Converting biowaste corncob residue into high value added porous carbon for supercapacitor electrodes

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HIGHLIGHTS

- Corncob residue was used to prepare porous carbon for supercapacitor electrodes.
- Green and low-cost steam activation without pre-carbonization was used.
- The obtained porous carbon achieves high surface area and high yield after ash-removal.
- The porous carbon exhibits a high capacitance of 314 F g^{-1} in 6 M KOH electrolyte.
- No capacitance decay was observed after 100,000 cycles for a symmetrical cell.

GRAPHICAL ABSTRACT

A high value added porous carbon was obtained from a corncob residue, which shows a superior capacitive performance compared to those polymer-based synthetic carbons as electrode material for a supercapacitor. The corresponding symmetrical cell shows a superb cycling stability. Almost no capacitance decay was observed after 100,000 cycles.
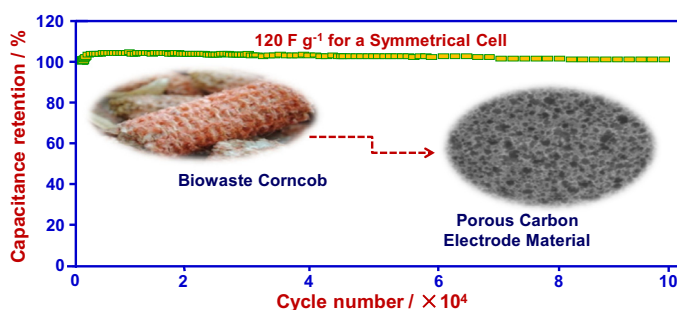
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ABSTRACT

In this report, corncob residue, the main by-product in the furfural industry, is used as a precursor to prepare porous carbon by a simple and direct thermal treatment: one-step activation without pre-carbonization. As a consequence, the corncob residue derived porous carbon achieves a high surface area of 1210 m^2 g^{-1} after ash-removal. The carbon material has the advantages of low cost and low environmental impact, with a superior electrochemical performance compared to those polymer-based synthetic carbons as electrode material for a supercapacitor. The carbon electrode exhibits a high capacitance of 314 F g^{-1} in 6 M KOH electrolyte. The corresponding sample also shows a superb cycling stability. Almost no capacitance decay was observed after 100,000 cycles. The excellent electrochemical performance is due to the combination of a high specific surface area with a fraction of mesopores and highly stable structure.

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1. Introduction

Electrical double layer capacitors (EDLC), also called supercapacitors, as a class of state-of-the-art energy storage devices, have been attracting significant research interest lately due to their wide range of applications in electrical vehicles, digital devices, pulsing techniques, etc (Choi et al., 2012; Dyatkin et al., 2013). The storage of electrical energy in supercapacitors is based on the electrostatic attraction of the opposite charges occurred on a double-layer at the electrode/electrolyte interface. Thus, supercapacitor is effective for instantaneous charge–discharge of

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large current supplies, compared to redox reaction based batteries. It exhibits a higher specific power ($\sim$10 kW kg^{-1}) and longer cycle life ($\sim$100,000 cycles) compared with other rechargeable electrochemical energy storage devices, such batteries and fuel cells.

Carbon-based materials are currently pursued as supercapacitor electrodes due to their large surface area, high electrical conductivity and good capacitive performance (Jiang et al., 2013; Zhang and Zhao, 2009). Considering the demand for sustainable eco-friendly resources and process, more and more attention has been focused on transforming biomass into valuable carbon materials, due to abundance and low cost of biomass precursors, such as beer waste (Hao et al., 2014), human hair (Saravanan and Kalaiselvi, 2015), nut shells (Xu et al., 2014), plant leaves (Biswal et al., 2013), pollens (Zhang et al., 2013), cotton stalk (Chen et al., 2012) and sugar cane bagasse (Rufford et al., 2010).

According to the recent report from United States Department of Agriculture (USDA), global corn production for 2013/14 reached 989.2 million metric tons. Assuming that all current corncobs are collected, 41.1–54.7 million metric tons of corncobs are annually available. As a widely available and environmentally friendly biomass, agricultural residue, corncob has been employed for the large-scale production of biofuels and varieties of high value added chemicals (Li et al., 2010; Mao et al., 2013). For example, using corncobs as the raw feedstock can product furfural, one of the most universal industrial chemicals (Li et al., 2014; Oh et al., 2013; Zhang et al., 2014). A million tons of corncob residues (by-product from the process of furfural production) are generated. It has been estimated that around 12–15 metric tons of residue is obtained after 1 metric ton of furfural is produced. An average of 23 million metric tons of corncob residues is available annually for alternative uses in China (Sun et al., 2011). Despite their abundance, the investigations on how to transform corncob residue into valuable products are still very limited. It is necessary to find green and simple solutions to turn such a significant amount of biomass residue into high value added materials. It has been reported that corncob residue can be used to prepare porous carbons for water pollutants removal and gas separation after chemical activation or a combination with microwave irradiation (Hou et al., 2013; Sun et al., 2012).

Corncob residue mainly composes of lignin and cellulose (Mamman et al., 2008; Zeitsch, 2000). Lignin is a three-dimensional, highly cross-linked poly-phenolic polymer without any ordered repeating units. Cellulose is a polysaccharide consisting of a linear chain of several hundred to many thousands of linked D-glucose units, which is organized into micro-fibrils surrounded by hemicellulose and encased inside a lignin matrix. The highly heterogeneous of corncob residue can cause preferential etch one or several of the phases in the process of pyrolysis and activation. Therefore, such multi-phase tissue is an ideal precursor to achieve porous carbon with a high porosity.

The conventional physical activation process is a two-step process: (i) pyrolysis in an inert atmosphere (usually nitrogen) of the precursor normally at 400–900 °C to eliminate the bulk of volatile matter; (ii) partial gasification using an oxidizing gas at 350–1000 °C to develop the porosity and surface area. The porous structure of obtained porous carbons depends on precursor, the temperature and degree of activation. Although this process has been sufficiently studied (Sevilla and Mokaya, 2014), the regimes of activation for different raw materials still requires optimization.

Considering the environmental concern and energy consumption, it is still a challenge to develop an easy and benign method to prepare porous carbons from biowaste corncob residue. Meanwhile, corncob residue derived porous carbon for supercapacitor electrodes was rarely reported. In this work, a one-step activation process is demonstrated for the preparation of porous carbons from corncob residue. The porous carbons can be made

with high surface area up to 1210 m^2 g^{-1}, and exhibit a high capacitance of 314 F g^{-1} at a scan rate of 5 mV s^{-1}, when they were used as an electrode material for supercapacitors. The capacitance is still 259 F g^{-1}, even at a high scan rate of 100 mV s^{-1}. The capacitance retention is as high as 82%. Almost no capacitance decay was observed after 100,000 cycles. The maximum energy density in aqueous and organic electrolyte is 6.8 Wh kg^{-1} and 17 Wh kg^{-1}, respectively. Such a remarkable performance shows that corncob residue derived porous carbon is a promising material for commercial supercapacitors. This study also opens a new approach for the preparation of high value added products from biowaste.

2. Methods

2.1. Materials

Corncob residues were obtained from a continuous acid hydrolysis process of corncob-to-furfural. Before processing, the corncob residue was water-rinsed to remove the residual acid, dried at 90 °C overnight, and then sieved for irregular granules with the size of ca. 150–250 μm. KOH (Sinopharm Chemical Reagent Co., Ltd., China, AR) was used as received without any further purification. Distilled water was used to prepare solutions and wash samples.

2.2. Proximate analysis of corncob residue

The proximate analysis of the corncob residue was carried out to estimate the characteristics. The moisture content was determined as the weight loss in an air oven at 110 °C until a constant weight. A silica crucible and a muffle furnace were used to estimate ash (heating up to 815 °C for 1 h) and volatile matter (heating up to 900°C for 7 min) contents. Fixed carbon content was calculated by the difference. All analyses were performed in triplicate.

2.3. Sample preparation

In a typical one-step activation process, i.e., steam activation without pre-carbonization, was conducted by directly activating corncob residues (CR) at 750, 800 or 850°C. The obtained carbons were accordingly denoted as CR-x, where x represented the activation temperature. CR-750, CR-800 and CR-850 were prepared by heating the raw material to a set activation temperature (750, 800 or 850°C) in a N$_2$ atmosphere, and then immediately switched to steam/N$_2$ at this temperature and maintained for 45 min. The steam used was generated by a steam generator at a constant 200 °C and carried into the reactor with nitrogen carrier gas.

CR-850 was further treated by ash removal with acid soaking, subsequent alkali immersing, deionized water washing and drying. The obtained sample was denoted CR-850-RA. For comparison, a control simple was prepared firstly by a pre-carbonization, which was heated up to 350 °C for 1 h. Subsequently, the sample was heated to 850 °C and activated by steam for 45 min (denoted CR-CA-850). All heating rates in the experiments are 5 °C min^{-1}.

2.4. Characterization

Thermo gravimetric analysis was performed in a temperature range of 25 °C to 800 °C under N$_2$ with a heating rate of 10 °C min^{-1} using a STA 449 F3 Jupiter thermo gravimetric analyzer (NETZSCH). Scanning electron microscopy (SEM) was carried out with a Hitachi S-4800 instrument. Nitrogen adsorption/desorption isotherms were measured with a Micromeritics TriStar 3000 physisorption analyzer. Prior to the test, the samples were degassed under vacuum at 200 °C for at least 4 h. The Brunauer–Emmett–Teller