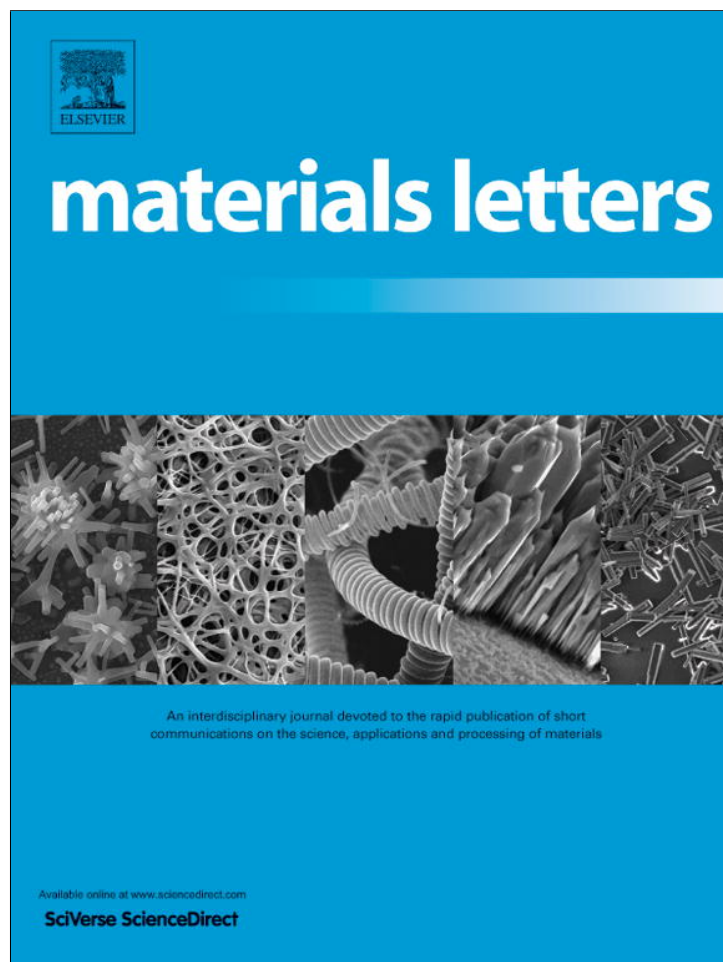


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One-step approach towards graphitic mesoporous carbon with a narrow pore size distribution

Zhihong Tang^a, Yan Song^b, Xing He^a, Junhe Yang^{a,*}

^a University of Shanghai for Science and Technology, School of Materials Science and Engineering, Shanghai 200093, China

^b Key Laboratory of Carbon Materials, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, China

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ABSTRACT

In this paper, a simple way was described for the synthesis of graphitic mesoporous carbons (GMCs) with a narrow pore size distribution. The material with a pore size of about 4 nm was obtained by one-step carbonization of the composite of thermosetting phenol resin (TPR) and ferrocene, which had a Brunauer–Emmett–Teller (BET) surface area of 248 m²/g and a d (002) spacing of 0.3386 nm. When ferrocene was changed to ferric nitrate, the pore size was also centered at 4 nm, but the BET surface area was increased to 607 m²/g, and the d (002) spacing was increased to 0.3427 nm. The effort of this work will pave the way for the preparation of GMCs in large scale.

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1. Introduction

Mesoporous carbons with graphitic structure and narrow pore size distribution are of great interest in many applications such as electrodes for double-layer capacitors and catalytic supports in fuel cells due to their high surface areas and good electronic conductivities. It is well known that high temperature treatment of graphitizable carbon precursors [1,2] and catalytic graphitization [3–8] are two effective ways towards graphitic carbons. Accordingly, template method combined with high temperature treatment or catalytic graphitization was used to synthesize graphitic mesoporous carbons (GMCs) with a narrow pore size distribution. For example, Fuertes et al. prepared ordered GMCs by high temperature heat treatment of templated carbons, the same group also combined template method with catalytic graphitization to prepare GMCs [2,3], their fabrication processes were fairly complicated. In order to simplify the preparation process, aromatic compounds were used as carbon precursors to prepare GMCs by the template method, but the aromatic compounds are poisonous, which could not be used extensively [1,4]. Consequently, Han et al. synthesized hollow graphitic nanoparticles by the catalytic method, but the Brunauer–Emmett–Teller (BET) surface area was only 88 m²/g [5].

In this paper, GMCs with a narrow pore size distribution were synthesized by one-step carbonization of the composite of thermosetting phenol resin (TPR)/iron salt (ferrocene or ferric nitrate), which not only shortened the preparation procedure dramatically,

but also enhanced the BET surface area greatly. The effort will make it possible for the preparation of GMCs in a large scale.

2. Experimental

In a typical synthesis, TPR and iron salt (ferrocene or ferric nitrate) were homogeneously mixed in ethanol, the composite (iron salt/TPR) was stabilized in air at 120 °C for 5 h after the solvent evaporation, then it was heat-treated in nitrogen at 700 °C for 1 h, the product was washed by 10% HCl solution, followed by washing

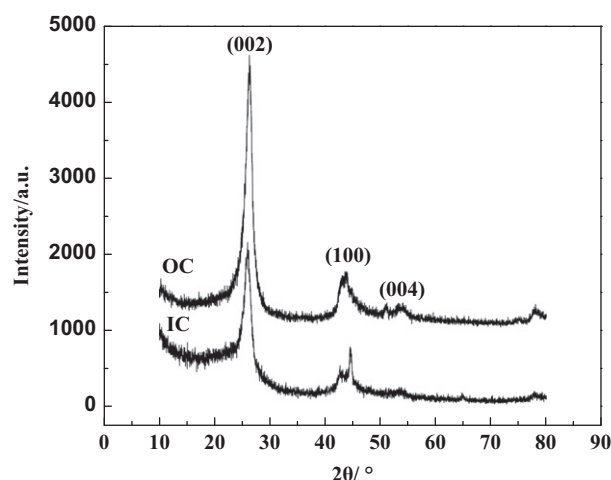


Fig. 1. XRD patterns of the samples.

* Corresponding author. Tel./fax: +86 21 55271723.
E-mail address: jhyang@usst.edu.cn (J. Yang).

with distilled water to neutral and drying at 110 °C for 48 h. The mass ratio of TPR to iron salt was 1. The carbon obtained by the addition of ferric nitrate and ferrocene was denoted as IC and OC, respectively, the carbon prepared without the addition of iron salt was signed as NC. The iron valence of the carbonized sample (M-500 Mossbauer) and properties of obtained carbons such as pore character (Micromeritics ASAP-2000) and crystal structure (Rigaku Dmax-rA X-ray diffraction analyzer) were determined.

Table 1
Pore character of obtained carbons.

| Sample name | S_{BET} (m^2/g) | V_{micro} (cm^3/g) | V_{meso} (cm^3/g) | V_{total} (cm^3/g) | Ratio _{meso} ^a (%) |
|-------------|--------------------------|-----------------------------|----------------------------|-----------------------------|--|
| NC | 52 | 0.01 | 0.03 | 0.04 | 75 |
| IC | 607 | 0.09 | 0.58 | 0.67 | 86 |
| OC | 248 | 0.03 | 0.27 | 0.30 | 90 |

^a Ratio_{meso} = $(V_{total} - V_{micro}) / V_{total}$.

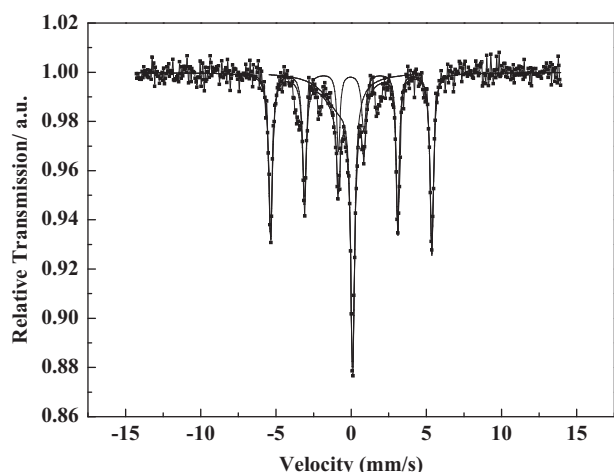


Fig. 2. Mossbauer spectra of carbonized composite of TPR/ferric nitrate.

3. Results and discussion

Fig. 1 displayed the X-ray diffraction (XRD) graph of OC and IC. From the graph it can be seen obvious (002) and (100) peaks of the two samples, which indicated that the non-graphitizable carbon precursor was catalytically graphitized even at a relatively low heat treatment temperature. Calculated from the XRD patterns, the $d(002)$ spacing of OC and IC was 0.3386 and 0.3427 nm, respectively, which of OC was closer to graphite than that of IC, which illuminated that the form of iron played an important role on the graphitization. Ferrocene was stable even at 470 °C, the deeper graphitization degree of OC was probably attributed to the high catalytic activity of ferrocene. According to the position and profile of $d(002)$ peaks, it can be deduced that the turbostratic structure was formed in the obtained carbons, which suggested that although the content of iron salts was fairly large, they were finely dispersed in the carbon precursor [6,7].

Table 1 summarized the pore character of as-prepared carbons. From the table it can be seen that the BET surface areas and pore volumes of OC and IC were much larger than those of NC, the mesopore ratio was also over 85% for OC and IC, which indicated that the iron salts not only graphitized the carbon precursor, but also promoted the formation of mesopores in the carbon matrix. However, the pore volume and surface area of IC were much higher than those of OC, which should be contributed to the different iron salt of ferric nitrate and ferrocene. Ferric nitrate was decomposed easily during carbonization (the decomposition temperature of ferric nitrate is about 125 °C), the decomposition product Fe_2O_3 , NO_2 and O_2 would react with carbon precursor in the carbonization step to form more mesopores.

The Mossbauer spectra of the carbonized composite of TPR/ferric nitrate (Fig. 2) proved the reaction between carbon precursor and ferric nitrate. There were a double-line peak and a six-line peak in the spectra, which indicated that Fe^{3+} (according to the double-line peak) and α -Fe (according to the six-line peak) existed in the carbonized sample. Calculated from the Mossbauer spectra, the content of α -Fe reached 39.5% in the carbonized sample. Since the decomposition product of ferric nitrate was Fe_2O_3 , the existence of α -Fe in the carbonized sample further

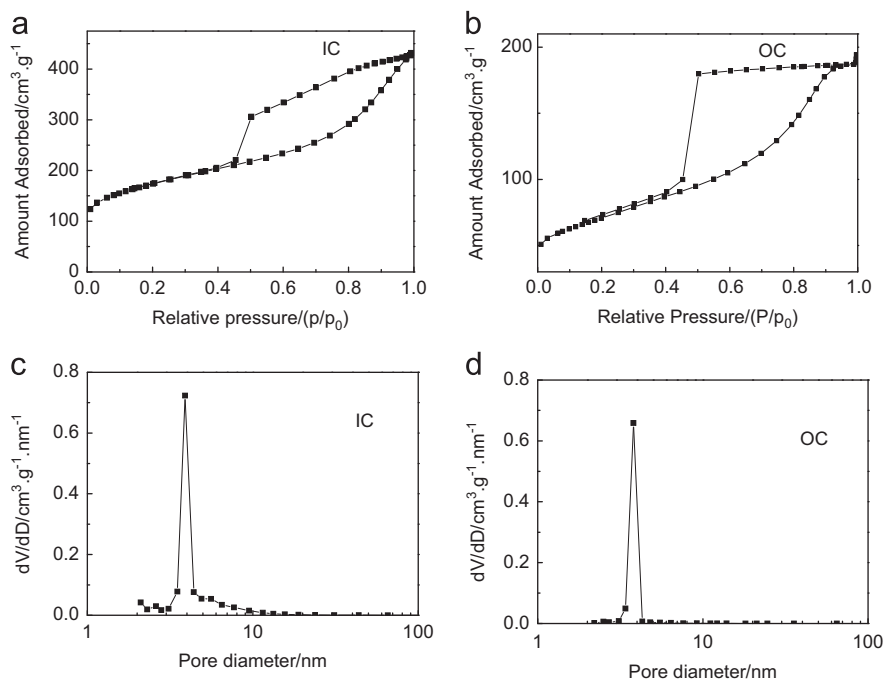


Fig. 3. Nitrogen adsorption–desorption curves and BJH pore size distributions of IC and OC.

proved the reaction between the iron oxide and amorphous carbon, then more carbon was burned during carbonization, and more pores were formed.

Mossbauer spectra of the sample proved the reaction happened between iron oxide and amorphous carbon, however, the pore structure developed in the carbon cannot be detected. Fig. 3a and b showed the nitrogen adsorption–desorption curves of IC and OC, which indicated that abundant mesoporous pores developed in the carbons, according to the shape of the adsorption–desorption curves, it can be deduced that there were abundant bottle-like pores in the obtained carbons. Fig. 3c and d demonstrated Barrett–Joyner–Halenda (BJH) pore size distributions of IC and OC from the desorption branch of the isotherms. There was a sharp peak at about 4 nm in the two graphs, which indicated that both carbons had a narrow pore size distribution centered at 4 nm. Combined with the nitrogen adsorption–desorption curves of IC and OC, it can be concluded that the pores developed in OC and IC were bottle-like and had a mouth of about 4 nm. Since the pores appeared after the addition of iron salt, the decomposition product of iron salt during carbonization would react with the amorphous carbon around it, and then left opened pores.

4. Conclusions

In conclusion, GMCs with a narrow pore size distribution have been successfully synthesized by one-step carbonization of the

composite of TPR/iron salt (ferrocene or ferric nitrate). Iron salt not only catalytically graphitized TPR at a low heat treatment temperature, but also promoted the formation of pores of about 4 nm in the obtained carbons.

Acknowledgments

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