

# Organic acid catalyzed carbon aerogels with freeze-drying

Yuelong Xu<sup>a,b</sup>, Meifang Yan<sup>a,b,c</sup> and Zhenfa Liu<sup>a,b</sup>

<sup>a</sup>Institute of Energy Resources, Hebei Academy of Sciences, Shijiazhuang 050081, China

<sup>b</sup>Hebei Engineering Research Center for Water Saving in Industry, Shijiazhuang 050081, China

<sup>c</sup>Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China

E-mail addresses: xudalong.cool@163.com (Y. Xu)

**Abstract.** Carbon aerogels (CAs) were synthesized via a sol–gel process by condensation-polymerization of phloroglucinol, resorcinol and formaldehyde using 2,4-dihydroxybenzoic acid as catalyst with freeze-drying. The effects of the freeze-drying method on the texture and pore structure were studied. Meanwhile the structure of carbon aerogels was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and a surface-area analyzer. The results show that the freeze-drying method and acid catalyst were good for the specific surface area of carbon aerogel, up to 765m<sup>2</sup> g<sup>-1</sup>, and pore size distribution.

## 1 Introduction

Carbon aerogels were first reported by Pekala in the 1990s, which has gotten more and more attention because of three-dimensional cross-linked porous structure and excellent electrochemical properties. Because of unusual chemical and textural properties, carbon aerogels have promising application in different fields with the development of carbon materials. These properties of interconnected primary particles have attracted widespread attention in the catalyst supports field, gas and metal adsorption fields.

CAs were first synthesized via a sol–gel process by condensation-polymerization of resorcinol and formaldehyde using sodium carbonate as a base catalyst with drying at room temperature. Currently, Freeze-drying and supercritical extraction of the solvent from the gel are among the most common processes to produce intact dried gel structures.

Organic acid catalyst has been reported for preparation of CAs in recent decades. Organic acid catalysts not only shorten the gel time but also improve the porous structure. Meanwhile the pore size distribution could be controlled. In this paper, CAs were synthesized via a sol–gel process by condensation-polymerization of phloroglucinol, resorcinol and formaldehyde using 2,4-dihydroxybenzoic acid as catalyst with freeze-drying. The effect of freeze-drying method on the porous structure is studied, the specific surface area, pore volume, pore size and structure properties of the carbon aerogels are investigated. Meanwhile, electrochemical properties of the carbon aerogels are investigated.



## 2 Experimental

### 2.1 Materials

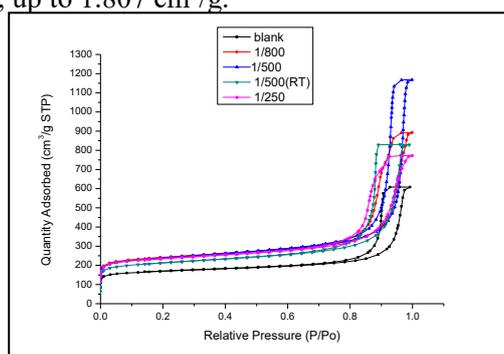
The chemical reagents used are analytical grade: phloroglucinol, resorcinol, formaldehyde (30%), and 2,4-dihydroxybenzoic acid (C). Ultima IV X-ray diffraction instrument (XRD, Rigaku, Japan), Specific surface analyzer ASAP2420 (micromeritics, USA), scanning electron microscope (SEM).

### 2.2 Synthesis of the carbon aerogels

Carbon aerogels were synthesized by polycondensation of phloroglucinol (P), resorcinol (R) and formaldehyde (F), using 2,4-dihydroxybenzoic acid as catalysts (C) and deionized water as the solvent. The molar ratio of P / R was 0.15, the molar ratio of (P + R)/F was 0.5, and the molar ratio of (P + R) / C was 250, 500 and 800, respectively. The concentration of raw material (P + R + F) in solution was 45 wt%. Phloroglucinol, resorcinol, formaldehyde, and 2,4-dihydroxybenzoic acid (C) catalyst were added into deionized water. Ultrasonic oscillator was used to dissolve the reactants to form a homogeneous solution in test tubes. Putting test tubes in water bath and keeping 50°C for some time until the hydrogels were obtained. The hydrogels were freeze-dried. The dried aerogels were carbonized at 900°C for 3 h with a heating rate of 2°C/min under a flowing nitrogen atmosphere (100 mL/min).

## 3 Results and discussion

The N<sub>2</sub> adsorption–desorption isotherms of different CAs are shown in Fig. 1. The specific surface area ( $S_{\text{BET}}$ ), micropore surface area ( $S_{\text{micro}}$ ), BJH desorption average pore diameter and ( $D_{\text{average}}$ ) and total pore volume ( $V_{\text{total}}$ ) of as-prepared CAs samples was listed in Table 1. The type-IV isotherms of are exhibit in Fig. 1, and all the as-prepared CAs samples exhibit similar shape. When  $p / p_0 < 0.01$ , the initial regions of the isotherms have a sharp rise which is indicative of the presence of micropores in as-prepared CAs samples. As shown in in Fig. 1, the 1/500 sample has the highest quantity adsorbed which is in accord with the maximum total pore volume. As shown in table 1, the samples with freeze-drying have the higher specific surface area. Meanwhile the organic acid catalysts also improve the specific surface area. The 1/500 sample has the highest specific surface area, up to 765 m<sup>2</sup>/g, and the highest total pore volume, up to 1.807 cm<sup>3</sup>/g.

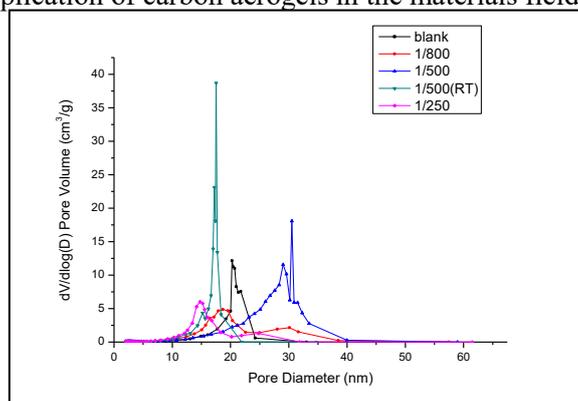


**Fig. 1** Nitrogen adsorption – desorption isotherms of different CAs samples(1/500(RT): acetone solvent exchanged and dried at room temperature)

**Table 1** textual properties of different CAs samples

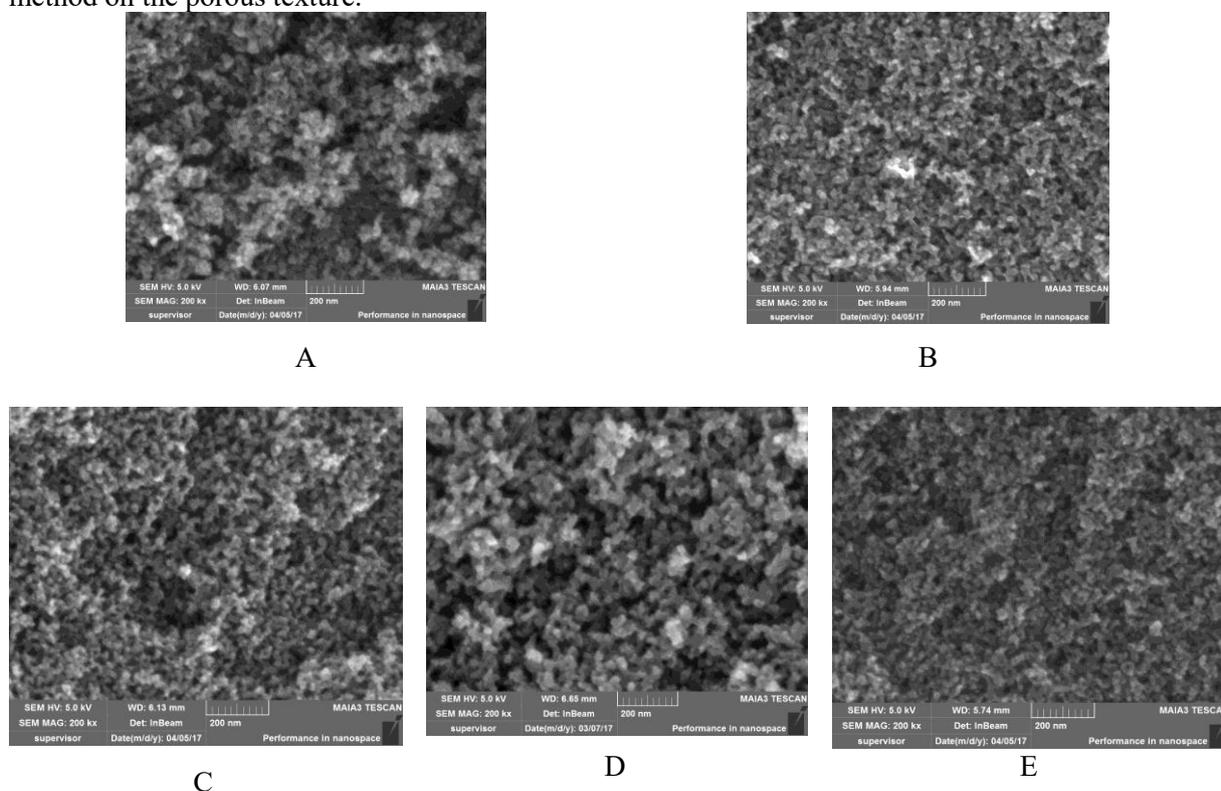
Entry	$S_{\text{BET}}$ (m <sup>2</sup> /g)	$S_{\text{micro}}$ (m <sup>2</sup> /g)	$D_{\text{average}}$ (nm)	$V_{\text{total}}$ (cm <sup>3</sup> /g)
Blank	593	389	7.01	0.941
1/800	758	463	7.21	1.381
1/500	765	496	9.53	1.807
1/500(RT)	678	417	7.56	1.282
1/250	745	491	6.41	1.195

The pore size distribution of as-prepared CAs samples were shown in Fig. 2. As shown in Fig. 2, the pore size has a narrow distribution. When the dosage of 2,4-dihydroxybenzoic acid was 1/500, the freeze-drying sample has the maximum pore size, the result is in good agreement with the result of table 1; the 1/500(RT) sample has the narrower distribution, the range of pore size is 10nm - 20nm. As shown in in Fig. 2, different pore size distribution could be obtained through this prepared method which is benefit for the application of carbon aerogels in the materials field.



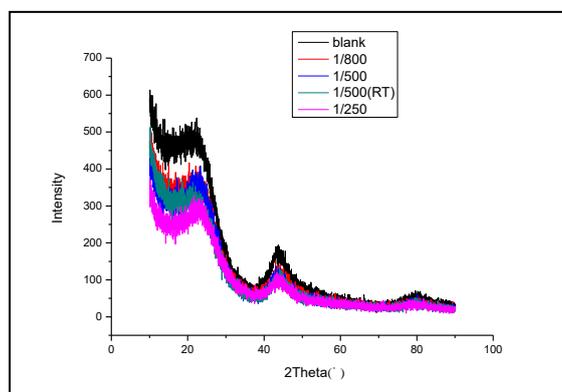
**Fig. 2** Pore size distribution of as - prepared CAs with freeze - drying(1/500(RT): acetone solvent exchanged and dried at room temperature)

Figures 3A–E show SEM-images of as - prepared CAs samples with freeze - drying and solvent exchanged drying. As shown in Figures 3A–E, Figures 3B, 3C and 3E have the dense micropore which is indicative of the presence of micropores in CAs. The freeze - drying method could be conducive to the generation of micropore and improve the specific surface area. The samples A and D have the larger pore size, the results illustrate the effect of organic acid catalyst and freeze - drying method on the porous texture.



**Fig. 3** SEM—images of as - prepared CAs with with freeze - drying(A: blank; B: 1/800; C: 1/500; D:

1/500 (RT); E: 1/250. 1/500(RT): acetone solvent exchanged and dried at room temperature)



**Fig. 4** XRD patterns of as - prepared CAs with freeze - drying(1/500(RT): acetone solvent exchanged and dried at room temperature)

The XRD patterns of as - prepared CAs samples are shown in Fig. 4. As shown in in Fig. 4, two diffraction peaks at the  $2\theta$  of  $23.5^\circ$  and  $43.8^\circ$  are exhibited in Fig. 4 which is corresponding to the (002) peak of graphite carbon and (101) peak of the crystal plane diffraction, respectively. The difference of all CAs samples XRD patterns could be found in in Fig. 4.

#### 4 Conclusions

Carbon aerogels were prepared through polycondensation of phloroglucinol, resorcinol and formaldehyde using 2,4-dihydroxybenzoic acid as the catalyst with freeze - drying. Organic acid and freeze - drying method can promote the porous texture and electrochemical properties of as - prepared carbon aerogels. When the dosage of 2,4-dihydroxybenzoic acid was 1/500 with freeze - drying, the specific surface area was up to  $765\text{m}^2\text{g}^{-1}$ , and pore size was about 30 nm. The controlled pore size has great potential application in the future. And the freeze - drying method could be used in the preparation carbon aerogels. This as - prepared carbon aerogels with excellent specific surface area and controlled pore size would attract more and more attention in the application of carbon material.

#### Acknowledgments

This work was financially supported by the Foundation of Hebei Academy of Sciences (17709) and Natural Science Foundation of Hebei Province (16214402D).

#### References

- [1] Pekala RW, Organic aerogels from the polycondensation of resorcinol with formaldehyde J. Mater. Sci., vol. 24, 1989, pp. 3221 - 3227.
- [2] C. Nguyen, D.D. Do, The Dubinin–Radushkevich equation and the underlying microscopic adsorption description, Carbon vol. 9, 2001, pp. 1327–1336,
- [3] Tamon H, Ishizaka H, Yamamoto T, Suzuki T. Influence of work. freeze-drying conditions on the mesoporosity of organic gels as carbon precursors. Carbon vol. 38, 2000, pp. 1099–1105.
- [4] Tamon H, Ishizaka H, Mikami M, Okazaki M. Porous structure of organic and carbon aerogels synthesized by sol–gel polycondensation of resorcinol with formaldehyde. Carbon vol. 35, 1997, pp. 791–796
- [5] Klemm D, Kramer F, Moritz S, Lindström T, Ankerfors M, Gray D, Dorris A Nanocelluloses: a new family of nature-based materials. Angew Chem Int Ed. Vol. 50, 2011, pp. 5438–5466.
- [6] Yao Y, Ma C, Wang J, Qiao W, Ling L, Long D Rational design of high-surface-area carbon nanotube/microporous carbon core–shell nanocomposites for supercapacitor electrodes. ACS Appl Mater Interfaces vol. 7, 2015, pp. 4817–4825.
- [7] Zhang K, Zhang Y, Wang S Enhancing thermoelectric properties of organic composites through hierarchical nanostructures. Sci Rep vol. 3, 2013, pp. 3448–3455.

- [8] Guo, B.; Wang, X.; Fulvio, P. F.; Chi, M.; Mahurin, S. M.; Dai, S. Soft-Templated Mesoporous Carbon-Carbon Nanotube Composites for High Performance Lithium-ion Batteries, *Adv. Mater.* Vol. 23, 2011, pp. 4661–4666.
- [9] Lijuan Zhao, Jinghong Zhao, Xijing Sun, Quan Li, Jinrong Wu and Aiping Zhang, Enhanced thermoelectric properties of hybridized conducting aerogels based on carbon nanotubes and pyrolyzed resorcinol – formaldehyde resin, *Synthetic Metals*, vol. 205, 2015, pp. 64–69.
- [10] Feng Li, Lijing Xie, Guohua Sun, Qingqiang Kong, Fangyuan Su, Hong Lei, Xiangyun Guo, Bingsen Zhang, Chengmeng Chen, Regulating pore structure of carbon aerogels by graphene oxide as ‘shape-directing’ agent. *Microporous Mesoporous Mater.* Vol. 240, 2017, pp. 145 - 148.