Industrial Crops and Products 65 (2015) 216–226

Contents lists available at ScienceDirect

Industrial Crops and Products

journal homepage: www.elsevier.com/locate/indcrop

Hydrothermal preparation of highly porous carbon spheres from hemp (*Cannabis sativa* L.) stem hemicellulose for use in energy-related applications

Yong Wang, Ru Yang*, Min Li, Zijian Zhao

State Key Laboratory of Chemical Resource Engineering, Beijing Key Laboratory of Electrochemical Process and Technology for Materials, Beijing University of Chemical Technology, Beijing 100029, China

ARTICLE INFO

Article history:
Received 18 August 2014
Received in revised form 1 December 2014
Accepted 4 December 2014

Keywords:
Hemicellulose
Hemp stem
Carbon sphere
Activation
Supercapacitor
Gas absorption

ABSTRACT

This work provides a new route for high-value-added utilization of hemicellulose extracted from agricultural crops. Hemp stem hemicellulose is chosen as precursor to prepare well-shaped carbon spheres with large surface area of up to 3062 $m^2 g^{-1}$ by an improved low-temperature hydrothermal carbonization method and KOH activation. A pre-carbonization strategy before activation is also employed to keep activated carbons in perfectly spherical morphology even at a high KOH/carbon ratio 5/1. The influence of KOH/carbon ratio on the structure, surface chemistry and application performance is systematically investigated. Due to abundant micropores and ample oxygen functionalities, the samples can achieve a high capacitance of 318 $F g^{-1}$ as electrode material in supercapacitors. The plentiful micropores also lead to excellent CO_2 and CH_4 adsorption capacities at ambient pressure and 0 °C. Hemicellulose-derived activated carbon spheres should be potentially sustainable materials applied in energy and environmental areas.

1. Introduction

Activated carbon spheres are attractive functional materials applied in blood purification, chemical protection, catalyst supports, gas storage and supercapacitor electrodes due to their uniformity, high mechanical strength, high thermostability, good fluidity, low pressure drop, large packing density, high micropore volume and large specific surface area (Romero-Anaya et al., 2014; Li et al., 2011a; Zhang et al., 2014). In particular, the regularly spherical shape can benefit the capacitive performance of supercapacitors because the homogeneous package can decrease the resistance of electrolyte diffusion, and the space between the spheres can make the electrolyte accessible to the electrode, both of which help to efficiently form the electric double layer (Du et al., 2010).

Pitch and synthetic ploymers are conventional precursors for carbon spheres, but with the progressive depletion of fossil resources, the abundant, renewable and inexpensive biomass becomes promising alternative. Hydrothermal carbonization (HTC) is an environmentally friendly and effective process employed to convert low value and widely available biomass into spherical carbon, in which carbohydrates treated at relatively low temperature (160 < T < 220 °C) in water in an autoclave can provide carbonaceous spheres after hydrolysis, dehydration, polymerization, and aromatization (Baccile et al., 2009; Titirici and Antonietti, 2010). In general, monosaccharides and disaccharides can be easily transformed into carbon spheres at higher than 160 °C, while polysaccharides need a temperature of around 200 °C. Even over 220 °C is required for cellulose forming well-shaped carbon spheres because the microcrystalline structure and intermolecular hydrogen bonds of cellulose holding the polymeric chains firmly together are hard to break (Sevilla and Fuertes, 2009). To date, various pure carbohydrates including glucose, sucrose, starch, cellulose and cyclodextrin have been extensively studied (Hu et al., 2010). It is very worthwhile to obtain carbon spheres from directly hydrothermal conversion of crude biomass instead of clean saccharides; however, only those "soft" plant tissues without an extended crystalline cellulose scaffold can lose their original structure, forming globular carbonaceous nanoparticles, and "hard" plant tissues can not form spheres (Hu et al., 2010). Therefore, crude biomass including various agricultural and forest residues are usually not for spherical carbon but for irregular-shaped activated carbon

* Corresponding author. Tel.: +86 10 64436736; fax: +86 10 64436736.
E-mail address: ruyang@mail.buct.edu.cn (R. Yang).

http://dx.doi.org/10.1016/j.indcrop.2014.12.008
0926-6690/

particles through direct pyrolysis and activation (Liu et al., 2014; Elmouwahidi et al., 2012; Karthikeyan et al., 2014).

To utilize crude biomass for carbon spheres, hemicellulose, as a kind of "soft" tissue, deserves our attention. Hemicellulose is a major constituent in the cell wall of lignocellulosic biomass, interconnected together with cellulose by physical intermixing and linked to lignin by covalent bonds (Freudenberg, 1965). It accounts for generally 25–30% of lignocellulosic biomass and has a much lower degree of polymerization compared with that of cellulose. Hemicellulose is characterized as a complex heteropolysaccharide mainly consisted of xylose, glucose, arabinose, galactose, mannose and uronic acid, and can be easily isolated by well-understood methods for producing chemicals and biofuels, in addition to traditional application in paper industry (Peng et al., 2012; Garde et al., 2002; Liu et al., 2012; Xing et al., 2011; Guo et al., 2012). However, there are very few reports on applying hemicellulose to preparation of functional carbon materials, although carbons derived from sustainable biomass are current research hotspots. In view of the above, preparation of carbon spheres by HTC of extracted hemicellulose should be an effective route for high-value-added utilization of lignocellulosic biomass, especially those agricultural wastes.

As commonly observed for HTC products, the hydrothermal carbon spheres have no relevant porosity, which hinders their potential application for gas adsorption and energy storage. To introduce porosity within the structure, KOH chemical activation is employed as a strategy to develop micropores in carbohydrate-derived carbon spheres. Sevilla et al. (2011b) prepared porous carbons from KOH activation of hydrothermally carbonized renewable resources, such as glucose, starch, cellulose and sawdust, but found that activation caused a morphological change. All KOH-activated samples exhibited irregular shaped particles, regardless of the hydrochar precursor. Li et al. (2011a) reported a KOH-activated carbon spheres prepared from glucose with perfectly spherical shapes and with a specific surface area of 1283 $m^2 g^{-1}$. Recently, Romero-Anaya et al. (2014) have studied the activation process of carbohydrate-derived carbon spheres with different activating agents, and found that KOH activation caused destruction of the spheres when KOH/carbon ratio was higher than 4/1 although a large surface area of over 3000 $m^2 g^{-1}$ was obtained. Falco et al. (2013b) have produced HTC carbon spheres from hydrolysis products of spruce and corncob at 200 °C, and also declared that KOH activation resulted in a complete disruption of spherical morphology. They speculated that such disruption may be caused by the meltdown of HTC products with a low degree of crystallinity in the activation process.

In this study, carbon spheres with good morphology and simultaneously with a large surface area of 3062 $m^2 g^{-1}$ are successfully prepared from hemicellulose extracted from the stem of *Cannabis sativa* L. *Cannabis sativa* L., an annual herbaceous plant of Cannabaceae family known as "hemp", is one of the oldest crops in the world. It is cultivated mostly in the EU, Central Asia, Philippines and China (Zhang et al., 2013). In its scientific name, L. stands for Linnaeus, and indicates the authority who first named the species. The bast of hemp is traditionally used for fiber production, and the seed is for oil, while hemp stem, as an agricultural residue, is of little use. Hemp can supply over 20 ton of dry matter per hectare, most of which are stems (González-García et al., 2010). Hemp stem consists of about 65% woody core, and the core contains 40–48% cellulose, 18–24% hemicellulose and 21–24% lignin (Gümüşkaya et al., 2007). It is a huge waste and an enormous pressure on the environment if hemp stem is burnt as low-rank fuel. Preparation of porous carbon materials from hemp gains more and more attentions. For instance, porous carbon nanosheets with outstanding performance in supercapacitors were prepared from hydrothermal carbonization and KOH activation of hemp bast (Wang et al., 2013). Super high-surface-area carbon powders with irregular shapes were produced from crude hemp stem (Yang et al., 2012). Despite those efforts, the development of new utilization of hemp will make perfect sense.

Extraction of hemicellulose for preparation of regular-shaped activated carbons provides a promising way of high-value-added utilization of hemp stem. Two improved strategies are attempted in the preparation process. Firstly, during HTC, dilute sulfuric acid is chosen as catalyst to accelerate the hydrolysis, dehydration and aromatization of hemicellulose at a lower temperature. Secondly, a pre-carbonization step which can enhance the crystallinity of HTC products is employed to avoid carbon spheres being powdered in the activation process. The influence of KOH/carbon ratio on the structure and surface chemistry of carbon spheres is systematically discussed. Electrochemical performance in supercapacitors and adsorption capacities of CO_2 and CH_4 are also evaluated. Hemp stem hemicellulose-derived carbon spheres should be potentially sustainable materials applied in energy and environmental areas.

2. Materials and methods

2.1. Preparation of materials

Hemp stems, taken from "Yunma 1" after the hemp harvest in Menghai County, Xishuangbanna Dai Autonomous Prefecture, Yunnan Province of China, were smashed into powder (400 mesh). Hemicellulose was extracted from hemp stem according to Sun's report (Xiao et al., 2001). Typically, 5 g of hemp stem power was soaked in 100 ml of 6 wt% NaOH with stirring at 40 °C for 12 h. The residue was filtered off, and the filtrate was neutralized to pH 5.5 with 6 M HCl. The dissolved hemicellulose was isolated by precipitation of filtrate with two volumes of ethanol. After centrifugal separation, the isolated hemicellulose was thoroughly washed with 70% ethanol, and then filtered for standby application.

The extracted hemicellulose was added into 80 ml of 5 wt% dilute sulfuric acid solution. Due to the high hydrophilia, hemicellulose could be easily dispersed in the solution. The homogeneous solution was placed in a Teflon-lined stainless steel autoclave at 160 °C for 12 h. Then the powder obtained was removed by centrifugation and washed with water and ethanol. After being dried in an 80 °C oven, the black powder was put in a tube furnace, heated to 600 °C at 5 °C min^{-1}, and pre-carbonized for 2 h. The carbonized product was mixed with KOH at the weight ratios of 1:1–1:5, and then activated in the tube furnace at 800 °C for 3.5 h. The resulting sample was washed with 1 M HCl solution and deionized water, and finally dried at 80 °C. Hemicellulose-derived activated carbon spheres were denoted as HACS-*r*, where *r* represented the KOH/carbon ratio.

2.2. Characterization

The morphology of product was examined using a Hitachi S-4700 scanning electron microscope (SEM) at 5–20 kV. The particle size distribution was measured on a OMEC Easysizer20 laser particle size analyzer. Fourier transform infrared spectra (FTIR) were acquired using a Nicolet 8700 FTIR spectrometer by averaging 256 scans in the 4000–400 cm^{-1} spectral range at 4 cm^{-1} resolution. X-ray photoelectron spectroscopy (XPS) was used to determine the surface atomic composition of carbons. XPS spectra were taken on a Thermo VG ESCALAB 250 spectrometer equipped with a monochromatic Mg Kα X-ray source (1253.6 eV). X-ray diffraction (XRD) was conducted using a Rigaku D/MAX-2500 with Cu Kα radiation.

N_2 adsorption–desorption (−196 °C) analysis was carried out on an Micromeritics ASAP 2020 surface area and porosity analyzer.