Journal of Alloys and Compounds 607 (2014) 23–31

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

Synthesis and supercapacitor application of nanoporous carbon by the direct carbonization of aluminium salicylate coordination polymer

Xing Hui Zhang [a], Zhong Jie Zhang [a,*], Dong Hua Xie [b], Xiang Ying Chen [b,*]

[a] College of Chemistry & Chemical Engineering, Anhui Province Key Laboratory of Environment – Friendly Polymer Materials, Anhui University, Hefei 230039, Anhui, PR China
[b] School of Chemical Engineering, Anhui Key Laboratory of Controllable Chemistry Reaction & Material Chemical Engineering, Hefei University of Technology, Hefei 230009, Anhui, PR China

ARTICLE INFO

Article history:
Received 25 February 2014
Received in revised form 9 April 2014
Accepted 10 April 2014
Available online 20 April 2014

Keywords:
Salicylate
Coordination polymer
Carbonization
Nanoporous carbon
Supercapacitor

ABSTRACT

Flake-like nanoporous carbon has been synthesized by the direct carbonization of aluminium salicylate coordination polymer that serves as hard templates and carbon sources. It reveals that the carbonization temperature plays a crucial role in the formation of nanoporous carbon. The correlation between specific surface areas, pore structures, surface functionalities and capacitive performances are investigated. The nanoporous carbon synthesized at 900 °C, named as **carbon-900**, exhibits high surface area of 1162 $m^2\ g^{-1}$ and large total pore volume of 0.80 $cm^3\ g^{-1}$. The electrochemical behaviors are measured in a three-electrode system. In details, high specific capacitance of 220.0 $F\ g^{-1}$ is achieved at a current density of 0.5 $A\ g^{-1}$, whereas it also delivers high energy density of 30.5 $W\ h\ kg^{-1}$, and long cycle stability (~88.57% retention after 3000 cycles).

1. Introduction

Recently, a great attention has been focused on the application of nanoporous carbons as electrode materials for supercapacitors due to their remarkable properties including accessibility, easy processability, and chemical stability in acidic or basic solutions and performance ability in a wide range of temperatures [1,2]. Nanoporous carbons are usually prepared by the carbonization of natural or synthetic precursors, followed by activation treatment. To improve/manipulate nanoporous structure, hard and soft templates, such as zeolite [3,4], $CaCO_3$ [5], NH_4Cl [6], have been used to guide the formation of pores during the carbonization process.

Coordination polymers, also known as metal–organic frameworks (MOFs), are comprised of metal–organic units linked together at least in one dimension to form an infinite array through extended covalent or coordinate interactions [7–9]. Coordination polymers have been implemented as novel templates to prepare porous carbons with the original nanoporous structures. For example, Yamauchi et al. developed a direct carbonization method for the synthesis of nanoporous carbon derived from Al-based porous coordination polymer [10–12] and zeolitic imidazolate framework [13]. Xu et al. reported Zn-based MOFs-templated microporous carbon, using furfuryl alcohol as carbon precursor [14,15]. Apart from these works, similar templates also appear in cases of IRMOF-1/3/8 [16], zinc-containing MOFs [17], and cobalt imidazolate framework [18]. The coordination polymers-based templates have advantages of synthesis of nanoporous carbons over other templates, such as good thermal stability and commercial availability [19]. Therefore, in-depth exploration of the porous carbon synthesis derived from coordination polymer is an interesting subject for material scientists.

On the other side, aluminum salicylate belongs to the salicylic acid group of substances, which can be used in creams, ointments or solution for the cleaning wounds and photoluminescent phosphor. Owing to its high carbon content stemmed from the phenyl group, aluminium salicylate is expected to produce nanoporous carbon through a direct carbonization process. Herein, we demonstrate a direct carbonization route to prepare porous carbons at elevated temperatures, using aluminium salicylate coordination polymer as carbon source and hard template. The effect of carbonization temperature upon the specific surface area, pore structures and capacitive performance was studied in detail, primarily revealing that the porous carbon sample obtained at 900 °C exhibits the utmost excellent behaviors.

---

* Corresponding authors. Tel./fax: +86 551 62901450 (X.Y. Chen).
E-mail addresses: zhangzj0603@126.com (Z.J. Zhang), cxyhfut@gmail.com (X.Y. Chen).

http://dx.doi.org/10.1016/j.jallcom.2014.04.074
0925-8388/© 2014 Elsevier B.V. All rights reserved.

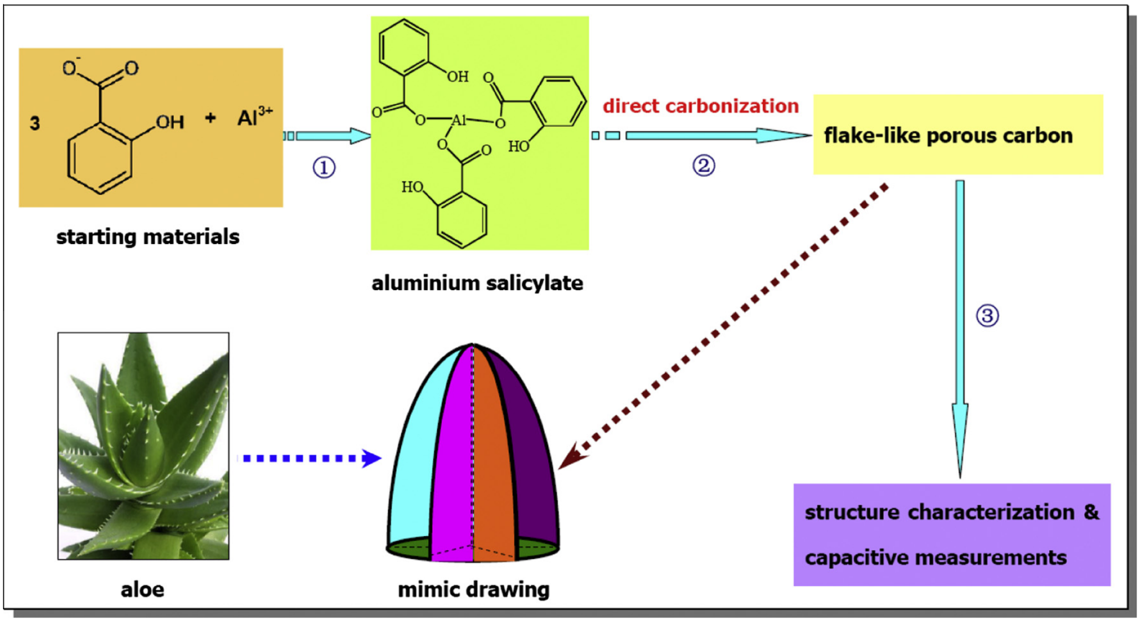

Fig. 1. Schematic illustration of the production of nanoporous carbon, primarily composed of flakes as those of natural aloe, by heating aluminium salicylate at 700/800/900 °C for 2 h under Ar flow.

2. Experiment

In a typical experiment, aluminium nitrate nonahydrate and sodium salicylate pre-dissolved in deionized water with designated molar ratio of 1:3 were mixed together to produce white aluminium salicylate coordination polymer. It was then converted into flake-like nanoporous carbon by a direct carbonization method at high temperatures of 700/800/900 °C, dominated as **carbon-700/800/900** for referring conveniences. More interestingly, the present carbon exhibits flake-like superstructures in shape, just like that of natural aloe. The overall schematic route is depicted in Fig. 1.

2.1. Typical room temperature synthesis procedure for aluminium salicylate coordination polymer

$Al(NO_3)_3 \cdot 9H_2O$ and sodium salicylate (molar ratio of 1:3) were dissolved in deionized water to form clear solutions. Then, the two solutions were mixed together under constant magnetic stirring for 2 h at room temperature, producing abundant white floccular precipitate. Then, the precipitate was filtered off, washed with deionized water and absolute ethanol for several times, and then dried under vacuum at 120 °C for 6 h.

2.2. Typical direct carbonization synthesis procedure for carbon sample

The above-prepared aluminium salicylate powder was first ground, and then placed in a porcelain boat, flushing with Ar flow for 30 min, and further heated in a horizontal tube furnace up to 700, 800, and 900 °C at a rate of 5 °C min^{-1} and maintained at this temperature for 2 h under Ar flow. The resultant product was immersed with dilute HCl solution to remove soluble/insoluble substances, subsequently washed with adequate deionized water. Finally, the sample was dried under vacuum at 120 °C for 12 h to obtain the **carbon-700/800/900** samples.

2.3. Characterization

X-ray diffraction (XRD) patterns were obtained on a Rigaku D/MAX2500V with Cu Kα radiation. Field emission scanning electron microscopy (FESEM) images were taken with a Hitachi S-4800 scanning electron microscope. Transmission electron microscope (TEM) and high-resolution transmission electron microscope (HRTEM) images, and fast Fourier transform (FFT) pattern were performed with a JEOL 2010 unit operated at 200 kV. X-ray photoelectron spectra (XPS) were obtained on a VG ESCALAB MK II X-ray photoelectron spectrometer with an exciting source of Mg Kα (1253.6 eV). The specific surface area and pore structure of the carbon samples were determined by N_2 adsorption–desorption isotherms at 77 K (Micrometrics ASAP 2020 system) after being vacuum-dried at 200 °C overnight. The specific surface area was calculated by the conventional Brunauer–Emmett–Teller method. The pore size distribution (PSD) plot was recorded from the adsorption branch of the isotherm based on the Barrett–Joyner–Halenda (BJH) model.

2.4. Electrochemical measurements

A mixture of 80 wt% the carbon sample (~4 mg), 15 wt% acetylene black and 5 wt% polytetrafluoroethylene (PTFE) binder was fabricated using ethanol as a solvent. Slurry of the above mixture was subsequently pressed onto nickel foam under

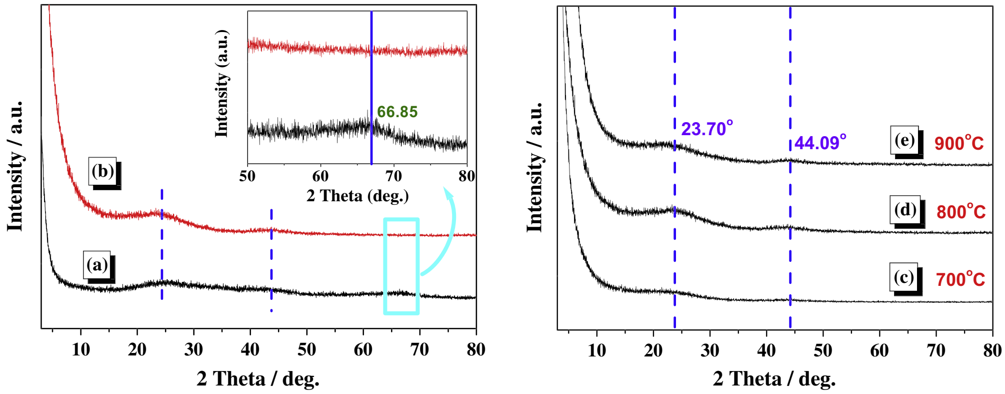

Fig. 2. XRD patterns of the **carbon-800** sample before (a) and after (b) being washed with aqueous HCl solution and deionized water to remove any unwanted impurities; together with the contrast XRD patterns of the (c) **carbon-700**, (d) **carbon-800** and (e) **carbon-900** samples. Notes: the inset in left figure shows the two theta scopes specifically ranging from 50° to 80°. The diffraction peak centering at 66.85° can be indexed as cubic γ-Al_2O_3 (JCPDS Card No. 29-0063), which was subsequently removed during aqueous workup.