J Mater Sci (2007) 42:3692–3694
DOI 10.1007/s10853-007-1711-x

LETTER

Synthesis of nanoporous carbons by an in situ template approach

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Received: 16 January 2007 / Accepted: 21 March 2007 / Published online: 26 April 2007
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A new approach for synthesis of nanoporous carbon is reported. This involves: (1) synthesis of the template of iron nanoparticles in situ with formation of carbon by chemical vapor decomposition of iron pentacarbonyl and ethanol, and (2) removal of the template by acid treatment. The present template approach is much simpler than previous ones involving separate procedures for preparation of template materials and graphitization and suitable for large-scale production.

A number of methods for the preparation of nanoporous carbon have been developed, with the traditional one being the carbonization–activation route used to produce activated carbon [1, 2]. However, since the carbon precursors were generally in solid state, the controllability of the pore size distribution of the porous carbon was limited [3]. The synthesis of the template is a separate step from the formation of carbon, and filling the template is always a sophisticated process. Additionally, the high chemical stability of the template previously used often made its removal insufficient by hydrofluoric acid treatment [4–6].

The growth of nanoporous carbon with a graphitic framework in gaseous phase usually takes place under harsh conditions. Such synthetic methods also have limitations in terms of scalability and economics because of the demanding synthetic conditions and generally low yields. The preparation of graphitic carbon in solid state often requires high temperature treatment. In addition, they lead to a significant reduction in the surface area and pore volume of the porous carbon. Nevertheless, all these methods include preparation of carbon precursors (carbon aerogel, resorcinol–formaldehyde gel, or polymer particles) and mixing the precursors with catalytic particles and thus suffer from time-consuming, incomplete graphitization, difficult purification of remaining amorphous carbon and surface areas generally lower less than 350 m^2/g.

The synthetic processes discussed above either require high temperatures or are rather time-consuming, and in most cases give rise to relatively low surface areas. In this study, we report a simple template approach for preparing nanoporous carbon. An iron template and carbon were uniformly mixed in situ by thermal pyrolysis of iron pentacarbonyl [$Fe(CO)_5$] and ethanol. The iron template could be easily removed from the carbon matrix by acid(HCl) treatment. This gives rise to an amorphous carbon with a surface area S_{BET} of 891 m^2/g at 500 °C, but a graphitic carbon with S_{BET} of 800 m^2/g at 600 °C and 558 m^2/g at 650 °C.

The initial and acid-treated samples were studied by transmission electron microscopy (TEM) and high resolution TEM (HRTEM). The sample prepared at 500 °C consisted of very fine nanoparticles. These particles tended to form chain-like aggregates of ~50 nm in size. XRD analysis illustrated the presence of peaks associated with Fe and Fe_3C phases and the absence of peaks related to graphite (Fig. 1). A typical TEM image of the sample prepared at 650 °C is shown in Fig. 1b. As can be seen, the sample consisted of well-dispersed nanoparticles with an average diameter of 30–50 nm. Furthermore, each nanoparticle had a core-shell structure with the core containing Fe and the shell being carbon.

After the treatment with HCl acid, the Fe and Fe_3C phases were eliminated with little remaining in the sample. In contrast with the as-prepared sample at 500 °C, the sample after acid treatment showed a porous structure with

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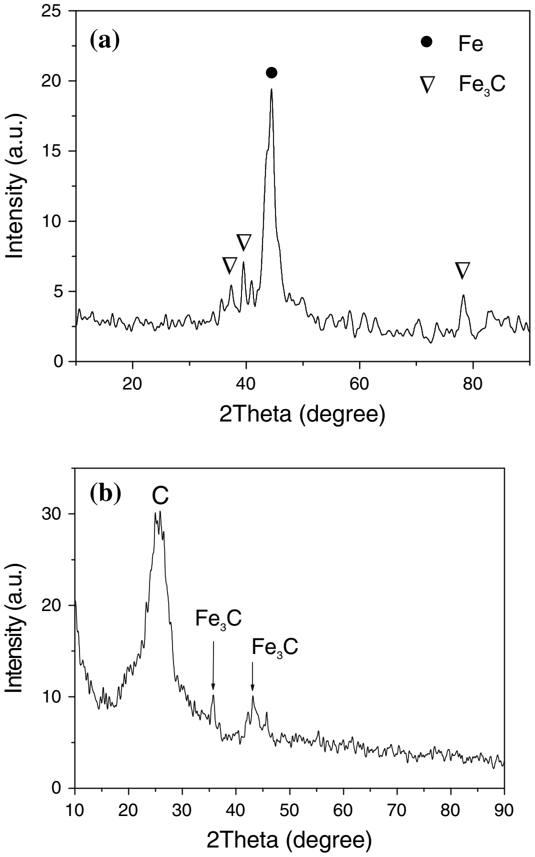

Fig. 1 The XRD pattern of the sample prepared at 500 °C (**a**) and 600 °C (**b**) sample after acid treatment

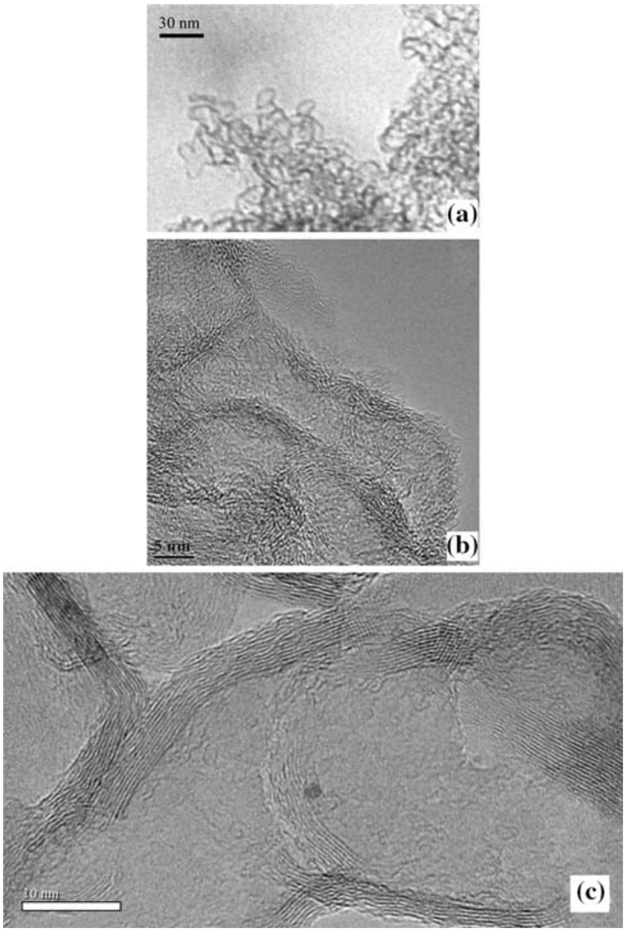

Fig. 2 TEM (**a**) and HRTEM (**b**) images of the sample prepared at 500 °C after acid treatment showing a nanoporous structure and low degree of graphitization. HRTEM (**c**) images of the sample prepared at 650 °C after acid treatment

pore sizes of 3–10 nm and the walls of pores were mainly amorphous with a low degree of graphitization (Fig. 2a). After the acid treatment of the 650 °C sample, the original Fe or Fe_3C phase could no longer be observed, but the carbon shells remained (Fig. 2b), showing a cage structure with a cage size of ~20–60 nm. HRTEM (Fig. 2c) illustrated that the shells of 3–6 nm thick were constituted by well-defined graphitic layers with a spacing of 0.34 nm. Such graphitization is also supported by the XRD result of the 600 °C sample showing a clear reflection that can be assigned to the (002) plane of graphite (Fig. 1b).

The particles without Fe and Fe_3C could be hollow. This suggestion is supported by the observations of the lack of structure and uniform translucent appearance to the electron beam in the core region, and similar structures of graphitic planes in multiple overlaid particles (Fig. 2c). If the cage-like particles were filled with amorphous carbon, then the cores will show variations of translucence and the structures behind the overlaid particles could not be clearly discerned due to the intervening crystalline material in the path of the electron beam.

The above results expressly reveal the morphology and the structure of the pores filled with the Fe or Fe_3C template. The formation of this core-shell structure may be related with the activities of the carbon source and metal particles. The decomposition of $Fe(CO)_5$ might yield iron nanoparticles that possessed a very high-catalytic activity for the decomposition of ethanol. At high temperature, the decomposed carbon could be dissolved in iron and form an Fe–C phase. As the temperature of the particles decreased, carbon would precipitate and deposit on the surface of the iron particles. Carbon atoms remained disordered because the temperature might not be high enough at 500 °C for them to crystallize. But at higher temperatures, atoms might be dissolved in iron, and they would precipitate on the surface of iron particles to form well-defined graphitic layers as the particles flowed out the furnace and thus their temperature decreased.

Several N_2 adsorption experiments were carried out to analyze the pore structures in the hollow cage samples synthesized at different temperatures (Fig. 3a). This observation suggests that there were micropores in all cage

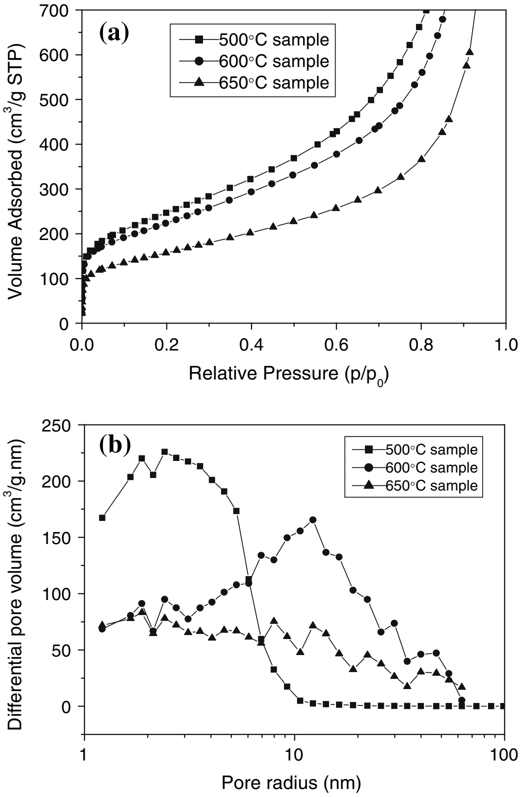

Fig. 3 N_2 adsorption isotherms showing a low uptake of N_2 in the low pressure region ($p/p_0 < 0.05$) but a much higher uptake in the high pressure region ($p/p_0 > 0.05$) (**a**), BJH plots illustrating mesopore size distributions (**b**)

samples. After the initial adsorption, however, the uptake of N_2 increased significantly in the region of high nitrogen pressure. Such a high uptake indicates the presence of mesopores in the samples.

Using these adsorption data, the total specific surface area S_{BET}, the samples originally synthesized at 500, 600 and 650 °C had a S_{BET} of 891, 800 and 558 m^2/g, respectively.

Figure 3b shows the mesopore size distribution. The samples synthesized at 500 and 600 °C present a strong distribution at pore sizes around 4–10 nm and 20–40 nm, respectively, compared with that synthesized at 650 °C. These sizes are close to the inner diameters of the cages observed by TEM (Fig. 2). Therefore, the pores of these sizes may result from the removal of the template inside the cages, and respond for the high S_{BET} values observed for the samples synthesized at 500 and 600 °C.

From the experimental observation and above analysis, some advantages of the present approach can be noted. In contrast with previous template methods for preparation of nanoporous carbon, the present one combines the synthesis of template, the introduction and formation of carbon into one step. That is, the template can be formed in situ with the formation of carbon. Additionally, by simply supplying ethanol and iron pentacarbonyl, porous carbon containing the Fe template can be fabricated continuously. Evidently, such a unique feature is beneficial to large-scale production.

At relatively higher temperatures of 600 and 650 °C, graphitic carbon can be produced also in situ with the template. Consequently, the previous time-consuming preparation of carbon precursors and separate step for graphitization are not required. Furthermore, since the whole process took place in short time, the size of the template was small, and the amount of carbon dissolved in the template was limited. All these led to particles of small size (<50 nm) and thin (<6 nm) graphitic shells (Fig. 2), and therefore high surface areas of 800–558 m^2/g. These values are much higher than previous ones generally less than 350 m^2/g for graphitic carbon.

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