J Mater Sci (2010) 45:4439–4443
DOI 10.1007/s10853-010-4526-0

Green and low-cost materials as carbon source for the synthesis of hierarchical porous carbons

Shidi Zuo · Yong Xiao · Yingliang Liu · Huihua Qiu · Qiu Guan · Mingtao Zheng

Received: 16 October 2009 / Accepted: 13 April 2010 / Published online: 28 April 2010

Abstract Hierarchical porous carbons (HPCs) were successfully synthesized using green and relatively low-cost materials as carbon source. The template of the macro- and large meso-pores was nickel hydroxide obtained from the reaction between sodium hydroxide and nickel nitrate, while the micro- and small meso-pores were formed during the dissipation of the gases produced in the reaction process. Different carbon sources were used for the formation of HPCs, and sucrose proved to be the best which had a Brunauer–Emmett–Teller (BET) surface area of 829 m^2/g. Besides, a possible mechanism for the formation of HPCs was hypothesized.

Introduction

Recently, carbon materials attract considerable attentions and have been widely investigated because of its potential advantages. Besides a variety of novel morphologies such as carbon nanotubes, flower-like carbon, graphene and porous carbons [1–4], they also show their unique physical and chemical properties, i.e., low mass density, high corrosion resistance, tailorable surface properties and excellent thermal stability [5–7]. All of these advantages above make them promising in many scientific realms such as catalysis, energy storage and adsorption [8–11].

The structure of hierarchical porous carbons (HPCs) is based on the body of mesoporous carbon materials, which can be treaded by various methods and then added with micro- and macro-pore structure for the formation of HPCs. Since HPCs have a special three-dimensional (3-D) structure, it could be widely used in many areas. For example, Wang et al. [12] recently synthesized a kind of HPCs which had a high energy and power density and can be used for electrochemical capacitive energy storage. Because of its special properties and promising applications, HPCs are receiving more and more attentions, and methods of preparing it are correspondingly various. Generally, the ways of making HPCs can be classified into two sorts, one of which is to treat carbon precursor directly to obtain HPCs, say, Wang et al. [12] used nickel hydroxide as template and phenolic resin as carbon source, and after a carbonization process, HPCs were obtained. The other way of preparing it is to add micro-pore structure into mesoporous carbon or to add micro- and meso-pore structure into macroporous carbon, for instance, Wang et al. used potassium hydroxide to activate the commercial activated carbons (ACs), and successfully added micropore into the commercial ACs and largely increased its BET surface area [13].

For the synthesis of porous carbon, a variety of materials, vary from saccharide to resin, low polymer to high polymer and artificial materials to natural materials, have been used as carbon source. However, for the synthesis of HPCs, only a minority kind of material is used. For example, saccharide, a kind of promising carbon source which is clean, low-cost and widely used for the synthesis of porous carbon, is rarely used for the formation of HPCs. Thus in this work, saccharide such as starch, sucrose and glucose is used instead of phenolic resin as carbon sources with the consideration that when phenolic resin is used, too much toxic organic gas will be produced and thus causes negative influence to the environment. Besides, from the point of economic benefit, phenolic resin is far more expensive than starch, sucrose and glucose, and the cost of

---

S. Zuo · Y. Xiao · Y. Liu (✉) · H. Qiu · Q. Guan · M. Zheng
Department of Chemistry, Institute of Nanochemistry, Jinan University, Guangzhou 510632, People's Republic of China
e-mail: tliuyl@163.com; sheedy.sczs@gmail.com

producing HPCs in a large-scale will be increased accordingly. So here we use saccharide as the carbon source to synthesize HPCs which display an excellent hierarchical porosity in the carbon body and has a BET surface area of 829 m^2/g.

Experimental section

Material synthesis

The HPCs were synthesized using nickel hydroxide as template and starch, sucrose or glucose as carbon source. Briefly, 50 g of 10 wt% sodium hydroxide aqueous solution was added with 25 g of 1 mol/L nickel nitrate aqueous solution drop by drop under stirring followed by a further continuous stirring for 6 h. Subsequently, 25 g of 20 wt% starch, sucrose or glucose aqueous solution was added. Then the mixed solution was evaporated until dryness in a 60 °C water bath under continuous stirring, after which, the solid composite was put in an oven at the temperature of 80 °C for 24 h to obtain the precursor. 2 g of the as-prepared precursor was put in a porcelain boat which was then heated to 200 °C and kept at 200 °C for 2 h, then heated to 400 °C and kept at 400 °C for 4 h at a heating ramps of 3 °C/min under nitrogen atmosphere in a tube furnace for the whole carbonization process. When the carbonization was done, the product was treated with 50 mL of 3 mol/L hydrochloric acid for 12 h under stirring. After filtration, the product was washed by distilled water twice and by ethanol once, finally dried in an oven at 80 °C for 48 h.

Structural and textual characterization

The samples were characterized by X-ray powder diffraction (XRD) performed on a MSAL-XD2 X-ray diffractometer with Cu Kα radiation (40 kV, 20 mA, $\lambda = 1.54051$ Å). The morphology observation of the samples was examined with scanning electron microscopy (SEM, Philips XL-30). The BET surface area, pore volume and pore size distribution were measured by the Micrometics TriStar 3000 Analyzer.

Results and discussion

A direct coprecipitation method is used to synthesize the carbon precursor of HPCs followed by a carbonization process. Starch, sucrose or glucose is used as carbon source to coprecipitate with nickel hydroxide to form the mixed composite. After carbonization, three kinds of HPCs are obtained named as HPC–ST, HPC–SU and HPC–GL in which ST (starch), SU (sucrose) and GL (glucose), respectively, represent the carbon source used in the formation of carbon precursor. As shown by the SEM images Fig. 1a–c, HPC–ST, HPC–SU and HPC–GL present a similar morphology, which is loose and porous with different size of pore in the body of HPCs that can be seen clearly. The macro-pores in the product have a tunnel structure with pore diameter of 400–600 nm and thousands of meso-pores with pore diameter of 30–40 nm on them which can be easily observed.

The powder XRD patterns of the HPCs are illustrated and compared in Fig. 2. There is a board peak at 24.5° and a small shoulder peak at 43.3° in the curves of the samples HPC–SU and HPC–GL which indicate the possible presence of an amorphous carbon phrase in the main body of

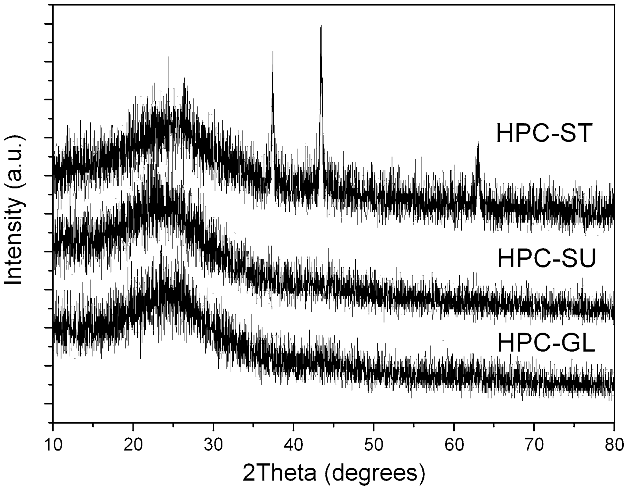

Fig. 2 XRD patterns of samples: HPC–ST, HPC–SU and HPC–GL

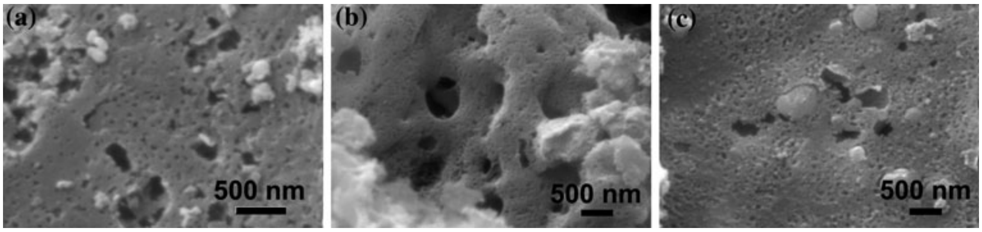

Fig. 1 SEM images of samples: HPC–ST (**a**), HPC–SU (**b**) and HPC–GL (**c**)

the HPCs [14]. Differs from the other two, the sample HPC–ST has three sharp peaks at 37.4°, 43.5° and 63.1°, respectively. These peaks have the typical feature of nickel oxide nanocrystals which are caused by the remains of the nickel oxide [15] derived from the nickel hydroxide during the carbonization process. The reason why the nickel oxide cannot be removed when washed with hydrochloric acid would probably be explained by the formation of a core–shell nanostructure in which the nickel oxide particles are coated with the carbons and it makes them irremovable from the acid. Since the synthesis conditions of the three samples are totally the same only except for the carbon sources used, we can believe that the difference is caused by the carbon sources we use in the formation of the precursor. Although all of the three are saccharide, as a kind of polysaccharide, starch is totally different in structure from sucrose and glucose which is disaccharide and monosaccharide, respectively. The poly structure of the starch makes it possible for the nickel oxide particles to be coated with the carbons during the carbonization process. The specific mechanism of the formation of the core–shell nanostructure still needs to be further studied in future works.

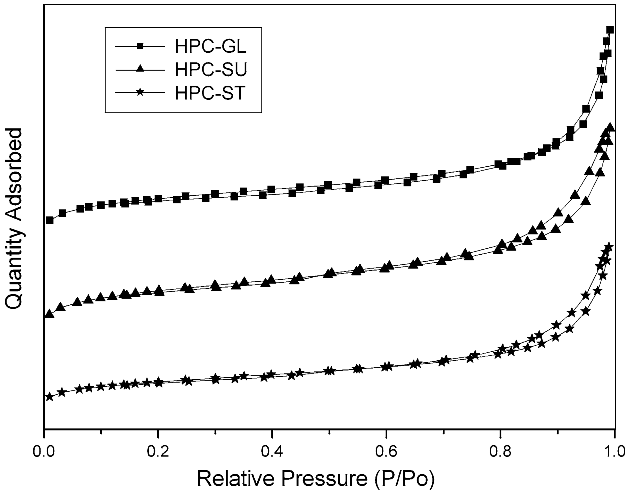

Fig. 3 Nitrogen adsorption–desorption isotherms of the samples: HPC–ST, HPC–SU and HPC–GL

Figure 3 shows the N_2 adsorption–desorption isotherms of the obtained HPCs. According to the isotherms of the samples, BET surface area, micro- and total-pore volume and pore size distribution of the samples are obtained and the results are shown in Table 1; Fig. 4. These isotherms in Fig. 3 vividly show that there are little differences between HPC–ST, HPC–SU and HPC–GL. All of the three curves show the combined characteristics of type I and type II with a hysteretic loop type of H3, which indicate the coexistence of pores with different size. Besides, it is worth noting that the adsorption isotherm and the desorption isotherm in all of the three figures have an intersection point at a relative pressure (P/P_0) = 0.6, 0.5, 0.9 for HPC–ST, HPC–SU and HPC–GL, respectively. When the given relative pressure is smaller than that of intersection point, the desorption isotherm is underneath the adsorption isotherm. These features also indicate that the as-prepared HPCs have macro- and meso-pore structure in their main body, which is in parallel with the results provided by the SEM analysis. The BET surface area of HPC–ST, HPC–SU and HPC–GL is 526, 829, 752 m^2/g, with a total-pore volume of 0.68, 0.94, 0.84 cm^3/g, a micro-pore volume of 0.08, 0.15, 0.13 cm^3/g and a micropore-to-total-pore volume ratio of 0.12, 0.16, 0.15, respectively. The total-pore volume of our sample HPC–SU and HPC–GL are far larger than that have been reported previously [11], and though the micropore-to-total-pore volume ratios are smaller, it can still reveals that large part of the pore volume in our samples is contributed by macro- and meso-pores. According to Wang's work, the use of alkali in the treatment of carbon materials with meso- and macro-pore structure can notably increases the micro-pore volume [12], which is to say, the samples synthesized in the present work have large potential in further treatment which could significantly improves the properties of the HPCs.

Table 1 Pore structure of as-prepared HPCs

Sample	S_{BET}[a] (m^2/g)	S_{micro}[b] (m^2/g)	V_t[c] (cm^3/g)	V_{micro}[d] (cm^3/g)	V_{micro}/V_t (%)	D_{BJH}[e] (nm)
HPC–ST	526	189	0.68	0.08	12	10.9
HPC–SU	829	328	0.94	0.15	16	9.3
HPC–GL	752	298	0.84	0.13	15	10.8

[a] The specific surface area (S_{BET}) is calculated by the Brunauer–Emmett–Teller (BET) method

[b] S_{micro} represents the microporous surface area

[c] V_t denotes the total-pore volume

[d] V_{micro} represents the micro pore volume

[e] D_{BJH} stands for the Barrett–Joyner–Halenda (BJH) desorption average pore width

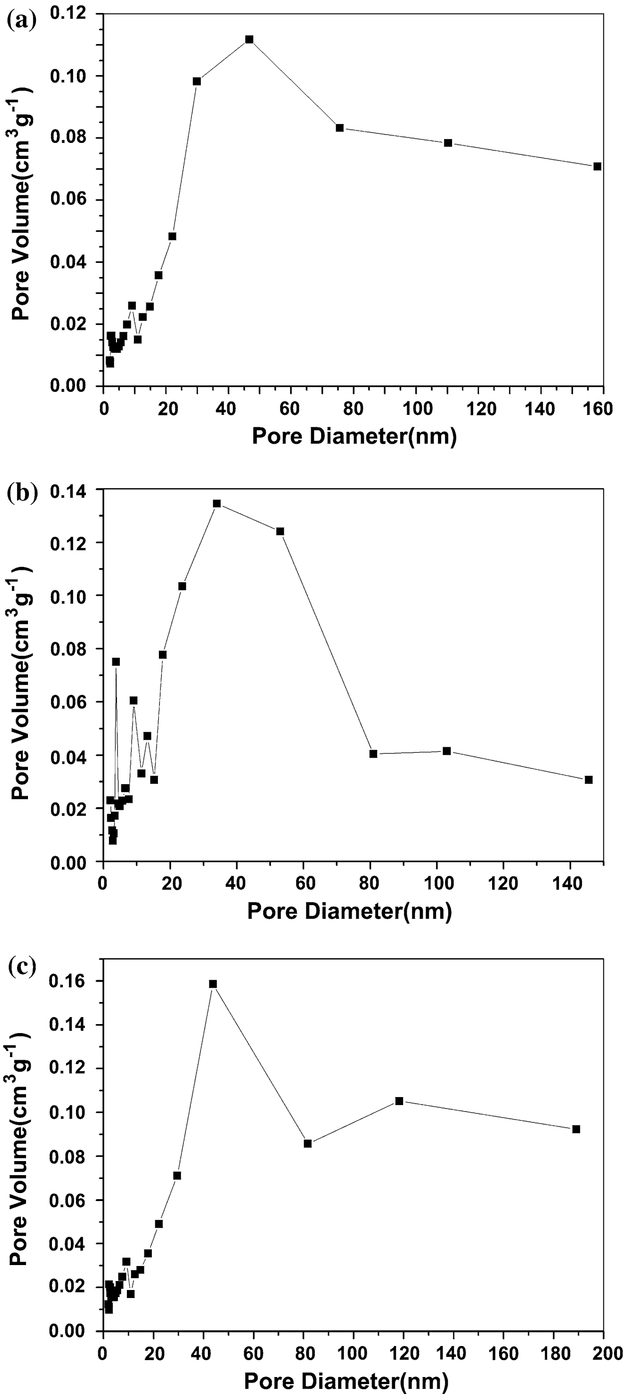

Fig. 4 Pore size distribution of the samples: HPC–ST (**a**), HPC–SU (**b**) and HPC–GL (**c**)

Figure 4 is pore size distribution curves of the samples HPC–ST, HPC–SU and HPC–GL, from which we can clearly found that the main kind of the pore is meso-pores range from 30 to 50 nm. Besides, HPC–SU also has a pore size distribution peak around 5 and 10 nm, which indicates that besides 30–50 nm meso-pore, this sample also has lots of meso-pore with pore diameters range from 5 to 10 nm. The analysis of pore size distribution curves are just in accordance with the SEM images as has been discussed above.

The results in Figs. 1, 2, 3 and 4, Table 1 clearly reveal that using starch, sucrose or glucose as carbon source, respectively, does not make any significant differences on the morphology of the as-prepared samples. All of the samples have an obvious hierarchical and irregular pore structure proved by the SEM images. However, the HPCs obtained from sucrose as carbon source, though with a similar appearance on the pore structure, shows better properties such as BET surface area, total-pore volume and percentage of micro-pore in the main body than the two obtained from starch and glucose, respectively, which means sucrose is a better carbon source to synthesize HPCs than that of starch and glucose.

A possible mechanism for the formation of hierarchical pores is shown in Fig. 5. The origin addition of the reactants is sodium hydroxide, nickel nitrate and carbon sources. Then the precursor which contains nickel hydroxide, sodium nitrate and carbon source is formed followed by the carbonization process step 1, step 2 and step 3. In step 1, when the reaction temperature increases above 340 °C (pyrolysis temperature of sodium nitrate), sodium nitrate begins to decompose and generate oxynitride, with the dissipation of which, micro-pore and meso-pore with small diameter will be left in the main body. In step 2, carbon source will be changed to carbon filled with nickel compounds and sodium oxide which would be washed away in step 3, leaving hierarchical pores in the carbon body.

Conclusions

Green and low-cost materials as carbon source to synthesize HPCs has been developed using nickel hydroxide as template and starch, sucrose or glucose as carbon source. By changing the carbon source, HPCs with different BET surface area are synthesized. The sample using sucrose as carbon source shows a BET surface area of 829 m^2/g which is larger than the other two, and it also means, among the three green and low-cost carbon sources, sucrose proves to be the best and the one that will have large application potential. Moreover, a possible mechanism for the formation of HPCs is given here for the first time which gives a good explanation about the formation mechanism of different size of pores in the main carbon body.

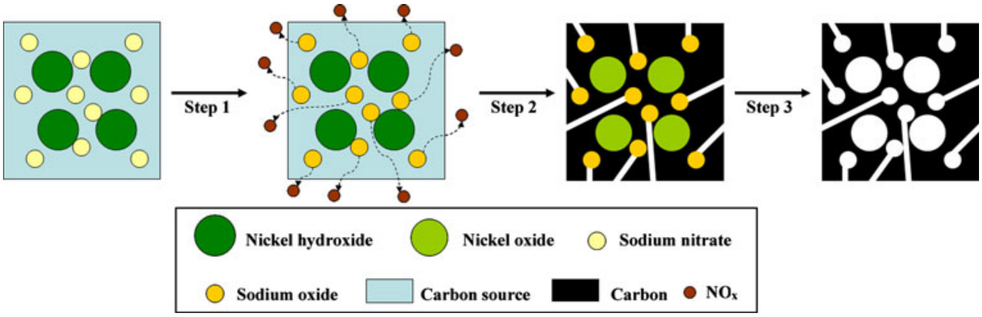

Fig. 5 Possible mechanism for the formation of HPCs

Acknowledgements This research was supported by the Natural Science Union Foundations of China and Guangdong Province (U0734005) and National Natural Science Foundation of China (20906037).

References

1. Iijima S (1991) Nature 354:56
2. Xiao Y, Liu YL, Yuan DS (2008) Carbon 46:559
3. Novoselov KS, Geim AK, Morozov SV, Jiang D, Zhang Y, Dubonos SV, Grigorieva IV, Firsov AA (2004) Science 306:666
4. Kim JY, Yoon SB, Yu JS (2003) Chem Mater 15:1932
5. Ryoo R, Joo SH, Kruk M, Jaroniec M (2001) Adv Mater 13:677
6. Lee J, Kim J, Hyeon T (2006) Adv Mater 18:2073
7. Wan Y, Shi YF, Zhao DY (2008) Chem Mater 20:932
8. Yuan ZY, Su BL (2006) J Mater Chem 16:663
9. Lu AH, Schueth F (2006) Adv Mater 18:1793
10. Wang YQ, Yang CM, Schmidt W, Spliethoff B, Bill E, Schueth F (2005) Adv Mater 17:53
11. Song C, Du JP, Zhao JH, Feng SA, Du GX, Zhu ZP (2009) Chem Mater 21:1524
12. Wang DW, Li F, Liu M, Lu GQ, Cheng HM (2008) Angew Chem Int Ed 47:373
13. Wang HL, Gao QM, Hu J (2009) J Am Chem Soc 131:7016
14. Zheng MT, Liu YL, Xiao Y, Zhu Y, Guan Q, Yuan DS, Zhang JX (2009) J Phys Chem C 113:8455
15. Wang DW, Li F, Cheng HM (2008) J Power Sources 185:1563