Accepted Manuscript

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PII:	S1001-8417(17)30458-8
DOI:	https://doi.org/10.1016/j.cclet.2017.10.041
Reference:	CCLET 4314
To appear in:	*Chinese Chemical Letters*
Received date:	13-9-2017
Revised date:	14-10-2017
Accepted date:	31-10-2017

Please cite this article as: Jinhui Xu, Wenli Zhang, Dianxun Hou, Weimin Huang, Haibo Lin, Hierarchical porous carbon derived from Allium cepa for supercapacitors through direct carbonization method with the assist of calcium acetate, Chinese Chemical Letters https://doi.org/10.1016/j.cclet.2017.10.041

Communication

Hierarchical porous carbon derived from *Allium cepa* for supercapacitors through direct carbonization method with the assist of calcium acetate

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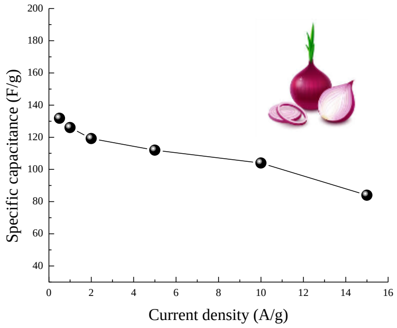
Graphical Abstract



Hierarchical porous carbon was prepared from onion through a direct carbonization method and it was used as suercapacitor electrode material.

ARTICLE INFO

Article history:
Received 13 September 2017
Received in revised form 14 October 2017
Accepted 24 October 2017
Available online

Keywords:
Porous carbon
Supercapacitor
Allium cepa
Hierarchical porous carbon
Direct pyrolysis
Biomass

ABSTRACT

In this paper, a direction carbonization method was used to prepare porous carbon from *Allium cepa* for supercapacitor applications. In this method, calcium acetate was used to assist carbonization process. Scanning electron microscope (SEM) and N_2 adsorption/desorption method were used to characterize the morphology, Brunauer-Emmett-Teller (BET) specific surface area and pore size distribution of porous carbon derived from *Allium cepa* (onion derived porous carbon, OPC). OPC is of hierarchical porous structure with high specific surface area and relatively high specific capacitance. OPC possesses relatively high specific surface area of 533.5 m^2/g. What's more, OPC possesses a specific capacitance of 133.5 F/g at scan rate of 5 mV/s.

During the past 20 years, research on supercapacitor has achieved great development. However, two major defects still remain in supercapacitor: (1) Low energy density; (2) High cost of electrode material, electrolyte and assembling progress [1]. These two defects limit the real-world applications of supercapacitor. In order to overcome these disadvantages, recent research mainly focuses on the areas of improving energy density, increasing cycle stability to extend life span and decreasing the cost of electrode materials.

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Porous carbon material is the commercial electrode materials for supercapacitors [2-6]. Traditional preparation method includes template method and activation method. Templates include hard template [7-8], soft template method [9-11] and dual template [12-13]. However, template methods are usually complicated and consume a large amount of chemicals. Activation method, usually referring to chemical activation method, is easy to obtain high surface area, controlled pore size and its distribution. Due to the sustainable nature of biomasses compared with petroleum products, biomass based porous carbon has obtained researcher's attention. Green, cheap and renewable biomass is treated as carbon precursor, for example rice husk, lignin, fish bone, banana peel *etc.* [14-18]. However, traditional activation method has two major drawbacks, it consumes a large amount of activation agent and is difficult to mix carbon precursor and activation agent homogeneously.

In this paper, using *Allium cepa* (usually called onion) as carbon precursor, a hierarchical porous carbon (onion derived porous carbon, OPC) was prepared through an easy, facile direct carbonization method with the assist of calcium acetate. OPC shows relatively high surface area and high specific capacitance with long-term stability. Detailed experimental procedure can be seen in Supporting information. All the electrochemical calculations are based on our previous study [17].

Fig. 1 displays the scanning electron microscope (SEM) images of three carbons. As can be seen in Fig. 1a, the morphology of OPC has a lamellar structure, as described in other literatures [19,20]. Fig. 1b indicates that the thickness of lamellar layer is of hundreds nanometers. In contrast, OC-1 (onion derived carbon, OC-1) (Fig. 1c) and OC-2（onion carbonized with calcium acetate solids, OC-2） (Fig. 1d) does not have similar lamellar structure and its morphology is in bulk particles.

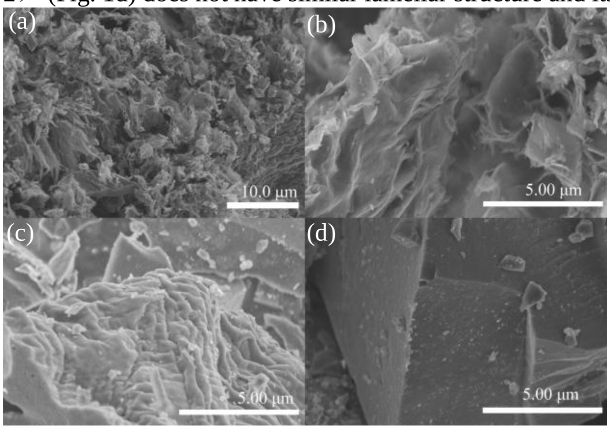

Fig. 1. (a) SEM image of OPC. (b) SEM image of OPC under high resolution. (c) SEM image of OC-1. (d) SEM imagine of OC-2.

The different morphology of OPC from OC-1 and OC-2 originates from the decomposition of $Ca(Ac)_2$ soaked into the onion. The decomposition of $Ca(Ac)_2$ forms $CaCO_3$. When $CaCO_3$ decomposes (825 ºC), the carbon skeleton of onion is already formed. The physical activation and evolution of CO_2 decomposed from $CaCO_3$ creates some pores in OPC. For OPC, due to well distribution of $Ca(Ac)_2$ among the onion tissues, evolution of CO_2 is able to separate the lamellar structure in onion, as a result the lamellar structure of OPC occurs. For OC-2, physical mixture of two solids is unable to allow $Ca(Ac)_2$ enter into onion tissues. SEM image of OC-2 is similar with OC-1, they are of large particles. N_2 adsorption/desorption experiments were carried out to analyze pore structure and specific surface area. OPC has a type I/IV adsorption isotherm (Fig. 2a) with a very steep increase in low pressure and a small hysteresis curve in high pressure, indicating the co-existence of micropores and mesopores in OPC. OPC has a Brunauer-Emmett-Teller (BET) area of 533.5 m^2/g with a microporous surface area of 348.8 m^2/g (Table 1). In contrast, OC-1 and OC-2 only have low BET area of 140.4 m^2/g and 158.8 m^2/g, respectively. According to pore size distribution of OPC (Fig. 2b and S1c in Supporting information), mesopores mainly distribute around 4 nm and mircropores distribute around 1.1 nm, indicating that OPC is a hierarchical porous carbon with micropores and mesopores. Besides, OC-1 and OC-2 are also hierarchical porous carbons but with less pore and smaller surface area. OC-1 and OC-2 have small micropores, mainly around 0.6 nm (Fig. S1d and e in Supporting information).

Table 1 Pore parameters of OPC, OC-1 and OC-2.

Samples	S_{BET} (m^2/g)	$S_{t\text{-}plots}$ (m^2/g)	$S_{t\text{-}plots}/S_{BET}$ (%)	V_{total} (cm^3/g)	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)
OPC	533.5	348.8	65.4	0.500	0.201	0.385
OC-1	140.4	114.7	81.7	0.090	0.038	0.061
OC-2	158.8	127.6	80.4	0.094	0.050	0.063

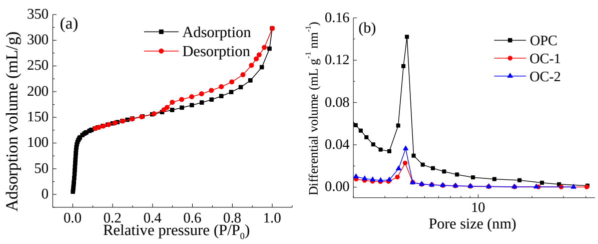

Fig. 2. (a) Adsorption-desorption isotherms of OPC. (b) Mesopore size distribution of OPC, OC-1 and OC-2.

To analyze the supercapacitive performance of OPC, CV （cyclic voltammetry, CV）analysis was carried out in a two electrode system. Fig. S2a (Supporting information) displays the cyclic votammograms of OPC under different scan rates. OPC exhibits a *quasi*-rectangular shape even at high scan rates, which indicates that a *quasi*-ideal capacitive behavior of OPC. At scan rate of 5 mV/s and 500 mV/s, the specific capacitance of OPC is 133.5 F/g and 58.4 F/g, respectively. In contrast, OC-1 and OC-2 have a much lower specific capacitance and poor abilities to retain *quasi*-rectangular shape at high rates (Fig. S2b and S3 in Supporting information). Specific capacitance of OC-1 and OC-2 is only 24.5 F/g and 32.5 F/g at 10 mV/s, respectively (Fig. S2c in Supporting information). The excellent supercapacitive performance of OPC can be attributed to high specific surface area and hierarchical porous structure of OPC. Abundant micropores endow OPC large surface area with excellent ion storage abilities to construct electric double layer. Mesopores allow fast ion transportation and electrolyte penetration [17].

Fig. S2d (Supporting information) is Nyquist plot of three carbon materials. As shown in Fig. S2d, OPC has a much smaller semi-circle radius than OC-1 and OC-2, indicating that charge transfer resistance (R_{ct}) of OPC is lower than OC. Small R_{ct} is also a reason for the high specific capacitance and great rectangular shape retaining ability of OPC, while high R_{ct} of OC causes low capacity and poor ability to retain rectangular.

GCD （galvanostatic charge and discharge, GCD） tests were carried out to test the supercapacitive performance of OPC (Fig. 3a). OPC shows outstanding rate performance and cycle stability. At a current density of 0.5 A/g, the specific capacitance of OPC is 131.8 F/g. The specific capacitance of OPC retains 84 F/g, at a high current density of 15 A/g (Fig. 3b). The capacitance retention ratio reaches as high as 73.7% compared with value at 0.5 A/g. Slight voltage drop in charge-discharge process indicates low equivalent series resistance of OPC. After 2000 GCD cycles at 2 A/g, the specific capacitance of OPC retains 99.7% (Fig. 3c).

Fig. 3d is the Nyquist plot of OPC before and after 2000 cycles. Equivalent circuit in reference [17] is used to simulate related electrical parameters. R_s stands for ohmic resistance. R_{ct} represents charge transfer resistance. Z_w is Warburg impedance. C stands for electric double layer capacitance. Q is constant phase element. According to data listed in Table S1 (Supporting information). R_{ct} only increases from 0.8314 Ω cm^2 to 0.9402 Ω cm^2, showing good cycling stability of OPC. However, R_s slightly decreases from 0.5967 Ω cm^2 to 0.5091 Ω cm^2. This phenomenon may be related to electrolyte penetration.

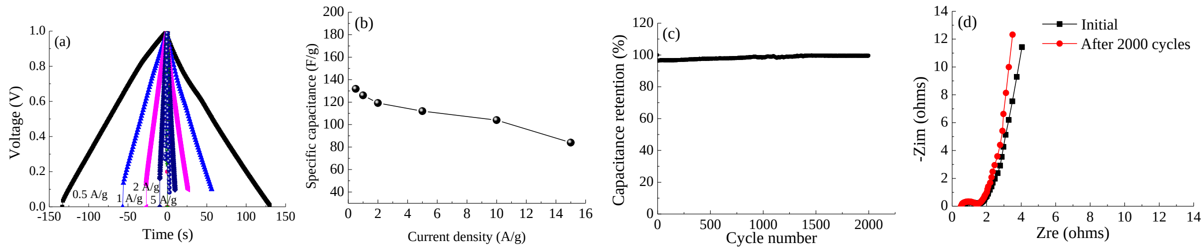

Fig. 3. (a) GCD curves of OPC at current densities ranging from 0.5 A/g to 15.0 A/g in 6 mol/L KOH solution. (b) Dependence of the specific capacitance of OPC on charge/discharge current density. (c) GCD cycling performance of OPC at 2.0 A/g in 6 mol/L KOH solution. (d) Nyquist plot before and after cycling test.

In Summary, OPC was prepared from *Allium cepa* by direct carbonization with the assist of $Ca(Ac)_2$. Solution saturating enable $Ca(Ac)_2$ to be evenly distributed in the tissues of Onion. Compared with carbon directly carbonized from dehydrated onion and the mixture of dehydrated onion and $Ca(Ac)_2$, OPC has lamellar structure and contains rich micropores and mesopores. Unique morphology and pore structure originate from the evolution and physical activation of CO_2 decomposed from $Ca(Ac)_2$ in onion tissues. Compared with other porous carbon obtained from direct carbonization method, OPC exhibits good supercapacitive performance and capacitance retention (Table S2 in Supporting information).

Acknowledgement

The research group acknowledges the financial support provided by National Natural Science Foundation of China (No. 21573093), National Key Research and Development Program (Nos. 2016YFC1102802, 2017YFB0307501) and Guangdong Innovative and Entrepreneurial Research Team Program (No. 2013C092).

References

[1] W. Zhang, N. Lin, D. Liu, et al., Energy 128 (2017) 618-625.
[2] Y. Li, G. Wang, T. Wei, et al., Nano Energy 19 (2016) 165-175.
[3] G. Zu, J. Shen, L. Zou, et al., Carbon 99 (2016) 203-211.
[4] J. Liu, X. Wang, J. Gao, et al., Electrochim. Acta 211 (2016) 183-192.
[5] W. Geng, F. Ma, G. Wu, et al., Electrochim. Acta 191 (2016) 854-863.
[6] Z. Chen, J. Wen, C. Yan, et al., Adv. Energy Mater. 1 (2011) 551-556.
[7] G.S. Chai, S.B. Yoon, J.S. Yu, et al., J. Phys. Chem. B 108 (2004) 7074-7079.
[8] A.A. Zakhidov, R.H. Baughman, Z. Iqbal, et al., Science 282 (1998) 897-901.
[9] Y. Xia, Z. Yang, R. Mokaya, et al., Adv. Energy Mater. 1 (2011) 678-683.
[10] J. Balach, L. Tamnorini, K. Sapag, et al., Colloids Surface A 415 (2012) 343-348.
[11] C. Huang, R. Doong, Microporous Mesoporous Mater. 147 (2012) 47-52.
[12] Y.H. Deng, C. Liu, T. Yu, et al., Chem. Mater. 19 (2007) 3271-3277.
[13] S.H. Du, L.Q. Wang, X.T. Fu, et al., Bioresource Technol. 139 (2013) 406-409.

[14] Y.K. Lv, L.H. Gan, M.X. Liu, et al., J. Power Sources 209 (2012) 152-157.
[15] W Chen, H. Zhang, Y. Huang, W. Wang, J. Mater. Chem. 20 (2010) 4773-4775.
[16] Z. Qiao, M. Chen, C. Wang, Y. Yuan, Bioresource Technol. 163 (2014) 386-389.
[17] W. Zhang, H. Lin, Z. Lin, et al., ChemSusChem 12 (2015) 2114–2122.
[18] W. Zhang, M. Zhao, et al., Colloid. Surface A 484 (2015) 518-527.
[19] T. Wei, X. Wei, L. Yang, et al., J. Power Sources 331 (2016) 373-381.
[20] J. Jin, L. Gu, L. Jiang, et al., Carbon 109 (2016) 306-313.