



Direct synthesis of porous carbon via carbonizing precursors of aluminum phosphate containing citric acid

Gang Liu, Yu Liu, Zhenlu Wang, Xiangzhou Liao, Shujie Wu, Wenxiang Zhang*, Mingjun Jia*

Key Laboratory of Surface and Interface Chemistry of Jilin Province, College of Chemistry, Jilin University, Changchun 130021, China

ARTICLE INFO

Article history:

Received 11 March 2008
Received in revised form 5 May 2008
Accepted 7 May 2008
Available online 25 May 2008

Keywords:

Porous carbon
Mesoporous material
Aluminophosphate
Citric acid
Hard template

ABSTRACT

A simple and efficient route is reported for the synthesis of porous carbon materials via carbonizing a kind of composite containing citric acid (CA) and aluminum phosphate (AIPO). The resulting carbon materials, bearing mesoporous and/or microporous characteristics, possess uniform pore size distribution and certain degree graphitic phase characteristic. The structural parameters of these materials, including mean pore sizes, pore volumes and specific surface areas, can be further tuned within a certain range by addition of suitable amount of sucrose (SU) into the CA/AIPO composite. The mesostructured AIPO, which is formed *in situ* during the carbonization, can be regarded as a hard-template for the formation of porous carbon material. We propose that the uniform distribution of CA, and the presence of suitable interaction between CA and aluminum phosphate are critical factors for the formation of mesoporous carbon network.

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1. Introduction

Synthesis of porous carbon materials is an important research subject, because these materials are extensively applied in various technological areas [1–4]. Recently, with the rapid development of novel means for the synthesis of various silica-based mesoporous materials, greater attention has focused on the synthesis of novel porous carbon materials with attractive characteristics, e.g. uniform mesoporous structure, graphitic phase, etc. [5–9].

The hard-template route was widely reported for synthesizing various uniform mesoporous carbon materials [10–12]. Different silica and aluminosilica mesoporous materials could be used as hard-templates for the synthesis of mesoporous carbon [7]. However, this route was generally required relatively complicate procedures, i.e. the extra step of preparation of the silica template, and infiltration of carbon precursor into the template pores prior to the carbonization [13,14]. Moreover, limited possibilities to tailor pore wall thickness in mesoporous silica [7,15,16] made it difficult to control pore size by this method. Hence, many efforts have been devoted to developing novel, simple and efficient methods for the synthesis of mesoporous carbon materials, and significant progress has already been marked in the past few years. For examples, Yoon et al. [17] and Kim et al. [18] reported independently a direct template carbonization method using as-synthesized mesostructured silica hosts to synthesize uniform mesoporous carbons. In their work, the surfactant occupying its mesopore channel was used di-

rectly as precursor of carbon. Besides, direct self-assembly of block co-polymers and resorcinol-formaldehyde resin, a so-called “soft-template” assembly route, was also reported recently in connection with generating an ordered mesoporous carbon structure [19,20]. Simultaneously, some mesoporous carbon materials of relatively low-ordered degree have also been synthesized by other direct synthesis methods [21–28]. For example, Kawashima et al. [21] prepared a porous carbon by using a simple sol-gel process with tetraethoxy silane (TEOS) in the presence of furfuryl alcohol. Pang et al. [25] and Zheng et al. [26] synthesized a kind of carbon material with mesocellular-foam-like characteristic by direct carbonizing a kind of composite containing polymer/silica/ $C_{16}H_{33}N(CH_3)_3Br$. Moreover, by using colloidal silica or colloidal silica aggregates as templates, mesoporous carbon with relatively large pore size and/or bimodal porosity could also be obtained [27,28].

Here, we report a simple, efficient method to synthesize porous carbon materials via direct carbonizing of a kind of composite containing citric acid (CA) and aluminum phosphate (AIPO). Previously, we have reported that thermally stable amorphous mesoporous AIPO could be synthesized by direct calcinations of the CA/AIPO composite, which is obtained by using CA as organic additive [29–31]. In the present work, the influence of citric acid amount and additional sucrose (as mixed carbon precursors) on the pore formation of the carbon materials is investigated. Various characterization means, such as N_2 adsorption, XRD, SEM, TEM and TG-DTA, are applied to obtain information of the texture and structure properties of porous carbon. Interestingly, carbon materials with mesoporous and/or microporous characteristics can be

* Corresponding authors. Tel.: +86 431 85155390; fax: +86 431 88499140.
E-mail addresses: zhwenx@jlu.edu.cn (W. Zhang), jiamj@jlu.edu.cn (M. Jia).

synthesized by using this method, and the structure parameters of these materials can be tuned in a certain range by changing the ratio of CA/Al, or by adding a certain amount of sucrose (SU) into the CA/AlPO composite.

2. Experimental

2.1. Synthesis

The CA/AlPO composite is prepared following a procedure described elsewhere [31]. Typically, H_3PO_4 (85 wt%) is dropped into a mixed aqueous solution of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and CA under vigorous stirring at ambient temperature, leading to a composition in molar ratio of $1.0:x:1.0:86 = \text{Al}(\text{NO}_3)_3/\text{CA}/\text{H}_3\text{PO}_4/\text{H}_2\text{O}$ ($x = 0.5, 1.0, 1.5$). After that, an aqueous ammonia solution (10 wt%) is used to adjust the pH value of the solution to 5.0. The solid CA/AlPO composite is formed after removing water and all other volatiles by heating the mixed solution at 363 K for 10 h.

The porous carbon material is obtained via the following steps: the CA/AlPO composite is first pretreated at 573 K in open air for a few minutes, then carbonization of the composite is carried out at 1073 K for 6 h under an argon flow. The black carbonized composite (denoted as NC-AlPO) is treated with 4 M HNO_3 solution at 323 K to remove AlPO component, and is filtered and dried at 383 K to obtain the resulting carbon materials (designated as NC-1). Another series of samples, which are prepared by introducing a certain amount of SU into the CA/AlPO composite, are labeled as NC-2. The experimental conditions and structural parameters of various porous carbon materials are shown in Table 1. Besides, a reference sample of mesoporous AlPO is also prepared by direct calcinations of a part of CA/AlPO composite (CA/Al = 1.5) at 873 K for 3 h in air.

2.2. Characterization

N_2 -adsorption/desorption isotherms were measured at 77 K, using a Micromeritics ASAP 2010N analyzer. Samples were degassed at 523 K for 8 h before measurements. Specific surface areas were calculated using the Brunauer–Emmett–Teller (BET) model. Pore volumes were estimated at a relative pressure of 0.94 (P/P_0), assuming full surface saturation with nitrogen. Pore size distributions were evaluated from desorption branches of nitrogen isotherms using the Barret–Joyner–Halenda (BJH) model. Powder X-ray diffraction (XRD) patterns were recorded on Shimadzu XRD-6000 diffractometer (40 kV, 30 mA) using Ni-filtered $\text{Cu K}\alpha$ radiation. Raman spectrum was recorded with a RENishaw in-via Raman spectrometer. Scanning electron microscopy (SEM) micrographs were obtained using a Shimadzu SSX-550 microscope. Transmission electron microscopy (TEM) images were

taken with a Mic HITACHI I-8100 electron microscope operating at 200 kV. Thermalgravimetry and differential thermal analysis (TG-DTA) experiments were performed using Shimadzu DTG-60 thermal station in flowing argon with a heating rate of 10 K min^{-1} , in the range from room temperature to 1123 K.

3. Results and discussion

3.1. Synthesis and characterization of porous carbon

The porous characteristic of the three NC-1 carbon materials (NC-1a, NC-1b and NC-1c) synthesized from the CA/AlPO composites with different CA/Al ratio is investigated by N_2 adsorption–desorption isotherms (Fig. 1). The samples of NC-1a (CA/Al = 0.5) and NC-1b (CA/Al = 1.0) exhibit type I + IV isotherms with a small hysteresis loop, implying the co-presence of micropores and mesopores [32]. This point can be further verified by BJH calculations (Fig. 1 inset). The sample of NC-1c (CA/Al = 1.5) shows a typical type IV isotherm, which is a characteristic of mesoporous materials [33]. The appearance of H2 hysteresis loops at relative pressure 0.4–0.7 indicates the presence of “ink-bottle” type pores in this material. The pore size distribution curve shows that NC-1c exhibits two sharp peaks in mesopore range centered at 3.5 and 2.2 nm, respectively (Fig. 1 inset). Analysis in micropore range shows that NC-1c also possesses a certain amount of micropore with mean pore diameter of 0.46 nm. Besides, the BET surface area and pore volume of NC-1a and NC-1b are $420 \text{ m}^2/\text{g}$, $0.07 \text{ cm}^3/\text{g}$ and $442 \text{ m}^2/\text{g}$, $0.14 \text{ cm}^3/\text{g}$, respectively, much lower than that of NC-1c ($738 \text{ m}^2/\text{g}$, $0.32 \text{ cm}^3/\text{g}$).

These results suggest that NC-1 carbon materials with mesoporous and/or micropores characteristics could be obtained by directly carbonizing the CA/AlPO composite, and the content of CA could considerably influence the pore size distributions and pore volume of the porous carbon materials.

Fig. 2 shows the N_2 adsorption–desorption isotherms and pore size distributions of five NC-2 samples prepared by the addition of different amounts of SU into the CA/AlPO composites (CA/Al = 0.5). The samples of NC-2a (SU/CA = 0.5/0.5) and NC-2b (SU/CA = 0.7/0.5) exhibit type IV curves with an H1-type hysteresis loop in the range 0.70–0.80, which is a mesoporous characteristic with relatively large pore size [33]. The pore size distribution curves show that NC-2a and NC-2b exhibit two peaks centered at

Table 1
Synthesis parameters and texture properties of carbon materials

| Sample | Composition of starting mixture (mol ratio) | S_{BET} ($\text{m}^2 \text{ g}^{-1}$) | Vol ($\text{cm}^3 \text{ g}^{-1}$) | Pore size ^a (nm) |
|---------|---|--|--------------------------------------|-----------------------------|
| NC-1a | CA/Al/P = 0.5/1/1 | 420 | 0.07 | 2.6 |
| NC-1b | CA/Al/P = 1.0/1/1 | 442 | 0.14 | 2.8 |
| NC-1c | CA/Al/P = 1.5/1/1 | 738 | 0.32 | 3.1 |
| NC-2a | SU/CA/ Al/P = 0.5/0.5/1/1 | 1018 | 1.10 | 5.3 |
| NC-2b | SU/CA/ Al/P = 0.7/0.5/1/1 | 1044 | 0.96 | 4.6 |
| NC-2c | SU/CA/ Al/P = 1.0/0.5/1/1 | 1072 | 0.91 | 3.4 |
| NC-2d | SU/CA/ Al/P = 1.2/0.5/1/1 | 1042 | 0.50 | 2.8 |
| NC-2e | SU/CA/ Al/P = 1.5/0.5/1/1 | 1051 | 0.25 | 2.0 |
| AlPO | CA/Al/P = 1.5/1/1 | 492 | 0.44 | 3.9 |
| NC-AlPO | CA/Al/P = 1.5/1/1 | 138 | 0.05 | 3.5 |

^a Average pore diameters calculated from desorption branches by using the BJH model.

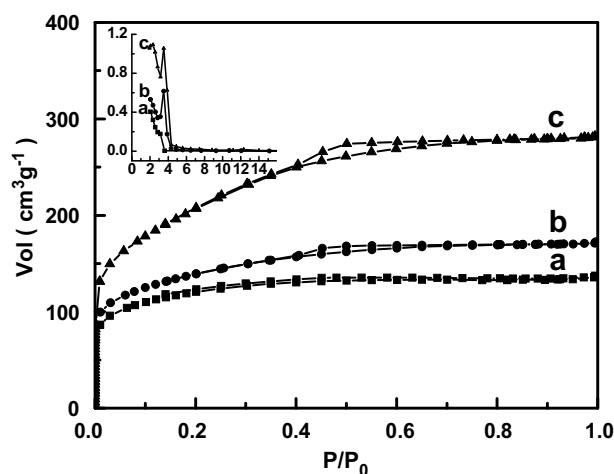


Fig. 1. N_2 adsorption–desorption isotherms and corresponding pore size distribution curves (inset) of (a) NC-1a, CA/Al = 0.5; (b) NC-1b, CA/Al = 1.0; (c) NC-1c, CA/Al = 1.5. Pore size distributions were evaluated from desorption branches of nitrogen isotherms using the BJH model.

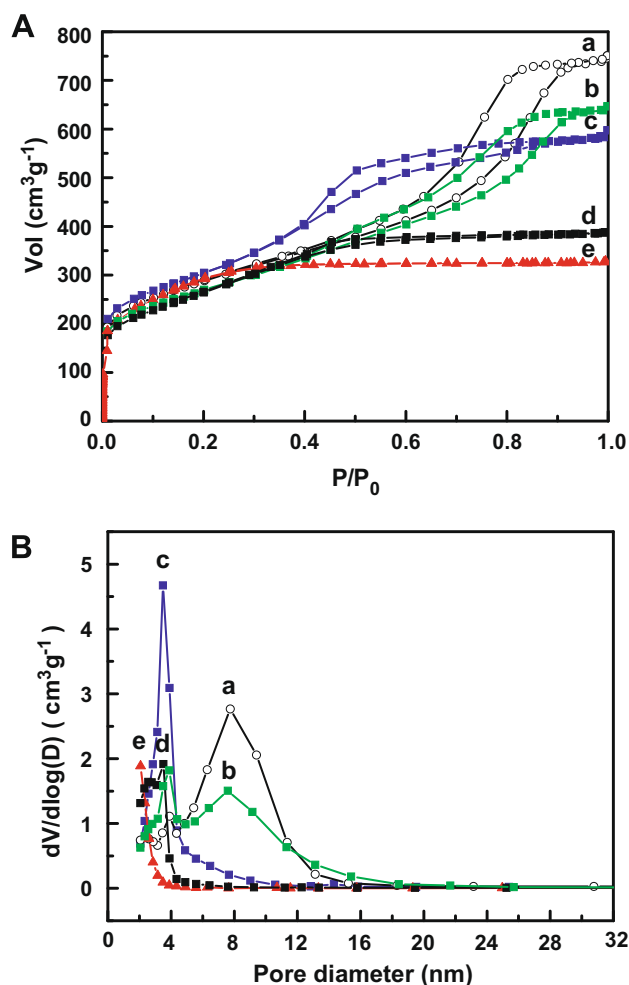


Fig. 2. N₂ adsorption–desorption isotherms (A) and corresponding pore size distribution curves (B) of (a) NC-2a, SU/CA = 0.5/0.5; (b) NC-2b, SU/CA = 0.7/0.5; (c) NC-2c, SU/CA = 1.0/0.5; (d) NC-2d, SU/CA = 1.2/0.5; (e) NC-2e, SU/CA = 1.5/0.5. Pore size distributions were evaluated from desorption branches of nitrogen isotherms using the BJH model.

3.8 and 7.6 nm, respectively. When the ratio of SU/CA increases to 1.0/0.5, the sample of NC-2c displays type IV isotherms with H2-type hysteresis loop, indicating the presence of “ink-bottle” type pores [33]. The pore size distribution curve of NC-2c shows a sharp peak centered at 3.8 nm. With further increasing the ratio of SU/CA to 1.5/0.5, the resultant sample of NC-2e exhibits type I isotherm with relatively small pore size (around 0.5 nm, calculated by Horvath–Kawazoe method), which is a characteristic of microporous materials [33]. These results suggest that the pore volumes and average pore sizes of NC-2 materials decrease with the increase of SU amount (see in Table 1). The largest values of pore volume and average pore size are obtained at the SU/CA ratio of 0.5/0.5, which are 1.10 cm³/g and 5.3 nm (calculated by using the BJH model), respectively. It should be noted that all the five samples of NC-2 exhibit much higher specific surface areas (above 1000 m²/g) and pore volumes than that of NC-1 samples, indicating that the addition of a certain amount of SU could be benefit to the formation of mesoporous channels of carbon materials.

The XRD patterns of a few representative samples of mesoporous carbon materials (NC-1c, NC-2a, NC-2c and NC-2e) are shown in Fig. 3. All the samples exhibit two broad diffraction peaks centered at 26° and 44°, which can be generally indexed to (002), (10) diffraction for glass-like carbons bearing graphitic characteristic [34]. The relatively broad signals suggest that the graphitization

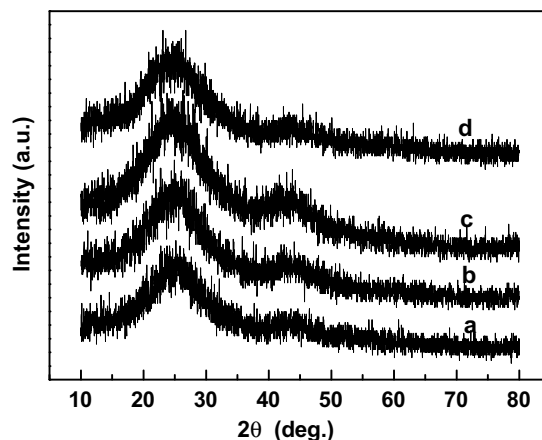


Fig. 3. XRD patterns of carbon materials: (a) NC-1c; (b) NC-2a; (c) NC-2c; (d) NC-2e.

level of these materials is very low. The d_{002} spacing obtained from the (002) peak is 3.42 Å, which is larger than that of ideal graphite (with $d_{002} = 3.35$ Å). The characterization of Raman spectra can further confirm the results of XRD. As shown in Fig. 4, both samples of NC-1c and NC-2c exhibit two peaks at around 1350 (D band) and 1590 cm⁻¹ (G band), indicating the presence of graphitic phase in these materials [34,35]. The relatively low intensity and broad signal of G band suggest that the graphitic level of these carbon materials is not very high [36].

Fig. 5 shows the representative SEM images of porous carbon NC-1c, NC-2a, NC-2c and NC-2e. The morphology of these carbon materials exhibits quite uniform film-like shape, indicating that carbon is present as a rigid continuous rather than isolate phase in these materials [22]. TEM images reveal that these materials possess disordered but uniform-size worm-like mesoporous structure, which is similar to that of mesoporous aluminophosphates (Fig. 6) [22].

Fig. 7 shows the DTA-TG profiles of the CA/AlPO composite (CA/Al = 1.5) recorded under argon atmosphere. The endothermic peak around 470 K along with the rapid weight loss can be ascribed to the partial decomposition of CA. The existence of a very strong exothermic peak at 530 K might be mainly caused by the decomposition of ammonium nitrates [29]. The gradual weight loss in the temperature range from 540 to 1000 K can be assigned to the continued carbonization of CA (mainly coordinated with Al species) and the condensation reaction of hydroxyls for the formation of

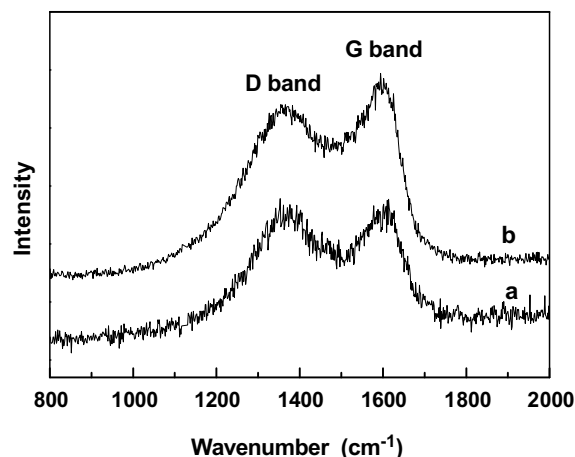


Fig. 4. Raman spectra of carbon materials: (a) NC-1c; (b) NC-2c.

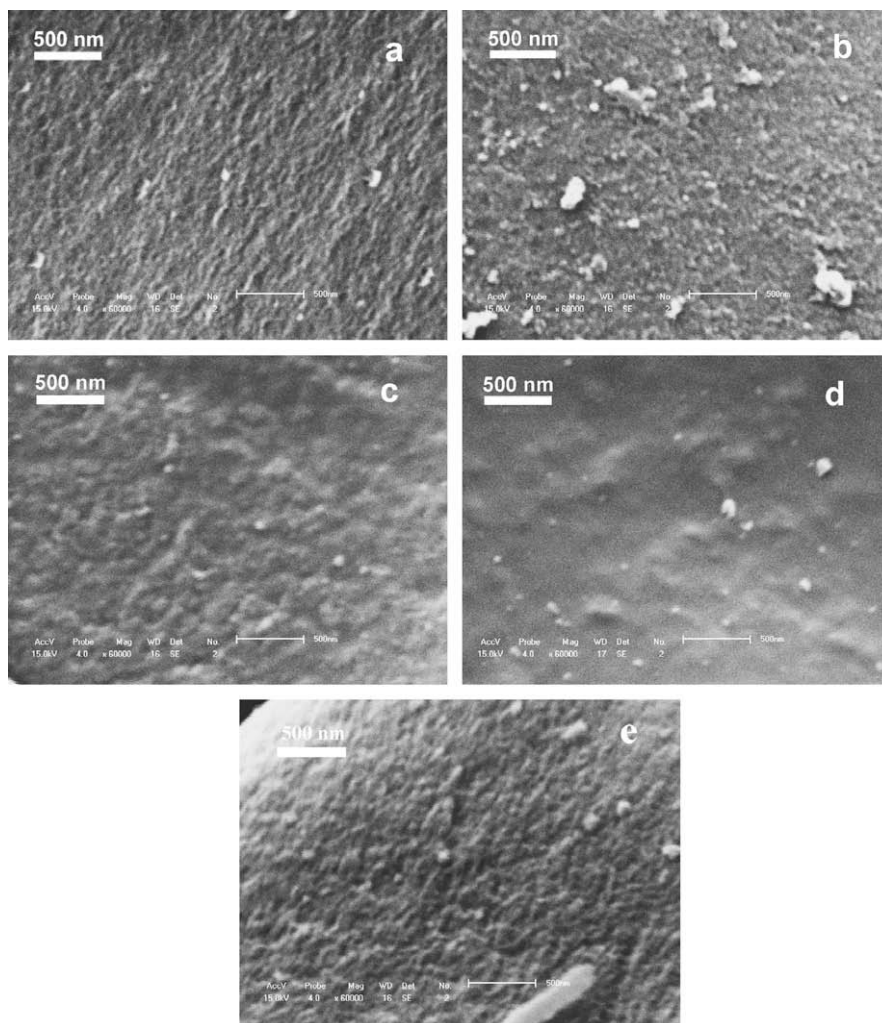


Fig. 5. SEM images of carbon materials: (a) NC-1c; (b) NC-2a; (c) NC-2c; (d) NC-2e; (e) AIPO.

AIPO framework [29]. We suppose that the strong exothermic process at around 530 K might be responsible for the formation of graphitic pore wall.

3.2. Discussion on the formation of porous carbon framework

For investigating the pore formation process, the N_2 -adsorption/desorption isotherms of mesoporous AIPO and the carbonized intermediated composite of NC-AIPO, which is derived from the same precursor of CA/AIPO for the synthesis of NC-1c, are given in Fig. 8. Both mesoporous AIPO and NC-AIPO samples exhibit mesoporous characters with narrow pore size distributions centered at 3.9 and 3.5 nm, respectively, which is consistent to the relatively large mesopore of NC-1c (see Fig. 1c). These results suggest that the mesopore of 3.5 nm in NC-1c has already formed during the carbonization, while the formation of relative small mesopores (2.2 nm) and a part of micropore in NC-1c should be mainly assigned to the removal of inorganic ingredient of AIPO after treating the NC-AIPO with HNO_3 .

Previously, we have proposed that the special coordination ability of CA is benefit to the formation of uniform complexes (such as $CA-Al-PO_4$) in the as-synthesized CA/AIPO composite, resulting in the presence of a suitable interaction between CA and AIPO framework for the formation of thermally stable mesoporous structures of AIPO [30]. Thus we had concluded that CA, as an organic additive, could function as a special template for the synthesis of

mesoporous AIPO materials [30,31]. In the present case, we think that the presence of uniform complexes in CA/AIPO composite can lead to uniform dispersion of carbon precursors, thus being benefit to the formation of continuous carbon network. Therefore, the presence of a suitable interaction between CA and AIPO should be also an important factor for the growth of carbon network of porous NC-1 during carbonization. It should be reasonable to propose that the thermal stable AIPO framework may function as scaffold or hard-template for the formation of carbon network during high-temperature carbonization, since we have found previously that the framework of mesoporous AIPO, already formed below 673 K, possess very high thermal stability (up to 1173 K) [31]. Considering the fact that corresponding porous material of NC-1 or mesoporous AIPO can be obtained by removing the opposite part via different post-treatment, we can also image that the carbon network should intercross with the AIPO framework in the carbonized NC-AIPO composite. This should be the main reason why NC-1 possesses a pore system of 3.5 nm, which is similar to that of mesoporous AIPO. Therefore, the concept of “mutual template” may be introduced here for understanding the pore formation mechanism of NC-1 and mesoporous AIPO materials.

For further confirming the special role of the interaction between CA and AIPO on the formation of porous carbon (NC-1), another two kinds of composites of CA/silica and SU/AIPO were also synthesized according to the procedure for the synthesis of CA/AIPO in this work. It was reported that CA can interact with silica

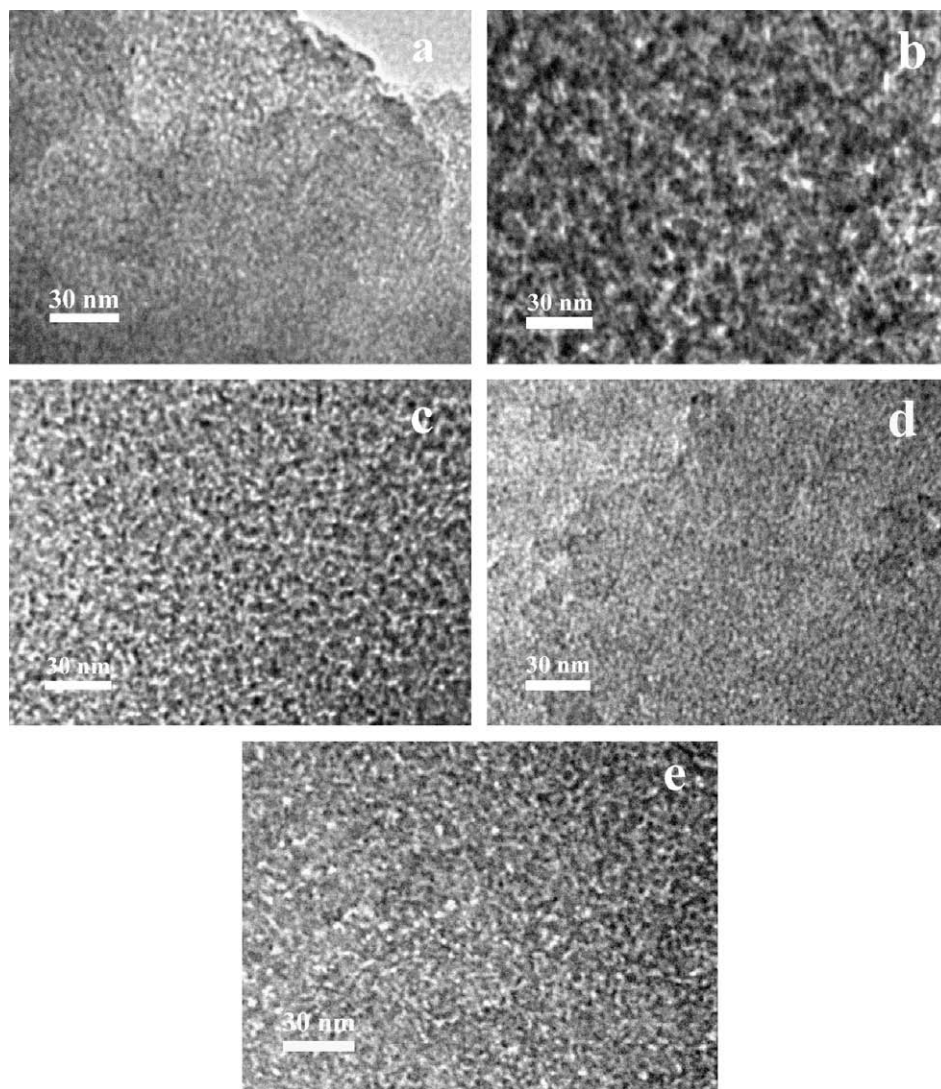


Fig. 6. TEM images of carbon materials: (a) NC-1c; (b) NC-2a; (c) NC-2c; (d) NC-2e; (e) AlPO.

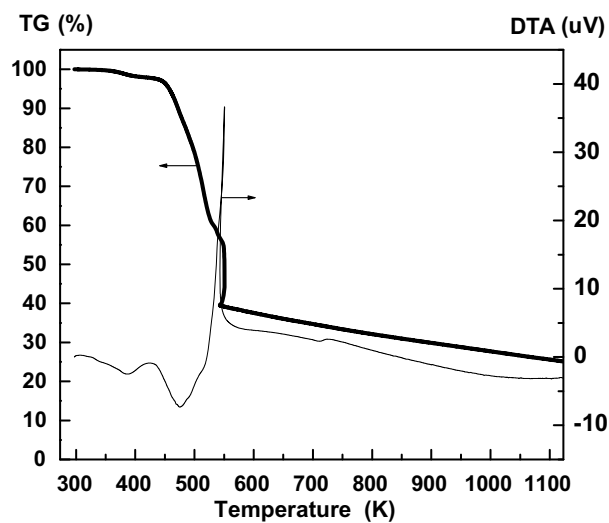


Fig. 7. TG-DTA profiles of as-synthesized CA/AlPO composite calcined under argon atmosphere.

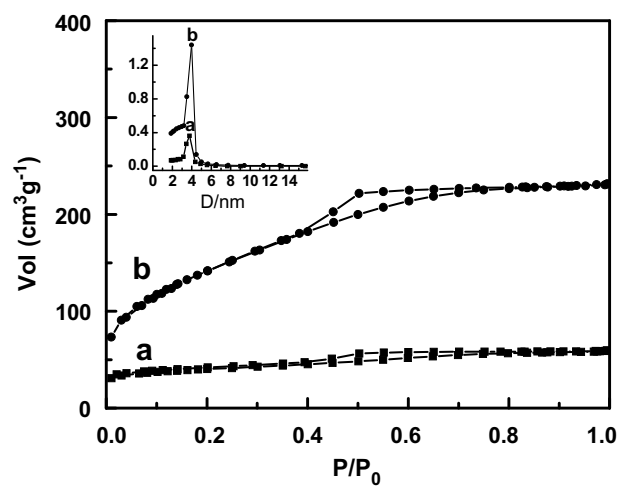


Fig. 8. N₂ adsorption-desorption isotherms and corresponding pore size distribution curves (inset) for (a) NC-AlPO and (b) AlPO.

by a weak hydrogen bonding, and mesoporous silica could be synthesized by direct calcination of the CA/silica composite [37]. However, we found that only trace amount of carbon powder, rather than porous carbon material could be obtained by carbonizing the CA/silica composite using similar carbonization conditions as the preparation of NC-1. Moreover, we found that direct carbonization of the SU/AlPO composite could not obtain porous carbon materials with uniform mesopore. These results confirm further that the presence of suitable interaction between CA and AlPO is indeed a crucial factor for the synthesis of porous carbon materials with mesoporous characteristic.

From above, we have also known that the addition of suitable amount of SU into the CA/AlPO composite could affect the structural characteristic of porous carbon materials. In fact, SU is well known the most commonly used carbon precursor for synthesize various porous carbon materials, since it is easily polymerized and convert to carbon under suitable carbonization conditions [38]. Therefore, we suppose that SU may mainly function as carbon precursor for building the “wall” of porous carbon materials by copolymerizing with the carbonized CA. The fact that pore volumes and pore sizes decrease with increasing the amount of sucrose, may be due to the formation of thicker walls as a result of higher degree of copolymerization between citric acid and sucrose. Besides, the “strain release” property of carbon obtained from sucrose may also cause the structural transformation of the result of carbon materials, which has been reported in the synthesis of mesoporous carbon CMK-1 and CKT-3 [11,39]. Moreover, our recent work indicates that some other organic compound such as hydroquinone and resorcin, could also be used as carbon precursors instead of SU for the synthesis of porous carbon materials. Further work is still required to clarify the concrete role of addition of different organic compound on the formation of porous carbon.

4. Conclusions

This work presents a simple and efficient way to synthesize porous carbon materials with mesoporous and/or microporous characteristic by carbonizing a kind of CA/AlPO composite. The structural parameters of these carbon materials can be further tuned in a certain range by the addition of suitable amount of SU. We believe that the physico-chemical properties of such materials could be further improved by optimizing synthesis conditions, thus providing numerous opportunities for application in the field of electrochemistry and catalysis science.

Acknowledgments

This work is supported by the Specialized Research Fund for the Doctoral Program of Higher Education (20040183003), Program for New Century Excellent Talents in University, State Basic Research

Project (2005CB221405), and National Natural Science Foundation of China (20403006, 20773050).

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