Novel pitch-based carbons with bimodal distribution of uniform mesopores

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A new method is proposed for the synthesis of pitch-based carbons with bimodal distribution of uniform mesopores formed by co-imprinting of spherical silica colloids and hexagonally ordered mesoporous particles of SBA-15 into mesophase pitch particles and subsequent silica dissolution.

Recently there is a great interest in mesoporous carbons because of their potential applications in adsorption of relatively large molecules, chromatographic separations, catalysis and electrochemistry. A significant breakthrough in this area was the templating synthesis of ordered mesoporous carbon (OMC) in 1999 by Ryoo *et al.*[1] Since 1999 various OMCs were synthesized *via* templating process, which usually involves the filling of mesopores of the ordered silica (OMS) such as MCM-48 and SBA-15 with carbon precursor, carbonization of the composite followed by silica dissolution (see review by Ryoo *et al.*[2] and references therein). Many other mesoporous silicas were used as templates including mesocellular foams (MCF),[3] MSU silicas with bimodal pore system,[4] colloidal silica crystals,[5] and silica colloids of different sizes in a non-agglomerated form.[6]

There are only few reports on the synthesis of mesoporous carbons with bimodal porous structure (here abbreviated as "bimodal carbons").[7–12] For instance, Lu *et al.* used SBA-15 silica as the template and loaded it with furfuryl alcohol (carbon precursor) to obtain a film of different thickness on the mesopore walls. After silica dissolution two types of pores were present; one type resulted from incomplete pore filling, another one from dissolution of the SBA-15 pore walls.[7] This group also synthesized polyacrylonitrile in the SBA-15 mesopores but in this case in addition to the mesopores created by dissolution of siliceous pore walls a noticeable fraction of larger mesopores was formed due to the lack of carbon in some regions of the SBA-15 mesopores.[8] The other works[9–12] report bimodal carbons with ordered–disordered mesoporous structures because of the difficulty to control the process of infiltration of mesopores with carbon precursor, which depends on the chemical nature of this precursor as well as synthesis conditions.

In this work we present an easy and inexpensive recipe for the synthesis of pitch-based bimodal carbons that contain both ordered mesopores being an inverse replica of the SBA-15 OMS and spherical mesopores formed after dissolution uniform silica colloids. It was shown previously[13–16] that the mesophase pitch is an attractive carbon precursor because it is a mixture of poly-aromatic hydrocarbons, which during carbonization form quite large graphite crystallites. SBA-15 served here as a template to form the structure of interconnected carbon nanorods, whereas uniform silica colloids were used to imprint larger spherical mesopores in pitch particles. This work shows that the use of a mixture of OMS particles and silica colloids leads to the formation of interconnected bimodal carbonaceous mesostructures.

The synthesis of bimodal carbons is illustrated in Scheme 1. The mixture of 0.2 g of mesophase pitch particles (synthetic pitch AR-24 from Mitsubishi; particle size <45 µm, softening point about 237 °C), 0.2 g of the SBA-15 particles[17] (surface area 780 m² g⁻¹, pore volume 1.0 cm³ g⁻¹, pore width 9.1 nm) and 0.2 g of commercial colloidal silica (Ludox AS-30 from Aldrich with a surface area about 230 m² g⁻¹ and particle size about 13 nm)
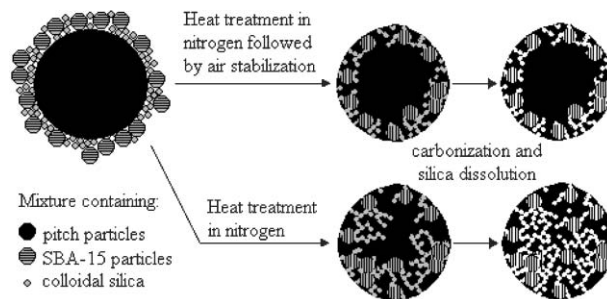
**Scheme 1** Illustration of the synthesis procedure of pitch-based carbons with bimodal mesoporous structure.

was dispersed in ethanol–water solution that was allowed to evaporate at about 60 °C after several hours stirring. The resulting solid mixture was heated with heating rate of 5 °C min⁻¹ to achieve the temperature specified in Table 1 (*i.e.*, 340, 400, 420 or 440 °C) and kept at this temperature for 2 or 3 h in flowing nitrogen. After this thermal treatment all samples were stabilized in flowing air at 220 °C for 10 h and carbonized in flowing nitrogen at 900 °C for 2 h. In the aforementioned processes a 5 °C min⁻¹ heating rate was used to achieve the temperature specified for a given process. Finally, silica templates were dissolved in 49% HF solution at room temperature (in this case special caution is recommended). The dissolution conditions were analogous as in previous works.[13,15] The resulting carbon samples are denoted C–T–t, where T and t refer to the thermal treatment temperature and time, respectively. They contained <2% of silica residue, which was estimated by thermogravimetric analysis in air at 800 °C. The SBA-15 template, which is hexagonally ordered mesoporous silica, was synthesized using the triblock copolymer $EO_{20}PO_{70}EO_{20}$ (Pluronic P123, BASF) and tetraethoxyorthosilicate (TEOS) according to the recipe reported elsewhere.[17]

The above scheme illustrates the consecutive steps of the synthesis of bimodal carbons. During thermal treatment at temperatures higher than the softening point, the mixture of the SBA-15 particles and silica colloids penetrated large pitch particles. If temperature of this treatment is high enough to ensure low viscosity of the pitch, the SBA-15 channels are also filled by pitch. Subsequent stabilization in air allows one to control the extent of

Table 1 The BET surface area (S), total pore volume (V_t), pore widths originating from the SBA-15 silica particles (w_1) and silica colloids (w_2), and the percentage of the pore volume obtained *via* replication of the SBA-15 (%)

Sample	S_{BET}[a]/m² g⁻¹	V_t/cm³	w_1[b]/nm	w_2[b]/nm	%[c]
C-340-2h	202	0.25	3.46	13.3	56.9
C-400-2h	274	0.38	4.09	13.2	56.7
C-440-2h	349	0.50	3.63	13.2	54.9
C-420-3h	390	0.56	3.47	13.4	54.8

[a] Calculated in the relative pressure range of 0.04–0.15. [b] Calculated at the maximum of pore size distribution (PSD). [c] Calculated by integration of PSD in the range below 6 nm.
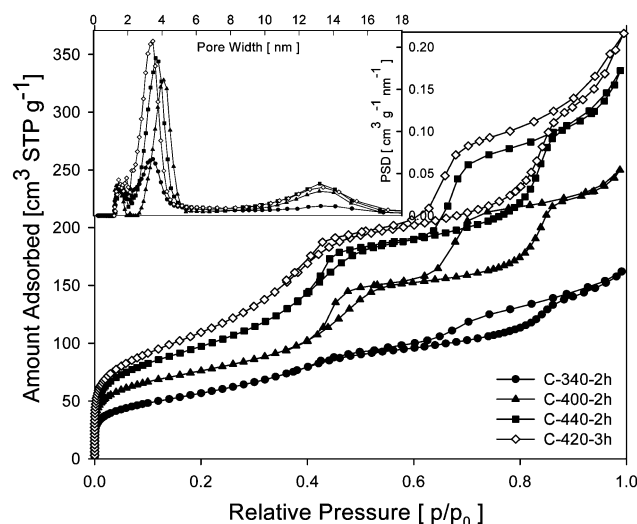
Fig. 1 Nitrogen adsorption isotherm at −196 °C and the corresponding pore size distributions (PSD) for the pitch-based carbons with bimodal mesoporous structure.

pitch–silica interpenetration. Otherwise this process would be continued during gradual heating of the mixture to achieve the carbonization temperature. The removal of silica from carbonized composite particles led to the formation of a bimodal meso-structure, which consists of ordered mesopores and uniform spherical mesopores that reflect the mesostructure of SBA-15 particles and the spherical shape of silica colloids, respectively.

Shown in Fig. 1 are nitrogen adsorption isotherms at −196 °C for the bimodal carbons studied. The inset in this figure shows the corresponding pore size distributions (PSD) calculated from the adsorption branch of the isotherms by using the modified BJH method (KJS method)[18] with the statistical film thickness obtained from nitrogen adsorption on the BP280 carbon black.[19] It is apparent that an increase in the thermal treatment temperature and time influences the interpenetration process of pitch and silica particles, which causes a gradual increase in the surface area and total pore volume of the resulting carbons (see Table 1). Adsorption analysis of the carbon samples revealed two distinct capillary condensation steps related to the mesopores formed after removal of the SBA-15 pore walls and spherical silica colloids. For carbons synthesized at higher temperatures (about 400 °C and higher) the position of the first step, which corresponds to the mesopores originated from the SBA-15 mesostructure, is shifted to the lower relative pressures with increasing temperature. This result may suggest that at higher temperature the pitch viscosity is low, which facilitates the filling of the SBA-15 channels, and leads to thicker carbon nanorods and consequently, smaller mesopores. Recent studies[20] indicate that the mesophase pitch molecules have tendency to orient perpendicularly to the axis of the SBA-15 channels favouring edge-on anchoring state. Presumably such an arrangement requires higher mobility of molecules, *i.e.*, lower viscosity of the pitch.

Among adsorption isotherms shown in Fig. 1 the isotherm curve for the C-420-3h carbon is the highest. The corresponding pore size distribution has a maximum about 3.5 nm, which is larger in comparison to 2.5 nm pore wall thickness of the SBA-15 silica.[21] This difference may be caused by overestimation of the size of pores located between carbon nanorods because the pore size analysis was done for cylindrical geometry[18] and/or some shrinkage of the pitch during stabilization and carbonization processes. Adsorption isotherms shown in Fig. 1 exhibit distinct capillary condensation steps and well-pronounced hysteresis loops for both types of mesopores indicating narrow pore size distribution and good pore

connectivity. The case of the sample C-340-2h fabricated at 340 °C, for which the diameter of ordered mesopores is smaller in comparison to that of other carbons studied, may imply high sensitivity of the synthesis carried out at relatively low temperatures. However, the distribution of ordered mesopores formed *via* replication of SBA-15 is relatively narrow and well separated from that reflecting spherical mesopores created after dissolution of silica colloids. As can be seen from Table 1 the mean pore width at the maximum of the PSD is about 13.3 nm and does not change much with thermal treatment temperature. Also, the latter value agrees well with the size of silica colloids used for creation of spherical mesopores in pitch particles. The volume ratio of ordered mesopores (calculated by integration of PSD in the range below 6 nm) to the spherical ones is about 55–57%, which corresponds well to the value of 51% estimated by assuming the 1 : 1 weight ratio of the SBA-15 and colloidal silica used in the synthesis. The microporosity in bimodal carbons is about 1–2%, which is analogous as in the colloid-imprinted carbons reported previously.[13]

In summary, the proposed method for the synthesis of pitch-based carbons affords materials with bimodal pore size distribution reflecting two types of mesopores: ordered ones formed *via* templating of SBA-15 and much larger spherical mesopores created by imprinting silica colloids of desired size in pitch particles. Both types of pores are well interconnected as evidenced by the shape of hysteresis loops characteristic for mesoporous structures without constrictions. The proposed method allows one to tailor the bimodal distribution of mesopores by selecting silica colloids of desired size and the SBA-15 particles of suitable pore wall thickness. Also, the fraction of both types of mesopores can be controlled by adjusting the SBA-15/colloidal silica ratio. The surface area and total pore volume of the resulting carbons can be controlled by temperature and time of the thermal treatment. In contrast to the previous reports this work shows a simple way to control accurately the size of larger pores by using commercially available silica colloids.

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