Carbohydrate Polymers 118 (2015) 115–118

Contents lists available at ScienceDirect

Carbohydrate Polymers

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

Short communication

Fabrication of hydrophobic, electrically conductive and flame-resistant carbon aerogels by pyrolysis of regenerated cellulose aerogels

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ARTICLE INFO

Article history:
Received 4 August 2014
Received in revised form 6 November 2014
Accepted 10 November 2014
Available online 16 November 2014

Keywords:
Carbon
Aerogels
Pyrolysis
Regenerated cellulose
Porous materials

ABSTRACT

In this paper, we reported miscellaneous carbon aerogels prepared by pyrolysis of regenerated cellulose aerogels that were fabricated by dissolution in a mild NaOH/PEG solution, freeze–thaw treatment, regeneration, and freeze drying. The as-prepared carbon aerogels were subsequently characterized by scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), nitrogen adsorption measurements, X-ray diffraction (XRD), Raman spectroscopy, and water contact angle (WCA) tests. The results showed that the carbon aerogels with pore diameters of 1–60 nm maintained interconnected three-dimensional (3D) network after the pyrolysis, and showed type-IV adsorption isotherm. The pyrolysis process leaded to the decomposition of oxygen-containing functional groups, the destruction of cellulose crystalline structure, and the formation of highly disordered amorphous graphite. Moreover, the carbon aerogels also had strong hydrophobicity, electrical conductivity and flame retardance, which held great potential in the fields of waterproof, electronic devices and fireproofing.

1. Introduction

Carbon aerogels with large specific surface area, high porosity and high electrical conductivity have been widely considered as promising high-performance materials for adsorbents, catalyst supports, artificial muscles, electrodes for electrical double-layer capacitors, and gas sensors (Li, Wang, Huang, Gamboa, & Sebastian, 2006; Moreno-Castilla & Maldonado-Hódar, 2005; Waghuley, Yenorkar, Yawale, & Yawale, 2008). Traditionally, carbon aerogels are synthesized by carbonization of organic aerogels, which are prepared by sol–gel procedure from polycondensation of different organic monomers (Moreno-Castilla & Maldonado-Hódar, 2005). Typically, resorcinol–formaldehyde system is the most extensively used raw materials for fabrication of carbon aerogels, and the resulting carbon aerogels have tunable surface properties related to the synthesis and processing conditions, which can design various materials with unique properties. Apart from the above-mentioned numerous merits, some defects of the resorcinol–formaldehyde organic aerogels, such as high density (100–800 mg cm^{-1}) (Fu et al., 2003; Wu, Fu, Dresselhaus, & Dresselhaus, 2006), fragility, toxicity and environmental pollution, dramatically hamper the development and industry application of this class of carbon aerogels. Recently, some novel carbon aerogels using natural polymers like glucose and bacterial cellulose as precursors have been prepared by pyrolysis, and show superior flexibility, adsorption properties, fire resistance, and electric properties (Chen et al., 2013; Liang, Guan, Chen, et al., 2012; Liang, Guan, Zhu, et al., 2012; Wu, Li, Liang, Chen, & Yu, 2013; Wu et al., 2014). Nevertheless, regenerated cellulose aerogels, composed of cross-linked three-dimensional (3D) network similar to bacterial cellulose, might also be ideal precursors for carbon aerogels.

Thereby, in this paper, versatile carbon aerogels were fabricated by pyrolysis of regenerated cellulose aerogels that were prepared following the procedures of dissolving cellulose in a green NaOH/PEG solution, freeze–thaw treatment, regeneration, and freeze drying. The as-prepared carbon aerogels were characterized by scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), nitrogen adsorption measurements, X-ray diffraction (XRD), Raman spectroscopy, and water contact angle (WCA) tests. Moreover, the resulting carbon aerogels showed strong hydrophobicity, electrical conductivity and flame retardance.

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http://dx.doi.org/10.1016/j.carbpol.2014.11.010

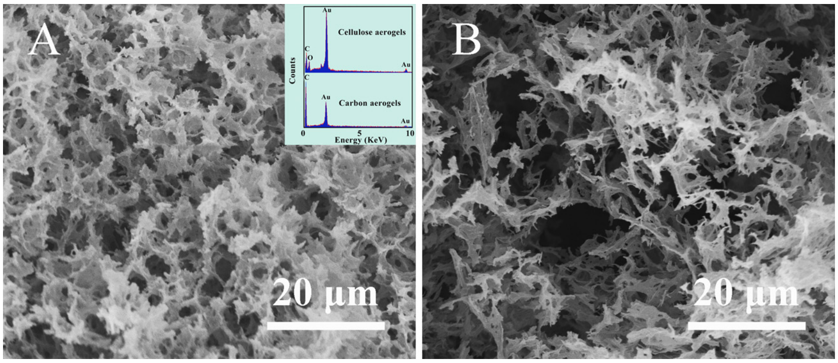

Fig. 1. SEM images of the cellulose aerogels (A) and the carbon aerogels (B). The inset showed the corresponding EDX spectra.

2. Materials and methods

2.1. Materials

Sixty-mesh powder of wheat straw after grinding and sieving was collected and dried in a vacuum at 60 °C for 24 h before used. All chemicals were supplied by Shanghai Boyle Chemical Co. Ltd. and used without further purification.

2.2. Fabrication of carbon aerogel via a pyrolysis method

The purified cellulose from the wheat straw powder was referred to our previous report via a chemical pretreatment process (Li, Wan, Lu, & Sun, 2014); meanwhile, the α-cellulose content of the obtained cellulose was determined by a modification of the TAPPI Method No. T 203 08-61 (Antrim, Chan, Crary, & Harris, 1980). The preparation of homogenous cellulose solution could be referred to the method based on the green NaOH/PEG solution (Yan and Gao, 2008). Briefly, the purified cellulose was mixed with a NaOH/PEG-4000 aqueous solution (9:1 by weight) with magnetic stirring for 6 h to form a 2 wt% cellulose solution. After being frozen at −15 °C for 12 h, the solution was thawed out at ambient temperature under vigorous stirring for 30 min, and the following homogenous cellulose solution was obtained. After being frozen at −15 °C for 3 h again, the frozen cellulose solution underwent a regeneration process by solvent exchange with 1% hydrochloric acid, distilled water and tert butyl alcohol in sequence until the formation of hydrogel without residual chlorine anions. Afterwards, the hydrogel was subjected to a freeze drying process at −35 °C for 48 h in a vacuum, and the following cellulose aerogel was pyrolyzed at 1000 °C under argon atmosphere to generate black carbon aerogel.

2.3. Characterizations

Micromorphology and surface chemical compositions were determined by SEM attached with EDX (FEI, Quanta 200). Nitrogen adsorption measurements were run on an accelerated surface area and porosimetry system (3H-2000PS2 unit, Beishide Instrument S&T Co. Ltd.), and pore characteristic parameters were calculated based on the Brunauer–Emmet–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods. Crystal structures were identified by XRD (Rigaku, D/MAX 2200). Raman spectra were performed using a Raman spectrometer (Renishaw, inVia). The wetting properties were characterized by a WCA analyzer (JC2000C).

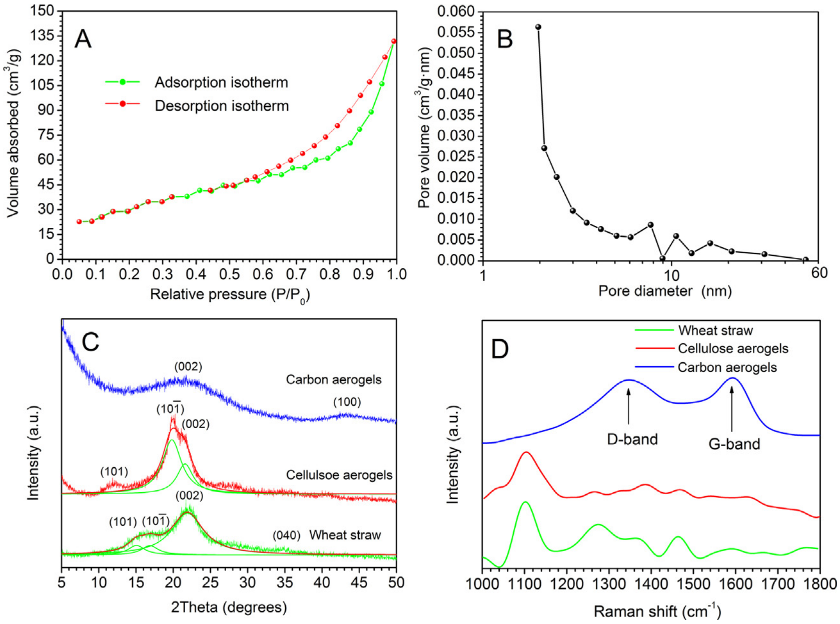

Fig. 2. (A) N_2 adsorption–desorption isotherms and (B) pore size distribution of the carbon aerogels. (C) XRD patterns and (D) Raman spectra of the wheat straw, the cellulose aerogels and the carbon aerogels.