On the use of mesophase pitch for the preparation of hierarchical porous carbon monoliths by nanocasting

Philipp Adelhelm¹, Karin Cabrera² and Bernd M Smarsly¹

¹ Institute of Physical Chemistry, Justus-Liebig-University Giessen, Heinrich-Buff-Ring 58, D-35392 Giessen, Germany
² Research and Development, Biochemistry and Separation, Merck KGaA, Frankfurter Strasse 250, D-64293 Darmstadt, Germany
E-mail: Bernd.Smarsly@phys.chemie.uni-giessen.de

Received 17 October 2011
Accepted for publication 5 December 2011
Published 9 February 2012
Online at stacks.iop.org/STAM/13/015010

Abstract
A detailed study is given on the synthesis of a hierarchical porous carbon, possessing both meso- and macropores, using a mesophase pitch (MP) as the carbon precursor. This carbon material is prepared by the nanocasting approach involving the replication of a porous silica monolith (hard templating). While this carbon material has already been tested in energy storage applications, various detailed aspects of its formation and structure are addressed in this study. Scanning electron microscopy (SEM), Hg porosimetry and N₂ physisorption are used to characterize the morphology and porosity of the carbon replica. A novel approach for the detailed analysis of wide-angle x-ray scattering (WAXS) from non-graphitic carbons is applied to quantitatively compare the graphene microstructures of carbons prepared using MP and furfuryl alcohol (FA). This WAXS analysis underlines the importance of the carbon precursor in the synthesis of templated porous carbon materials via the nanocasting route. Our study demonstrates that a mesophase pitch is a superior precursor whenever a high-purity, low-micropore-content and well-developed graphene structure is desired.

Keywords: mesophase pitch, nanocasting, carbon structure, hierarchical porosity

1. Introduction
Porous carbon materials are used in many applications, such as purification materials, printing inks, batteries, capacitors and catalyst supports. The specific properties of different carbon materials (e.g. carbon black, activated carbons, carbon nanotubes, carbon nanofibers and graphite) are mainly determined by the chemistry and structure on the nanoscale. Although the synthesis of microporous carbon materials (pore size \( d < 2 \text{ nm} \), specific surface area \( S > 500 \text{ m}^2 \text{ g}^{-1} \)) is straightforward, e.g., by steam activation, mesoporous carbon materials \((d = 2 \text{ to } 50 \text{ nm})\) were more difficult to produce until the work of Ryoo et al [1] spurred research on carbon materials with defined mesoporosity using the nanocasting ('hard templating') approach. Progress in this field is summarized in reviews [2–4].

Briefly, the synthesis of mesoporous carbons using the hard templating approach is conducted by the infiltration of a porous silica template with a carbon precursor. After the carbonization of the hybrid material, the porous carbon replica is obtained by removing the silica template. The principle is well illustrated by the replication of SBA-15 (a mesoporous silica with ordered pores of defined size and wall thickness in the nanometer range) to obtain CMK-3 [5]. Ideally, the wall thickness of the template determines the pore size of the carbon replica.

In many applications, fast access to the nanopores is required, and transport properties can be improved by adding pores in the macropore size range \((d > 50 \text{ nm})\). Ideally, a hierarchical, interconnected pore structure that allows continuous transport through a large volume is desired. Adequate silica templates can be synthesized in
a monolithic form by the ‘Nakanishi process’ based on the spinodal decomposition of a silica precursor with a polymer template [6]. Several monolithic carbon materials with hierarchical porosity were prepared either using these templates or by molding a carbon precursor with hard templates of different sizes [7–15].

The pore size and structure of the carbon material can be conveniently adjusted using an appropriate template. However, it is important to note that the carbon microstructure itself and thus most of its physical and chemical properties depend on the type of carbon precursor used. In the hard templating approach, furfuryl alcohol and sucrose (in aqueous solution) are typically chosen as carbon precursors because their low viscosity facilitates the infiltration of the template. On the other hand, these precursors produce a poorly defined, defect-rich carbon microstructure with inherent microporosity and a large amount of atomic impurities, mainly oxygen and hydrogen. Thus, other carbon precursors are used when a high electrical conductivity and a low microporosity are desired.

Pitches are excellent carbon precursors as they consist of carbon-rich, condensed, polyaromatic moieties that transform into a well-defined and ordered graphene structure. However, pitches are difficult to use in the hard templating approach as their melt is relatively viscous and their solubility is usually poor. Still, several pitch-based mesoporous carbon materials have been prepared by melt impregnation, colloidal imprinting or conversion of aromatic compounds to pitch in the silica template itself [16–19]. Alternative syntheses involving vapor deposition have also been reported [20]. However, the resulting materials are powders and do not exhibit an interconnected, hierarchical pore structure.

Recently, we have reported the use of a pitch-based, hierarchical porous carbon as an active anode material in lithium and sodium-ion batteries [21–23]. High capacity and excellent rate capabilities, which are likely related to the characteristic pore structure and the carbon precursor, were found. Also, we have used the same material as a support for polyaniline (supercapacitor applications) [24] and LiFePO₄ (battery applications) [25] as active electrode materials, illustrating its applicability in different research areas.

Although this particular mesophase-pitch-based hierarchical carbon has thus been used in various studies and applications, details of its formation and structure have not been clarified yet. In particular, the development of the graphene microstructure during heat treatment has not been studied as a function of the type of precursor used for the templating approach. We therefore applied a recently developed method for the analysis of the wide-angle x-ray scattering (WAXS) from non-graphitic carbons [26] to the WAXS of carbons based on mesophase pitch (MP) and furfuryl alcohol (FA), providing valuable insights into the fine details of the carbon microstructure as a function of the type of carbon precursor used. We further discuss the specific nanocasting process and address the special role of using MP as the carbon precursor by comparing it with other standard precursors.

2. Experimental details

2.1. Synthesis

Silica monoliths were provided by Merck KGaA. Mesophase pitch AR (Mitsubishi Chemical Company) was dissolved in tetrahydrofuran (THF) at a weight ratio of 1:3 by intense agitation for 3 days. The dispersion was centrifuged (5500 rpm, 5 min) and the soluble fraction (containing about 10 wt% MP) was used to infiltrate porous silica monoliths. Thereafter, the solution and the monolith were placed in an open glass vessel at a weight ratio of 80:1. The THF was slowly evaporated under mild agitation on a horizontal shaker. The resulting hybrid monolith was kept for 1 day in a quartz tube at room temperature for complete drying. The hybrid monolith was then carbonized under protective N₂ atmosphere in a Nabertherm muffle oven at 700 °C (heating time: 6 h, dwell time: 6 h). The silica template was removed in a 4 M solution of ammonium hydrogen difluoride (NH₄HF₂, >98.5%, Fluka) and the resulting carbon replica was washed with deionized water and ethanol. Carbon samples prepared by carbonization of precursors in their bulk form (absence of silica template) are denoted as bulk samples. The other types of carbon precursor used were starch (Fluka), α-Naphthol (>98%, Aldrich), sucrose (> 99.5%, Sigma) and furfuryl alcohol (>98%, Aldrich).

2.2. Characterization

A D8 machine from Bruker Instruments (CuKα radiation) was used for WAXS measurements in an angular range of 2θ = 10–100°. Nitrogen physisorption measurements and micropore analysis were conducted at 77 K with a Quantachrome Autosorb-1 system. Samples were pre-dried under vacuum at 100 °C overnight. Pore size distributions were calculated from the desorption branches (equilibrium model) of the isotherms using the non-local density functional theory (NLDFT). The adsorption branch was used for micropore analysis. A setup from CE Instruments was used for mercury porosimetry measurements. SEM images were acquired with a Gemini Leo 1550 microscope. XPS measurements were performed using a Physical Electronics ESCA 5600 spectrometer equipped with a monochromatic Al-K x-ray source (200 W, 14 kV) and a multichannel OmniiV detector. Thermogravimetric experiments were conducted using a TG 209 F1 setup from Netzsch. A vario Micro cube system from Elementaranalyse GmbH was used for the elemental (C, H, O) analysis of the samples.

3. Synthesis and morphology

Monolithic carbon replicas were prepared using a solution impregnation approach, as illustrated in figure 1. MP is dissolved in THF to obtain a solution (~10 wt% MP) of low viscosity. The solution is then poured into an open glass vessel and the porous silica monolith is infiltrated under mild horizontal agitation. The combination of agitation and continuous evaporation of the solvent allows continuous accumulation of the MP molecules in the porous template.
Figure 1. Synthesis of hierarchical porous carbon monoliths using silica as hard template and MP as carbon precursor.

1. A hierarchical porous silica monolith is placed into an open glass vessel.
2. A diluted MP solution is added. The monolith is infiltrated by mild horizontal agitation while the solvent evaporates and the MP concentration increases.
3. The silica-MP hybrid is slowly dried in a quartz tube to prevent cracking.
4. The hybrid material is carbonized under protective atmosphere.
5. The hierarchical porous carbon monolith is obtained by the dissolution of the template.

After the evaporation of the solvent, the infiltrated silica/MP hybrid material is taken out of the vessel and dried in a quartz tube of similar size. This ensures the drying process to be slow enough to prevent cracking of the monolith and also helps retaining the shape of the monolith. The drying process is followed by the carbonization of the hybrid material under nitrogen flow at 700 °C and the porous carbon replica is subsequently obtained by dissolving the silica template in an aqueous solution of ammonium hydrogen difluoride (NH₄HF₂). The synthesized monoliths are mechanically stable and in most cases crack-free. In principle, the silica monoliths can also be infiltrated by melt infiltration; however, our attempts so far did not provide satisfactory results owing to the high viscosity of the melt and the condensation of the pitch at elevated temperatures.

Figure 2(a) shows a photograph of the synthesized carbon monolith, several cm in length. SEM images reveal that the high integrity of the silica structure was successfully transformed into the carbon replica, and continuous macroporous frameworks with 1–3 µm pores...
are found for both systems (figures 2(b) and (c)). The macroscopic silica and carbon frameworks exhibit additional porosity in the mesopore range, as discussed in the following section. Such an interconnected hierarchical porous system provides optimized transport properties compared to bulk or purely meso- or microporous materials and can serve as an ideal reference system to study porosity and size effects owing to its defined geometry.

The situation is different when MP is heat-treated in absence of the silica template (bulk MP), as the carbonization process is accompanied by a large volume expansion leading to pores in the mm range (inset in figure 2(a)). In this case the carbon structure itself is non-porous on the µm scale as demonstrated by the SEM image in figure 2(d). Such a volume expansion is not observed during the nanocasting process and indicates that the carbonization process for bulk material is very different from that of MP in a confined space.

A closer look at the silica template and carbon replica, however, shows that the carbon replica cannot be considered as an ideal replica of the silica template. This issue is discussed below in more detail. XPS and energy-dispersive x-ray spectroscopy (EDX) measurements confirmed the high purity of the carbon monolith, revealing that the silica template was completely removed by dissolution. A carbon content of 95.5 at% and an oxygen content of 4.5 at% were estimated by XPS.

4. Porosity measurements and clarification of the nanocasting process

The porosity at different synthesis steps was first evaluated by Hg porosimetry (figure 3). The pore size distributions of the silica template and the carbon replica exhibit two well-defined maxima in the meso- and macropore size ranges. An average mesopore size of ∼6 nm and a macropore size of 2 µm are observed in the carbon monolith, confirming SEM results. The total pore volume is 1.18 cm³ g⁻¹ with mesopores contributing ∼20 vol%. Slightly larger average pore diameters (10 nm and 3 µm) are observed in the silica template.

Figure 3(b) shows the porosity measured after infiltration. Only a small fraction of mesopores is detected, indicating an almost complete filling of the silica mesopores with MP. The macropores are not completely filled, but the average macropore diameter is slightly smaller than that of the template; thus part of the porous silica framework is covered with a layer of MP. This shows that the replication process is not perfect on the µm scale and cannot be considered as volume templating only, in line with the findings from Lu et al on FA based carbons [8].

The underlying nanocasting processes are better described by a combination of surface and volume templating processes, as illustrated in figure 4: (1) The macro- and mesopores of the silica template are completely filled with a solution of MP dissolved in THF. (2) Drying off the solvent leads to an incomplete filling of the macropores, as confirmed by Hg porosimetry and SEM results. As the macropore walls are covered with MP, the term ‘surface templating’ is used in this case. Volume templating occurs within the mesopores of the silica matrix. (3) MP carbonization is associated with a certain weight loss and shrinkage, eventually leading to the formation of additional pores. (4) The carbon replica with macro- and mesopores is obtained by dissolving the template. The presence of macropores in the replica, which are then slightly smaller compared to the template, is only due to the combination of surface and volume templating processes, i.e. the carbon replica is not an ideal replica of the silica template.

This model of the templating process is further supported by the cumulative pore volumes: The silica template exhibits a pore volume of 2.25 cm³ g⁻¹. Assuming roughly equal densities for the nonporous silica and carbon materials (ρ = 2.2 g cm⁻³), the corresponding ideal carbon replica should exhibit a total pore volume of 0.09 cm³ g⁻¹. Instead, a pore volume of ∼1.2 cm³ g⁻¹ is observed, which is primarily related to the aforementioned incomplete pore filling of the silica pores with MP and the weight loss observed
Figure 4. Diagram of nanocasting process. The structure of the carbon replica is a result of combined surface and volume templating processes.

during carbonization. As a result of the nanocasting process, the monolithic carbon structure should comprise a highly mesoporous inner part, covered by a less porous shell. However, observing this feature unequivocally by SEM has not yet been possible.

As small mesopores and micropores cannot be detected by Hg porosimetry, the samples were further investigated by nitrogen physisorption. Figure 5(a) shows the isotherms of the silica template and the carbon replica. Both samples show a type IV isotherm typical of a mesoporous material. During infiltration, the mesoporosity vanishes as a result of the complete pore filling with MP. The silica template exhibits a BET surface area of 340 m$^2$ g$^{-1}$ and an average pore size of ~14.0 nm, as estimated using the NLDFT. The average pore size of the carbon replica is determined to be 7.3 nm as a result of the wall thickness of the template. In both cases, the pore size distributions are well defined, proving the possibility of excellent pore size control similar to that in ordered mesoporous materials (e.g. CMK-3), despite the disordered pore structure. A BET surface area of approximately 300 m$^2$ g$^{-1}$ is typically observed in carbon replicas. The volume templating process is confirmed by the porosity loss observed during carbonization (figures 5(a) and (b)).

Additional micropores can also develop during the carbonization of the carbon precursor itself. Micropore analysis evidenced a negligible micropore content in MP (figure 5(c)). For comparison, a carbon monolith was also synthesized using FA as the carbon precursor. This resulted in a high intrinsic micropore content, proving the exceptional carbonization behavior of MP. For the MP-based sample, the micropores ($d < 2$ nm) contribute only 2.6 vol% to the total pore volume of pores smaller than 50 nm; in contrast, 19 vol% is measured for the FA-based sample. These results reveal that the micropore content (and thus the carbon microstructure) strongly depends on the type of carbon precursor used. The impact of the type of carbon precursor on the carbon microstructure is discussed in the following section.

5. Impact of the type of carbon precursor on the carbon microstructure

The microstructure of carbon materials depends to a large extent on the type of carbon precursor. FA or sucrose is typically used as the carbon precursor in the hard templating approach. Table 1 shows the compositions of different types of carbon precursors and their weight losses observed during carbonization. The carbonization of most precursors is accompanied by a significant weight loss due to the high oxygen and hydrogen contents. Therefore, multiple infiltrations are often required to obtain a carbon replica with sufficient stability; the final product containing many heteroatoms. Moreover, a catalyst is often required to facilitate the carbonization process.

In this respect, MP is a superior type of carbon precursor as it can yield a well-defined graphene microstructure owing to its polyaromatic molecular structure showing a high carbon content. Also, the weight loss observed during carbonization is relatively small, even without additional catalysts, allowing an improved template replication. The carbon content after carbonization was determined by elemental analysis. As expected, the carbonized material is more carbon-rich in the case of MP (97.2 wt%) compared to when other type
of precursors are used (92.7 wt% for starch, 94.0 wt% for naphthol, 95.1 wt% for FA and 96.0 wt% for sucrose). While these values refer to the total composition of the samples, structural differences in the local carbon microstructure can be revealed by WAXS analysis.

Carbonization of the above-mentioned type of carbon precursors leads to a so-called ‘non-graphitic’ carbon microstructure, as illustrated in figure 6(a). Several graphene layers of random size, shape and orientation form stacks of a few nm height (in the direction perpendicular to the graphene layers) and the ‘gaps’ in between form micropores. Unless these structures are connected to each other, their graphene layers (and the ‘gaps’ in between) form micropores. Thus, we see a pronounced micropore content. Figure 6(b) shows the WAXS patterns of the carbonized bulk MP and FA. The carbonized FA serves also as an example for the other type of carbon precursors that show similar WAXS patterns after carbonization. Clearly, the MP-based samples exhibit a more defined carbon microstructure. The diffraction line at \(2\theta = 25.7^\circ\) originates from the interlayer scattering of graphene stacks and its intensity is higher in the MP-based samples. The maximum around \(2\theta = 42–47^\circ\) results from the intralayer scattering of graphenes. Quantitative information on the average stack dimensions and their polydispersities was derived from WAXS data using the method developed by Ruland and Smarsly [26]. A comparison of this method with standard techniques, such as Raman spectroscopy, can be found in reference [28]. As shown in figure 6(b), the calculated WAXS patterns match the experimental data over the entire angular range, and the results are summarized in table 2. The \(L_\alpha\) values observed in bulk MP are larger than those in bulk FA, although the obtained \(L_\sigma\) values are similar. The average interlayer spacing \(a_3\) is smaller in the pitch-based samples, indicating a less disordered graphene structure (the interlayer spacing for graphite is \(a_3 = 0.335\) nm).

The superior carbonization behavior of MP can be followed by comparing the stack dimensions and their

Table 1. Compositions of carbon precursors commonly used in synthesis of mesoporous materials and their weight losses observed upon carbonization under nitrogen atmosphere (6 h at 700 °C).

| Formula  | C (wt%) | H (wt%) | O (wt%) | Weight loss upon carbonization (wt%) |
|----------|---------|---------|---------|-------------------------------------|
| Mesophase C\(_6\)H\(_{46}\) | 94.8    | 5.2     | 0       | 21.9                                |
| Furfuryl alcohol\(^a\) | 61.2    | 6.2     | 32.6    | 86.7                                |
| Sucrose C\(_{12}\)H\(_{22}\)O\(_4\) | 42.1    | 6.5     | 51.4    | 75.0                                |
| Naphthol\(^b\) | 83.3    | 5.6     | 11.1    | 75.0                                |
| Starch C\(_7\)H\(_{10}\)O\(_5\) | 44.4    | 6.2     | 49.4    | 76.6                                |

\(^a\)Carbonization activated by catalyst: oxalic acid for furfuryl alcohol and sulfuric acid for naphthol.

Table 2. Results from WAXS analysis: stack dimensions and polydispersity values of carbon samples produced from MP and FA, and carbonized at different temperatures.

| Sample, carbonization temperature (°C) | \(L_\alpha\) (nm) | \(L_\sigma\) (nm) | \(a_3\) (nm) | \(\langle N\rangle^a\) | \(\kappa_a^b\) | \(\kappa_c^c\) |
|----------------------------------------|------------------|------------------|--------------|----------------------|-------------|-------------|
| Bulk MP, 700                           | 1.1              | 0.98             | 0.343        | 1.94                 | 0.26        | 0.48        |
| Bulk MP, 1000                          | 2.28             | 1.42             | 0.346        | 3.07                 | 0.12        | 0.34        |
| Bulk MP, 1500                          | 7.39             | 7.38             | 0.345        | 17.97                | 0.08        | 0.17        |
| Mon MP, 1000                           | 2.48             | 0.81             | 0.349        | 0.69                 | 0.19        | 0.48        |
| Bulk FA, 700                           | 1.33             | 0.45             | 0.364        | 0.68                 | 0.24        | 0.77        |
| Bulk FA, 1000                          | 2.65             | 0.68             | 0.351        | 1.38                 | 0.29        | 0.41        |
| Bulk FA, 1500                          | 6.0              | 0.78             | 0.347        | 1.44                 | 0.18        | 0.57        |

\(^a\)Average number of graphene layers per stack.

\(^b\)Polydispersity of chord-length distribution within layer plane.

\(^c\)Polydispersity of distribution of stack height.

\(^d\)For this sample, a relatively large value of \(\kappa_c\) was obtained; since the model is only meaningful for small values of polydispersity, the value is not listed.
polydispersities after carbonization at different temperatures. The change in $L_c$ is significant in the MP-based sample and an increase from 0.98 nm (700°C) to 7.38 nm (1500°C) is observed. The average number of graphene layers $\langle N \rangle$ forming one stack increases by a factor of more than 9. In contrast, the $L_c$ increase is negligible in the FA-based sample, and comparably large polydispersities are found. This result clearly demonstrates that a well-defined graphene structure can only be achieved when pitch-based carbon precursors are used.

From the observations described above (see figure 2) it is expected that the carbonization of the bulk material is different from carbonization in the confinement of the silica matrix during the nanocasting process, where the development of a defined carbon microstructure is constrained by geometry. This can be clearly observed from the results of the WAXS analysis of the prepared carbon monolith (‘mon MP’, figure 6(b)) where growth perpendicular to the graphene planes is hindered ($L_c = 0.81$ nm compared with $L_c = 1.42$ nm for the bulk MP carbonized at the 1000°C), while the $L_a$ values are similar. Comparing the $L_c$ values, the microstructure of mon MP ($L_c = 0.81$ nm) is more defined than that of bulk FA ($L_c = 0.68$ nm). Note that, however, the average number of layers $\langle N \rangle$ per stack is higher for bulk FA than for mon MP at 1000°C (table 2), which is in apparent contradiction to the $L_c$ values. This discrepancy can be explained by the fact that $L_c$ is not only determined by $\langle N \rangle$ and $\bar{d}_3$, but also the polydispersity parameter $\kappa_c$ [26].

A more defined carbon microstructure (i.e. larger $L_a$ and $L_c$ values) can also be realized by further increasing the carbonization temperature, but the use of silica as the hard template limits the carbonization temperature in the nanocasting process to $\sim$1200°C owing to SiC formation [29].

As an example for the effect of the local microstructure on the physical and chemical properties, thermogravimetric analysis (TGA) was carried out in order to determine the thermal stability of the carbon replicas. As can be seen from figure 6(c), the onset of decomposition under $N_2/O_2$-atmosphere starts at higher temperatures when MP is used as carbon precursor (onset at 546°C compared with 523°C found for the FA-based sample).

6. Conclusions

We have discussed the preparation of monolithic carbon materials with tailored porosity by the simple one-step solution impregnation of silica templates with a mesophase pitch dissolved in THF. The monoliths exhibit a hierarchical and interconnected structure with defined pores in the meso- and macropore ranges and are formed by combined surface and volume templating processes. Although the meso- and macroporosities are mainly determined by the template, we have shown through WAXS analysis that the local carbon microstructure is mainly defined by the type of carbon precursor, which affects the final properties of the material. Typically, sucrose and furfuryl alcohol are used as carbon precursors for the synthesis of the defined carbon nanostructures by the hard templating approach; however, they are not suitable if a low micropore content, a high purity level and improved chemical stability are desired. In these
cases, a mesophase pitch is better suited as a carbon precursor for the synthesis of well-defined model systems.

Acknowledgments

We thank Mitsubishi Gas Chemical Company for providing mesophase pitch and Merck KGaA for providing silica templates and financial support. We are indebted to the Max Planck Society and acknowledge support in the framework of the ENERCHEM project.

References

[1] Ryoo R, Joo S H and Jun S 1999 J. Phys. Chem. B 103 7743
[2] Ryoo R, Joo S H, Kruk M and Jaroniec M 2001 Adv. Mater. 13 677
[3] Xia Y D, Yang Z X and Mokaya R 2010 Nanoscale 2 639
[4] Sakintuna B and Yurum Y 2005 Ind. Eng. Chem. Res. 44 2893
[5] Jun S, Joo S H, Ryoo R, Kruk M, Jaroniec M, Liu Z, Ohsuna T and Terasaki O 2000 J. Am. Chem. Soc. 122 10712
[6] Tanaka N, Kobayashi H, Ishizuka N, Minakuchi H, Nakanishi K, Hosoya K and Ikegami T 2002 J. Chromatogr. A 965 35
[7] Taguchi A, Smatt J H and Linden M 2003 Adv. Mater. 15 1209
[8] Lu A H, Smatt J H and Linden M 2005 Adv. Funct. Mater. 15 865
[9] Han B H, Zhou W Z and Sayari A 2003 J. Am. Chem. Soc. 125 3444
[10] Lu A H, Li W C, Schmidt W and Schuth F 2006 Microporous Mesoporous Mater. 95 187
[11] Wang L F, Lin S, Lin K F, Yin C Y, Liang D S, Di Y, Fan P W, Jiang D Z and Xiao F S 2005 Microporous Mesoporous Mater. 85 136
[12] Alvarez S, Esquena J, Solans C and Fuertes A B 2004 Adv. Eng. Mater. 6 897
[13] Kim Y-S, Guo X-F and Kim G-J 2010 Catal. Today 150 91
[14] Lu A H, Smatt J H, Linden M and Schuth F 2003 New Carbon Mater. 18 265
[15] Yang H F, Shi Q H, Liu X Y, Xie S H, Jiang D C, Zhang F Q, Yu C Z, Tu B and Zhao D Y 2002 Chem. Commun. 2842
[16] Li Z J and Jaroniec M 2001 J. Am. Chem. Soc. 123 9208
[17] Kim T W, Park I S and Ryoo R 2003 Angew. Chem., Int. Ed. Engl. 42 4375
[18] Yang H F, Yan Y, Liu Y, Zhang F Q, Zhang R Y, Meng Y, Li M, Xie S H, Tu B and Zhao D Y 2004 J. Phys. Chem. B 108 17320
[19] Qiao W M, Song Y, Hong S H, Lim S Y, Yoon S H, Korai Y and Mochida I 2006 Langmuir 22 3791
[20] Xia Y D and Mokaya R 2004 Adv. Mater. 16 1553
[21] Hu Y S, Adelhelm P, Smarsly B M, Hore S, Antonietti M and Maier J 2007 Adv. Funct. Mater. 17 1873
[22] Adelhelm P, Hu Y S, Chunchom L, Antonietti M, Smarsly B M and Maier J 2007 Adv. Mater. 19 4012
[23] Wenzel S, Hara T, Janek J and Adelhelm P 2011 Energy Environ. Sci. 4 3342
[24] Fan L Z, Hu Y S, Maier J, Adelhelm P, Smarsly B M and Antonietti M 2007 Adv. Funct. Mater. 17 3083
[25] Doherty C M, Caruso R A, Smarsly B M, Adelhelm P and Drummond C J 2009 Chem. Mater. 21 5300
[26] Ruland W and Smarsly B M 2002 J. Appl. Crystallogr. 35 624
[27] Rodriguez-Reinoso F and Molina-Sabio M 1998 Adv. Colloid Interface Sci. 76 271
[28] Zickler G A, Smarsly B M, Gierlinger N, Peterlik H and Paris O 2006 Carbon 44 3239
[29] Sonnenburg K, Adelhelm P, Antonietti M, Smarsly B M, Noske R and Strauch P 2006 Phys. Chem. Chem. Phys. 8 3561