PGCs are mainly prepared by two methods: the conventional high temperature treatment (>2500 °C) and catalytic graphitization. The former is energy consuming, and usually leads to the surface area shrinkage of the obtained material. In contrast, the temperature of graphitization can be reduced to ~1000 °C or lower with the aid of catalysts (i.e. Fe, Co, Ni, Mn, etc). As the porosity of

the obtained materials greatly depends on their precursors, catalytic graphitization combining template technique has recently been adopted widely to obtain materials with both graphitic nanostructure and various porosities [4–6]. The template technique includes hard template [7,8] and soft template [9–11] methods. Besides, some other methods were also reported, such as foaming technique [12], microwave plasma enhanced chemical vapor deposition [13], combination of chemical activation and catalytic graphitization [4], pyrolysis of ammonium bicarbonate [14], and so on [15]. However, the precursors in these reports are exclusively carbonized and graphitized in furnace, which requires hours of heat treatment under inert gas atmosphere. Wang et al. [16] developed a microwave-assisted method to transform wood, cotton and filter paper, which containing cellulose, hemicellulose and lignin, into porous graphitic carbon nanostructures within just a few minutes. The method is energy saving and needs much less inert gas.

Biomass is a promising resource for the production of carbonaceous materials, as it is cheap, eco-friendly and renewable. The report about PGCs from biomass with microwave irradiation is very limited. Herein, we prepared two PGCs from cornstarch. The starch was pretreated via simple physical methods: gelatinization and retrogradation. Starch gelatinization is a process disordering the starch molecules. It breaks down the intermolecular bonds of starch molecules in the presence of water and heat. When native

\* Corresponding author. Tel.: +86 816 2419209; fax: +86 816 2419201.

E-mail address: [honglei117@163.com](mailto:honglei117@163.com) (H. Lei).

starch is heated and dissolves in water, the crystalline structure of amylose and amylopectin molecules is lost. Retrogradation, however, is just opposite to gelatinization. If the gelatinized starch is cooled or left at lower temperature for a long enough time, the linear molecules (amylose and linear parts of amylopectin molecules) retrograde and rearrange themselves again to a more crystalline structure. The linear chains place themselves parallel and form hydrogen bridges. Using gelatinized and retrograded starch as precursors, we prepared the PGCs by combining microwave-assisted catalytic graphitization and chemical activation. Results proved that the structure and morphology of the carbonaceous materials were affected by the molecular arrangement of the precursors, even though the chemical composition of the precursors was not changed. It also indicated that starch was a promising material to produce carbonaceous materials with different structure and morphology. The prepared PGCs with narrowly distributed hierarchical pores showed good electrochemical property. They have potential to be applied in many areas, like separation, catalyst supports, specific adsorbents or electrode material.

## 2. Materials and methods

### 2.1. Materials

Cornstarch (amylose content, ~25%) was purchased from the local market of Mianyang (Sichuan, China). Other chemical reagents used in this study, ethanol (95%),  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (AR),  $\text{ZnCl}_2$  (AR), pyrrole (AR), concentrated hydrochloric acid (AR), were purchased from Tianjin Kermel Chemical Reagent Co., Ltd. (Tianjin, China).

### 2.2. Experimental procedure

The two PGCs prepared in this study were denoted as PGC-1 and PGC-2. The only difference in the preparation of PGC-1 and PGC-2 was that different starch precursors were used. New gelatinized cornstarch was used to prepare PGC-1, and cornstarch after gelatinization and retrogradation was used to prepare PGC-2. The detailed procedure was as follow.

#### 2.2.1. Gelatinization

The cornstarch was suspended in distilled water in a weight ratio of 1:10. Then, the cornstarch was gelatinized under continuously agitation at 75 °C in a water bath. After 1 h of gelatinization, the gelatinized starch was freeze-dried, and the precursor for PGC-1 was prepared.

#### 2.2.2. Retrogradation (this step was only for PGC-2)

The precursor for PGC-2 was prepared by putting the freeze-dried starch in a desiccator and keeping it at ambient temperature for two weeks.

#### 2.2.3. Preparation of PGCs

Ethanol solution (10 mL) containing 0.81 g of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (graphitization catalyst) and 1.00 g of  $\text{ZnCl}_2$  (activation agent) was firstly prepared. Then, 1.00 g of the as prepared precursor was impregnated in the ethanol solution. After 24 h of impregnation, the solution was filtered and the precursor was oven-dried at 80 °C. Then the Fe-impregnated precursor was exposed to pyrrole vapor in a sealed flask for vapor-phase polymerization. Herein, the iron species catalyzed the polymerization of pyrrole, and they also served as the catalyst for the pyrolysis of carbon in the subsequent step [16]. Polypyrrole, on the other hand, is a conducting polymer used as a microwave absorber. It will be burned off in the pyrolysis process. The vapor-phase polymerization was operated at room temperature for three days. The obtained composite was put in a

ceramic crucible, which was then filled with nitrogen gas and capped. The composite was carbonized and graphitized with the assistance microwave irradiation in a microwave oven (Galanz WG700TL 2011-K6, 700 W, 2450 MHz) for 5 min. After removing the Fe and Zn species with concentrated hydrochloric acid, washing the product with distilled water to neutral and oven-drying at 120 °C, the final product was produced.

### 2.3. Characterization

The morphology and microstructure of the PGCs were studied by scanning electron microscope (SEM, S440, Leica Cambridge, Ltd., England) and transmission electron microscope (TEM, Libra 200FE, Carl Zeiss SMT Pte Ltd). X-ray diffraction (XRD) patterns were obtained on an X'Pert PRO (PANalytical B.V.) operating at 40 kV and 40 mA, using  $\text{Cu K}\alpha$  radiation ( $\lambda = 0.154$  nm). The dimension perpendicular to the basal plane of graphite ( $L_c$ ) and plane spacing  $d_{002}$  of the PGCs were calculated according to literature [17]. The PGCs were also characterized by thermogravimetric-differential scanning calorimetry (TG-DSC) (Q200, TA instruments, US) in an air flow (flow rate: 50  $\text{cm}^3/\text{min}$ , heating ramp: 5 °C/min). The Raman spectra were recorded with an InVia Raman microscope (Renishaw). The radiation source was a laser operating at a wavelength of 514 nm. Nitrogen adsorption-desorption isotherms of the PGCs were collected at 77 K using  $\text{N}_2$  adsorption analyzer (Auto-sorb-1MP, Quantachrome). The specific surface area, pore size distribution (PSD) and total pore volume were ascertained by Density Functional Theory (DFT) model. The DFT software available from Quantachrome was used for calculations. The cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were tested in an electrochemical workstation (CHI-760C, China) using three-electrode system in 6 mol/L KOH solution. The electrode for CV and EIS test was prepared by pasting the mixture of PGC, polytetrafluoroethylene (PTFE) and carbon black (8:1:1 in weight ratio) on a nickel foam (1 cm  $\times$  1 cm). The gravimetric capacitance ( $C_g$ ) and area capacitance ( $C_s$ ) of the electrode were calculated according to Eq. (1) and Eq. (2) as previous report [18,19]:

$$C_g = \left( \int IdV \right) / (vmV) \quad (1)$$

$$C_s = C_g / S \quad (2)$$

where  $I$  is the response current density,  $V$  is the potential,  $v$  is the potential scan rate,  $m$  is the mass of active materials and  $S$  is the specific surface area of active materials, respectively.

## 3. Results and discussion

### 3.1. Structural characterization

Fig. 1 shows the SEM images of the gelatinized cornstarch right after freeze-drying (Fig. 1a), gelatinized cornstarch after retrogradation (Fig. 1b), PGC-1 (Fig. 1c) and PGC-2 (Fig. 1d). As shown in Fig. 1a, the fresh dried cornstarch after gelatinization is composed of many scattered flakes. The planar size of the flakes is about 30–50  $\mu\text{m}$ . Some aggregates of the flakes can also be observed. The insert of Fig. 1a illustrates one of them. After thorough retrogradation, the starch molecules rearranged. The flakes transformed to starch blocks (Fig. 1b). Besides the morphology transformation, the structure of the gelatinized starch also changed with retrogradation. Fig. S1 (Supporting information) shows the XRD patterns of the new gelatinized cornstarch and the retrograded cornstarch. It can be seen that the retrograded cornstarch has a stronger

Download English Version:

<https://daneshyari.com/en/article/6533001>

Download Persian Version:

<https://daneshyari.com/article/6533001>

[Daneshyari.com](https://daneshyari.com)