New mesoporous carbon prepared by a simultaneous synthetic template carbonization method

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Mostly microporous in nature (with pore diameters less than 2 nm), porous carbon materials are widely used in adsorption, purification processes, chromatographic separation, etc. Although the microporosity is a highly desirable feature of carbons in many applications, e.g., in adsorption of small molecules, mesoporous carbons present distinct advantages not only for the adsorption of large molecules, but also for some new applications such as support for catalysts, and as electrodes of an electrochemical capacitor [1–4]. Development of industrial technology provides a strong demand for mesoporous carbons. An ongoing research in this field has been conducted for more than two decades. Many novel methods, such as catalytic activation [5, 6], carbonization of polymer blends and organic gels [7–11], and template carbonization [12–19], have been proposed to prepare mesoporous carbons and control their pore structure.

A conventional template carbonization method is described as follows: (1) introduce an organic compound into the nano-pores of a template inorganic matrix either by impregnation of polymer solution, CVD or synthetic method; (2) carbonize the organic–inorganic composite; and (3) liberate the resulting carbons from the templates. Inorganic host matrices which can be used as templates include layered materials [12, 13], zeolites [14], porous silica [15], anodic aluminum oxides [16], etc. Such spatial regulation of the carbonization process by the nanospace makes it possible to control the structure of carbon materials at nanometer level by changing either the size or the shape of nanospace. However, the structure of the obtained carbons is undoubtedly governed by the properties of the inorganic matrix [17]. For example, the carbon resulting from poly(furfuryl alcohol) (PFA) pyrolysis between the lamellae of clays [18] is quite different from that resulting from the pyrolysis of this same precursor in zeolite [14], or in the uniform and straight channels of an anodic aluminum oxide [16]. This method leaves no options for controlling the product's pore structure for the unchangeable fabric of the template substance. We may call the conventional template carbonization method as "inherent template carbonization method."

It is well known that the sol–gel process is a useful technique to prepare nano-composites of organic and inorganic materials with precisely controllable structure. If two sol–gel reactions, one of which is the synthesis of the template material, the other the synthesis of the carbon precursor polymer, could occur simultaneously in a reactor, the texture characteristics of both the template and the carbon precursor could be controlled synchronously by modifying the sol–gel reaction conditions. After the template framework is removed from the composite, a carbon that reflects the template framework can be obtained. The simultaneous sol–gel process, compared with the "inherent template carbonization method," makes it possible to obtain more tunable pore structures of the resultant carbons. We may call this method as "simultaneous synthetic template carbonization method" (SSTCM). Kawashima and his co-workers, using this method, prepared mesoporous carbon from PFA/sol–gel silica hybrids by the simultaneous formation of a crosslinked PFA and the silica phase during the sol–gel process [19].

Tetraethoxy silane (TEOS) has often been used as a silica precursor for the production of nano-composites by the sol–gel process. The shape and size of silica obtained could be tuned by the sol–gel reaction conditions [20, 21]. Investigation into resorcinol-formaldehyde (RF) gels and their carbonized products indicated that their particle size and pore structure showed sharply different characteristics under different processing conditions [9–11]. To the best of our knowledge, the preparation of mesoporous carbons with a combination of the above two sol–gel reactions by simultaneous synthetic template carbonization has not been reported.

The procedure of preparing carbons in this work is as follows: (1) the homogeneous mixture of TEOS, ethyl alcohol, deionized water, and HCl was added to a sealed reaction vessel and cured at 65 °C in a water bath for several hours to obtain the precursor sol of silica template; (2) the as-prepared sol was allowed to cool in an ice bath; (3) resorcinol (R) and formaldehyde (F) were directly solved in deionized water with a fixed molar ratio of 1:2; (4) the RF solution was added to the silica sol while stirring and the initial pH of the mixture was adjusted to 7.5 with dilute ammonia; (5) the mixture was put into a sealed bottle and cured for 7 days at 85 °C in a water bath to obtain mixing aquagels. During this treatment, both the gelation of TEOS and the polycondensation of RF took place; (6) after curing, the gel was removed from the sealed bottle and dried in air at 80 °C. Then, the mixing xerogel was further heat-treated at 1000 °C for 2 hr under nitrogen atmosphere to carbonize the polymer in the mixture; (7) the resultant carbon/silica composite was washed with HF to extract carbon from the silica framework; and finally (8) SSTM carbon was obtained by thoroughly washing

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TABLE I Pore structural parameters derived from nitrogen adsorption at −196 °C of the samples investigated

Si/R ratio	Treating time of silica solution	S_{BET} ($m^2 \cdot g^{-1}$)	Micropore volume ($cm^3 \cdot g^{-1}$)	Mesopore volume ($cm^3 \cdot g^{-1}$)	Average pore diameter (nm)
0:1	–	185	0.16	–	–
1:1	3	722	0.2	0.68	5.5
1:1	6	942	0.32	0.64	4.4
1:1	9	1554	0.52	0.92	3.8
2:1	6	1100	0.12	0.9	6.8
3:1	6	1313	0.31	1.74	10

with deionized water and drying. To primarily investigate the effect of the silica framework on the structure of the carbons, the mole ratio of TEOS to resorcinol (Si/R ratio hereafter) varied from 0 to 3 and the TEOS mixtures were treated at 65 °C before mixing with RF solutions for different times, such as 3, 6, 9 hr, to obtain different precursor sols of silica template.

The resulting SSTCM carbons exhibited well-developed mesoporosity, which was characterized by nitrogen adsorption isotherms at −196 °C (see the pore structure parameters listed in Table I). The ratio Si/R = 0:1 denotes that the carbon was produced only by carbonizing the RF xerogel without mixing the silica template. Figs 1 and 2 show the nitrogen adsorption isotherms for the carbon samples mentioned in Table I. According to the IUPAC classifications [22], the adsorption isotherms exhibit type IV characteristics with the exception of the carbon prepared when Si/R = 0:1, indicating that the SSTM carbons are typical mesoporous materials. Hysteresis is clearly visible in the regime of mesopore filling and shows H1 characteristics which can be attributed to cylindrical pores.

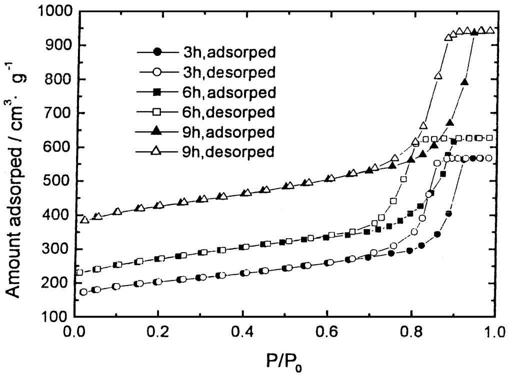

Figure 1 Nitrogen adsorption isotherms of the carbons prepared when silica sols were treated at 65 °C for 3, 6, 9 hr, respectively, and Si/R = 1.

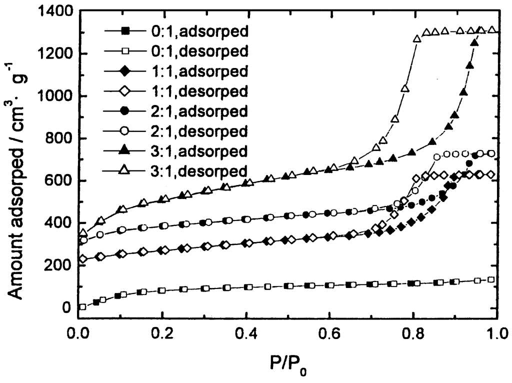

Figure 2 Nitrogen adsorption isotherms of the carbons prepared when Si/R were 0, 1, 2, 3, respectively, and the treating time of silica sols at 65 °C was 6 hr.

As is shown in Fig. 1 and Table I, on increasing the treatment time of the precursor sols of silica template, the S_{BET} increases sharply and the hysteresis shifts to lower relative pressure, indicating the depressing of the mesopore size. No agreement has yet been reached upon the complicated sol–gel reaction mechanism of TEOS so far. In the present work, the reaction mechanism might be more complicated since the two sol–gel reactions were simultaneously performed. However, investigation into silica aerogels by a two-step sol–gel process from TEOS showed that prehydrolysis of TEOS under acidic conditions led to small, partly condensed silica particles [23]. These silica particles may be the active sources of the subsequent condensation in a basic medium. The hydrolysis rate of TEOS under acidic conditions is so slow that hydrolysis cannot be accomplished within several hours [24]. Therefore, the shorter the hydrolysis time, the less the amount of reactive sites and hence, the larger the particle size of the silica. After the silica particle is removed, larger pores will be left in the carbon matrix. According to Fig. 2, these isotherms exhibit gradually increasing hysteresis loops, reflecting a rather broad distribution of mesopore with the increase of the Si/R ratio. The isotherm of the carbon prepared when Si/R = 0:1 shows type I characteristics. The absence of desorption hysteresis implies that only micropores exist in this sample. The sorption isotherm data overall suggest that the mesoporous structure of the SSTM carbons originated from the silica template framework which are removed by HF, and the pore structure can be effectively tailored by the adjustment of the processing conditions.

In summary, mesoporous carbons were obtained by the simultaneous synthetic template carbonization method. The pore structure of these carbons could be optionally and effectively controlled for the tunable silica template synthesized simultaneously with the carbon precursor polymer. Typical mesoporous structure makes these carbons promising materials for the adsorption of large molecules, chromatographic separation, and also for use in electrochemical capacitors and batteries.

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