J Mater Sci (2009) 44:4750–4753
DOI 10.1007/s10853-009-3710-6

LETTER

Preparation of spherical activated carbon with hierarchical porous texture

**Yue Liu · Kaixi Li · Jianlong Wang ·
Guohua Sun · Chenggong Sun**

Received: 2 April 2009 / Accepted: 26 June 2009 / Published online: 9 July 2009

Introduction

Hierarchical porous carbons can exhibit excellent adsorption performance due to their high connectivity of narrow pores provided by the textural transport pores that allowing rapidly deep penetration of adsorbate molecules into the pore network [1, 2]. They have been attracting widespread attention due to their potential technological applications, such as in adsorption of harmful materials in liquid or gas phase, in catalyst support, and as carbon electrode for supercapacitors [3–11]. The hierarchical micro/meso-porous carbons have been prepared by CO_2 activation of ordered mesoporous carbon and utilized as the electrode material for supercapacitor [12]. Meanwhile, a hierarchical meso/macro-porous carbon monolith has been obtained by using Pluronic F127 and SiO_2 opal as the templates [13]. In addition, a 3D aperiodic hierarchical porous graphitic carbon material has also been reported [14]. All of these porous carbons exhibited notable electrochemical double-layer performance.

In this study, we report a new method to prepare hierarchical porous activated carbon spheres (HPACSs) in which the commercial phenol-formaldehyde resins were used as carbon precursor. The prepared HPACSs exhibited a uniquely hierarchically porous structure and showed the high Brunauer-Emmett-Teller (BET) surface area as well as the specific pore volume. The mechanism of pore formation in HPACSs was also proposed.

Experiment

The novolac-type phenol-formaldehyde resins and hexamethylenetetramine were first dissolved in methanol, and then poured in an aqueous solution of polyvinyl alcohol (PVA) in a high-pressure reactor. The mixture was heated from room temperature to 403 K at a rate of 5 K/min and kept at this temperature for 60 min during which the mixture was actively stirred under a pressure to ensure the phenol resins were dispersed homogeneously. Then, after the reaction mixture cooling down to the room temperature naturally, the phenol-formaldehyde resin spheres (PFSs) were obtained via solid–liquid separation, followed by washing with distilled water to remove the excess polyvinyl alcohol (PVA) and drying at 383 K for 24 h.

To prepare the hierarchical porous activated carbon spheres (HPACSs), the PFSs were firstly preoxidized at 573 K for 120 min in air, and then heated up to 1123 K under a nitrogen atmosphere to activate PFSs for 60 min under a stream of steam at a flow rate of 20 mL/min.

The surface area and pore structure of prepared HPACSs were characterized using nitrogen adsorption at 77 K (Micromeritics ASAP-2020) as well as mercury

---

Electronic supplementary material The online version of this article (doi:10.1007/s10853-009-3710-6) contains supplementary material, which is available to authorized users.

Y. Liu · K. Li (✉) · J. Wang · G. Sun
Key Laboratory of Carbon Materials, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, China
e-mail: likx99@yahoo.com

Y. Liu
Graduate School of the Chinese Academy of Sciences, Beijing 100039, China

C. Sun
School of Chemical, Environmental and Mining Engineering, University of Nottingham, University Park,
Nottingham NG7 2RD, UK

porosimetry (Micromeritics AUTOPORE II 9220). The size and morphology of the samples were examined using scanning electron microscopy (SEM,LEO 438 VP).

Results and discussion

The nitrogen adsorption–desorption isotherms and the pore size distribution of HPACSs are shown in Fig. 1. Specifically, the HPACSs exhibited a type IV isotherm with an H1-type hysteresis loop and three uptake phases (Fig. 1a). At the very low relative pressures, there was a steep rise shown in Fig. 1b, indicating the presence of some micropores generated probably during the carbonization and activation of the precursor. Then, with the increase of the relative pressure, the N_2 adsorption amounts increased gradually, implying the existence of some micro/mesopores of a variety of sizes. Finally, at high relative pressures ($P/P_0 = 0.85$–0.97), the very presence of a hysteresis loop with a sharp capillary condensation indicated the existence of some large size pores. Furthermore, it has been found that the prepared HPACSs had a broad pore size distribution with a mean pore size 24 nm (Fig. 1c), as calculated using the Barrett-Joyner-Halenda (BJH) method from the adsorption isotherm. In addition, a nitrogen adsorption uptake has been observed in the adsorption isotherm at the relative pressures as high as $P/P_0 > 0.9$, indicating the presence of channels connecting the macropores [15].

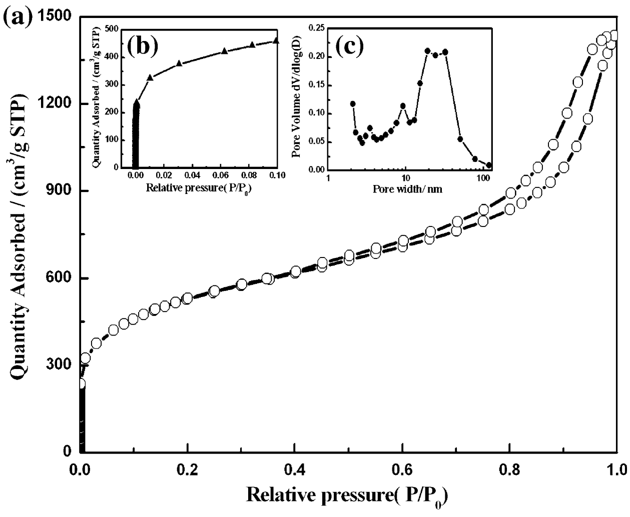

Fig. 1 N_2 adsorption–desorption isotherms (**a**), enlarged image of N_2 isotherms at the low relative pressures (**b**) and BJH pore size distributions (**c**) of HPACSs

The size distribution of the pores in the prepared HPACSs, particularly, the large mesopores and macropores, has been measured using mercury porosimetry too. The result is shown in Fig. 2. Specifically, a steep rise of cumulative pore volume was clearly evident at low pressures, as shown in Fig. 2a, indicating the presence of numerous macropores, while with the further increase of the pressure, the cumulative pore volume increased, implying the existence of some mesopores. Finally, as shown in Fig. 2b, the prepared HPACSs had a broad pore size distribution and had the pores of various sizes from the mesopores, the macropores to the ultra-macropores [16].

The BET surface area and the total pore volume of the prepared HPACSs were found to be as high as 1897 m^2/g and 2.22 cm^3/g, respectively. Meanwhile, its mesopore-to-total volume ratio was up to 92.3%. However, the micropore volume of the prepared HPACSs was only 0.16 cm^3/g, which can be attributed to the collapse and widening of the micropores as well as the closed mesopore opening. We studied the effects of preoxidation temperature on the structure of activated carbon spheres and did the repeat experiments (see supplementary information). The primary physical properties of the prepared samples are listed in Table 1.

The morphology of the prepared HPACSs is shown in Fig. 3. Specifically, the prepared HPACS showed a well spherical structure with a rough exterior surface. The macropores and the ultra-macropores were indicated by arrows in Fig. 3b, c, and particularly, in Fig. 3c. Particularly, as indicated by the arrows in Fig. 3c, it can be seen clearly that the walls of ultra-macropores actually contained many sub-pores and these sub-pores connected the

Fig. 2 Mercury adsorption curves (**a**) and pore size distributions (**b**) of HPACSs

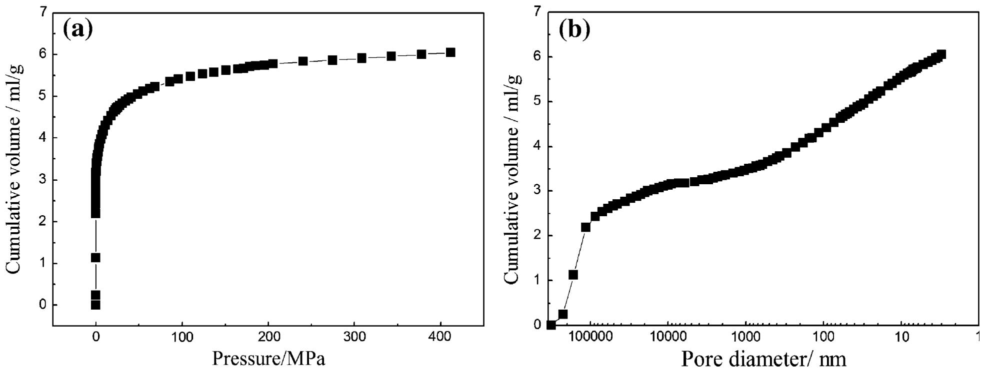

Table 1 The physical properties of the samples

Sample	S_{BET} (m^2/g)	V_{total} (cm^3/g)	S_{micr} (cm^3/g)	Ratio$_{meso}$ (%)	Pore size (nm)
ACSs	1196	0.86	0.42	51.2	2.89
HPACSs	1897	2.22	0.17	92.3	4.67

S_{BET} BET surface area, V_{total} total pore volume, measured at P/P =0.995, V_{micro} micropore volume, V_{meso} mesopore volume, Ratio$_{meso}$= V_{meso} / V_{total}, Pore size, adsorption average pore width (4V/A by BET)

ACSs, HPACSs are the activated samples for the original resin spheres and oxidized phenolic resin spheres at 573 K

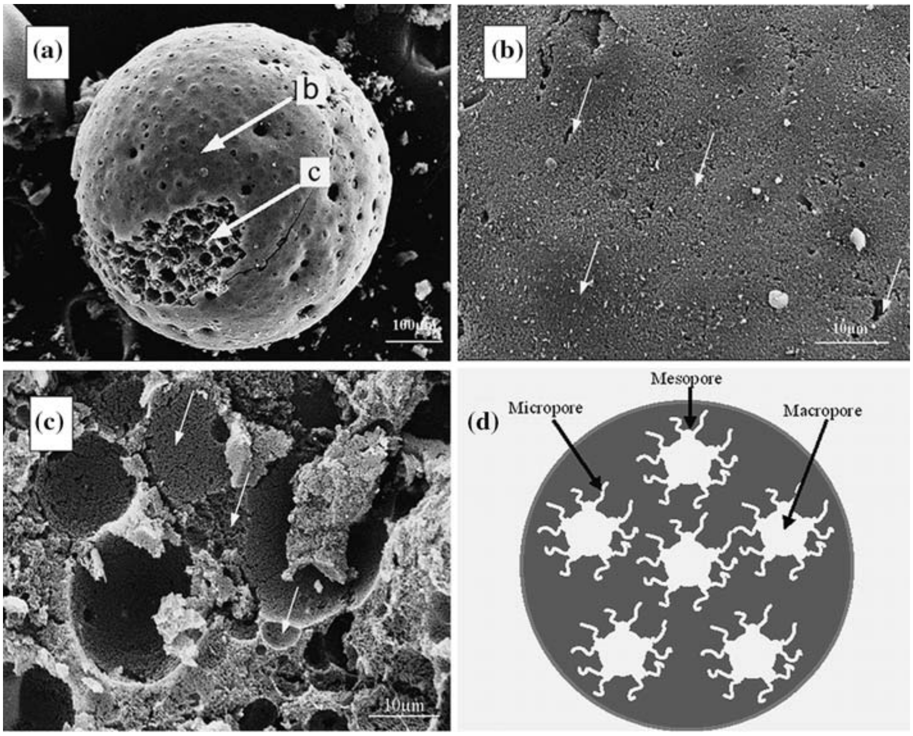

Fig. 3 SEM images of the samples, the particle (**a**), the exterior surface (**b**), the cross section (**c**), and the schematic representation (**d**) of hierarchical porous texture

macropores in the interior of the prepared HPACSs. These results along with the results of nitrogen adsorption and mercury porosimetry revealed clearly that the prepared activated carbon spheres exhibited a hierarchical structure thereafter can be called the hierarchical porous carbons. A schematic representation of the structure, i.e., a macroporous network with meso-microporous walls, is shown in Fig. 3d [14].

The formation mechanism of hierarchically structured pores may be as follows. The macropores were probably formed as a result of the solvent volatilization during the balling and curing of phenolic resins. Meanwhile, PVA, as surfactant ensuring that phenol resins were dispersed homogeneously, can definitely exert some influences on the formation of macropores. However, the solvent volatilization may play a crucial role here. The mesopores and the macropores on the PFSs surface were generated during the heat treatment in air at 573 K, meanwhile, many closed pores inside the PFSs were also opened to the surface during the heat treatment. Consequently, during PFSs activation process, small molecules can be removed more easily from the interior of resin particles while the activator can enter the interior of the resin spheres more quickly, thereafter facilitates the formation of internal micropores and mesopores. Simultaneously, the intermolecular cross-linking as well as the rearrangement reaction of phenolic resin also occurred. All of these eventually resulted in the increase of porosity. A more detailed study of the mechanism is underway.

Conclusions

The hierarchical porous activated carbon spheres have been successfully prepared via the preoxidation and activation, in which the cheap commercial phenolic resins were used as carbon precursor. The results showed that the preoxidation played crucial roles in determining the structure of HPACSs, which produced new pores on PFSs surface, opened the closed pores of PFSs, facilitated the further activation of PFSs, and eventually resulted in the formation of hierarchically porous structure, i.e., a macroporous network with meso-microporous walls. It has been found that the prepared HPACSs had a high specific surface area of 1897 m^2/g, a large total pore volume of 2.22 cm^3/g and a high mesopore ratio of 92.3%. All of these results indicated that the prepared HPACSs were promising in many applications such as the carbon electrode for supercapacitors.

Acknowledgements This study is financially supported by National Nature Science Foundation of China (No. 50272070).

References

1. Stein A, Wang ZY, Fierke MA (2009) Adv Mater 21:265
2. Gun'ko VM, Kozynchenko OP, Turov VV, Tennison SR, Zarko VI, Nychiporuk YM et al (2008) Colloids Surf A Physicochem Eng Asp 317:377
3. Tang DY, Zheng Z, Lin K, Luan JF, Zhang JB (2007) J Hazard Mater 143:49
4. Mirzaeian M, Hall PJ (2009) J Mater Sci 44:2705. doi:10.1007/s10853-009-3355-5
5. Shen WZ, Wang H, Guan RG, Li ZJ (2008) Coll Surf A 331:263
6. Tamai H, Kunihiro M, Morita M, Yasuda H (2005) J Mater Sci 40:3703. doi:10.1007/s10853-005-2838-2
7. Kötz R, Carlen M (2000) Electrochim Acta 45:2483
8. Qu D, Shi H (1998) J Power Sources 74:99
9. Frackowiak E, Béguin F (2001) Carbon 39:937
10. Zhang M, Hou YG, Yan GJ (2008) J Mater Sci 43:1376. doi:10.1007/s10853-007-2305-3
11. Tseng HH, Wey MY, Fu CH (2003) Carbon 41:139
12. Xia KS, Gao QM, Jiang JH, Hu J (2008) Carbon 46:1718
13. Zhao Y, Zheng MB, Cao JM, Ke XF, Liu JS, Chen YP et al (2008) Mater Lett 62:548
14. Wang DW, Li F, Liu M, Lu GQ, Cheng HM (2008) Angew Chem Int Ed 47:373
15. Alvarez S, Esquena J, Solans C, Fuertes AB (2004) Adv Eng Mat 6:897
16. Ecsedi Z, Lazău I, Păcurariu C (2009) Microporous Mesoporous Mater 118:453