Rational design of ordered mesoporous carbon with controlled bimodal porosity *via* dual silica templating route†

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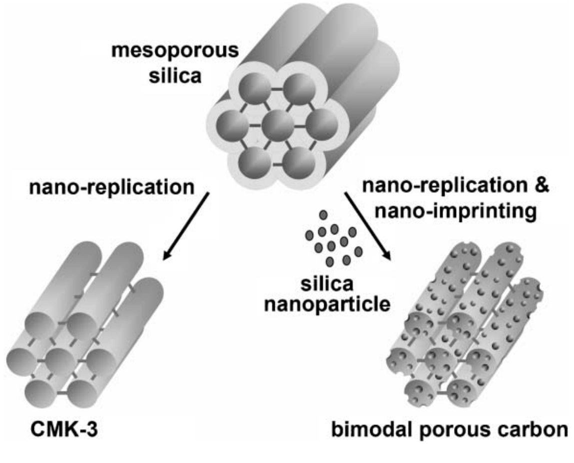
Combining both nano-replication and nano-imprinting techniques using dual silica templates provides a simple way to synthesize ordered mesoporous carbons with bimodal pore size distributions ($\sim$1.5 nm and $\sim$3.5 nm).

Recently, the preparation of a new series of ordered mesoporous carbon (OMC) materials has been reported *via* nano-replication technique using mesoporous silica as the templates.[1–4] Insertion of carbon precursors within the ordered mesopores of the silica materials, carbonization at high temperature and subsequent removal of the silica template result in the OMC materials. Compared with the typical porous carbon materials such as activated carbon, the OMC materials promise to be suitable as adsorbents, catalyst supports, templates for nano-structure materials, and advanced materials for electronics applications due to high surface area and uniform mesopores.[5–13] However, the control of pore size is yet of limited success in the synthesis of OMC materials, compared with tunable pore sizes of the mesoporous silica.[14] Because the wall of the mesoporous silica turns to the void mesopore of the OMC material, one should vary the wall thickness of the silica template in order to control the pore size.[15] The synthesis of the CMK-3 with pore diameters between 3.0 nm and 6.5 nm has also been reported by using mesoporous silicas with different pore sizes.[6] Alternatively, there are some reports concerning bimodal mesoporous carbons.[16–26] The internal pipe diameter can be controlled in CMK-5 carbon material, which has bimodal mesoporosity, *via* surface templating carbonization[16] or controlled catalytic chemical vapor deposition.[17] Bimodal OMC materials can also be obtained by choosing a proper mesoporous silica as the template and by controlled synthetic procedures.[18–22] Nano-imprinting routes for preparation of mesoporous carbons using colloidal silica particles have been reported, giving irregular mesostuctures.[23–25] A combined use of colloidal silica as well as mesoporous silica as the templates are also reported, which is an excellent route for the synthesis of bimodal mesoporous carbons.[25,26] A synthesis of pitch-based carbons with bimodal distribution of uniform mesopores formed by co-imprinting of spherical silica colloids and SBA-15 in to mesophase pitch particles and subsequent silica dissolution.[26] However, previously reported bimodal mesoporous carbon materials exhibit a mesopore in the range of 3–4 nm, which is produced from dissolution of mesoporous silica framework, and the other with larger pore size, from colloidal silica templates, inter-particular spaces, or partially infiltrated carbon precursors.

Here, we propose a facile synthetic strategy to obtain OMC materials with bimodal porosity, a mesopore in the range of 3–4 nm and the other around 1.5 nm that is the boundary between micro- and mesoporous regions, *via* nano-replication and nano-imprinting techniques using dual silica templates: both mesoporous silica and silica nanoparticles. This approach for the synthesis of OMC materials involves the creation not only of periodic mesopores but also of a tunable pore system within the carbon frameworks of OMC materials. As shown in Scheme 1, the periodic mesopores of the OMC materials are formed from the mesoporous silica template, and the tunable pores within the carbon frameworks are generated from the silica nanoparticles, which can be mixed with carbon precursor and introduced in the pores of mesoporous silica. This tunable pore in the range of 1–2 nm can be controlled by the amount as well as the size of the silica nanoparticles through the present synthesis strategy.

Synthesis of mesoporous silica template, SBA-15, was performed following the procedures described elsewhere[27] using triblock polymer Pluronic P123 ($EO_{20}PO_{70}EO_{20}$) as the



Scheme 1 Dual silica templated synthesis for ordered mesoporous carbons with bimodal porosity.

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structure-directing agent and tetraethylorthosilicate (TEOS) as the silica source. Silica nanoparticles (SNP) were prepared by typical sol–gel technique. TEOS was dissolved in the mixture of ethanol and 10^{-3} M HCl aqueous solution, giving a molar composition of 1.0 TEOS : 0.083 HCl : 4.5 H_2O : 4.5 EtOH. After continuous stirring at 313 K for a certain period, the mixture was directly used as the silica nanoparticle template. Synthesis of OMC materials is very similar to that of CMK-3 materials,[3] except that the SNP was mixed with the carbon precursors. The weight ratio of SNP/(SNP + sucrose) was varied in the range of 0–60 wt%, where the weight of SNP was calculated by the amount of TEOS in the SNP solution. The mesopores of the SBA-15 were filled with the mixture of the sucrose, sulfuric acid and SNP by impregnation method. The mixtures were dried at 373 K and subsequently at 433 K, and then the impregnation/drying step was repeated once more. The carbonization was carried out with heating to 1173 K under nitrogen flow, and finally the silica templates were dissolved at room temperature in a water–ethanol solution of HF. Elemental and thermogravimetric analyses indicated that the OMC materials contained below than 1 wt% of silica residue. The OMC materials thus obtained are denoted OMC-*x*-*y*, where the *x* means the oligomerization time for the silica nanoparticles and the *y* indicates the weight percentage of silica nanoparticles.

Fig. 1 shows the X-ray diffraction (XRD) patterns, N_2 adsorption–desorption isotherms and corresponding BJH pore size distribution curves for the OMC-21-*y* materials. The OMC materials give typical XRD patterns of 2-d hexagonal (*P*6*mm*) structure, similar to that of mesoporous carbon CMK-3.[3] Further evidence for the 2-d hexagonal structures of the material is provided by the transmission electron microscopy (See Fig. S1 of ESI†). The XRD patterns for the OMC-21-*y* materials in Fig. 1 represent the gradual decrease in structural order with increasing amount (*y*) of SNP. The SNP can be added to as much as about 40 wt% of carbon without destruction of ordered mesostructure, as shown in the XRD patterns. It is reasonable that the loss of periodic mesostructures beyond 50 wt% of silica nanoparticles may occur because the amount of void volume within the carbon frameworks is too great for the structure to be maintained. There is also a decrease of the (100) peak intensity as *y* increases, which indicates that void volumes within the carbon frameworks, templated by the silica nanoparticles, result in a decrease of the apparent density of the carbon wall, similar to CMK-5.[3]

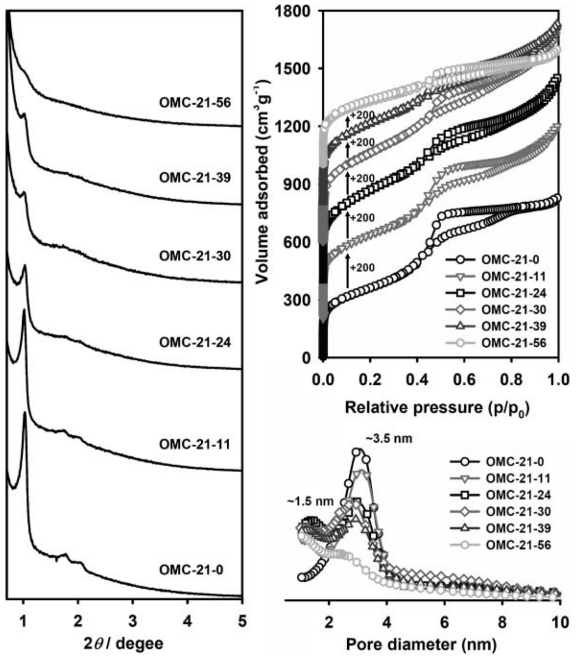

Fig. 1 XRD patterns, N_2 adsorption–desorption isotherms and corresponding pore size distribution curves for the OCM-21-*y* materials.

The BJH pore size distribution curves, obtained from N_2 adsorption branches, for the OMC-21-*y* materials exhibit two peaks, with the maxima corresponding to the inside diameter within the carbon frameworks ($\sim$1.5 nm) and the pores formed between the adjacent frameworks ($\sim$3.5 nm), respectively. As *y* increase to 30 wt%, the peak intensity corresponding to the pores within the framework ($\sim$1.5 nm) gradually increases. The pore volume of pores of less than 2 nm diameter also increases by the addition of SNP (Table 1 and Fig. S2†) until the amount of SNP reaches 30 wt%, whereas the pore volume of pores of diameter 2–10 nm is almost constant regardless of the amount of SNP. The theoretical volume of SNP can be calculated by the SNP weight and SiO_2 density (2.2 g cm^{-1}). The increasing amounts of pore volumes of OMC-21-*y* materials below 2 nm pore diameter, which are obtained by comparing with the pore volume of OMC-21-0, are very similar to the calculated SNP volumes until $y = 24$ (See Fig. S2 of ESI†). These results are clear evidence that the tunable pores ($\sim$1.5 nm) within the carbon frameworks are formed by the addition of SNP. The surface areas also increase from 1279 m^2 g^{-1} to 1688 m^2 g^{-1} due to the formation of additional pores within the carbon framework (Table 1). However, high loading of SNP results in a decrease in pore volume and surface area, as well as in structural integrity.

Fig. 2 shows high resolution SEM images for the OMC-21-*y* materials. As shown in the SEM images, the morphologies of OMC materials are very similar to that of SBA-15, which indicates that nano-replication from mesoporous silica to mesoporous carbon is successful even though the SNP is added to the carbon precursor. Until $y = 39$, the SEM images exhibit hexagonally arranged carbon rods, generated from mesopores of SBA-15. Unfortunately, the SEM and TEM experiments do not give clear evidence for the tunable pores within the carbon frameworks. From the SEM images with low magnification (See Fig. S3 of ESI†), the overall morphologies of OMC-21-11 and OMC-21-24 are very uniform and very similar to SBA-15 and OMC-21-0 materials. According to our observations, there is no additional formation of carbon phases which are templated only by SNP. As

Table 1 Physical properties of OMC-21-*y* materials

Sample	$S_{BET}{}^a$/ m^2 g^{-1}	$V_{<2\ nm}{}^b$/ cm^3 g^{-1}	$V_{2\text{–}10\ nm}{}^c$/ cm^3 g^{-1}	$V_{tot}{}^d$/ cm^3 g^{-1}
OMC-21-0	1279	0.53	0.59	1.31
OMC-21-11	1557	0.64	0.56	1.59
OMC-21-24	1688	0.69	0.54	1.62
OMC-21-30	1635	0.69	0.59	1.63
OMC-21-39	1480	0.61	0.47	1.42
OMC-21-56	1167	0.49	0.28	0.95

[a] Calculated in the range of relative pressure (p/p_0) = 0.05–0.20. [b] Less than 2 nm of pore diameter calculated at $p/p_0 = 0.16$ using Horvath–Kawazoe formula. [c] 2–10 nm of pore diameter calculated at $p/p_0 = 0.16$–0.78. [d] Measured at $p/p_0 = 0.99$.

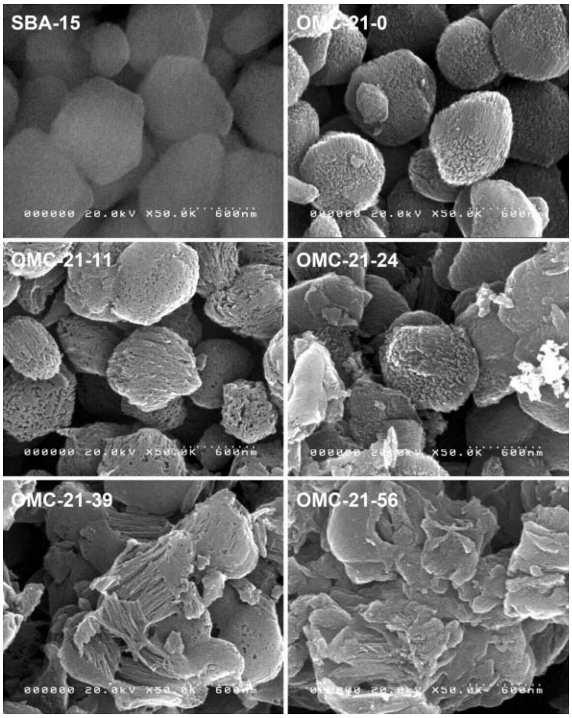

Fig. 2 SEM images for the SBA-15 and OCM-21-*y* materials.

shown in Fig. 2 and Fig. S3†, higher than 40 wt% loading of SNP gives morphological changes that may result from the destruction of the mesostructure of OMC materials or from the formation of the other carbon phases outside of SBA-15.

The pore sizes within the carbon frameworks are slightly tunable in the range of 1.3–1.9 nm by the choice of SNP, of which sizes can be controlled by the oligomerization time. The size of SNP is too small to template the mesopore inside the carbon frameworks when the oligomerization time is below 10 h. The small-sized particle may be embedded within the micropores, which come of themselves during the formation of the carbon framework, or template the additional micropores. Long oligomerization times (> 50 h) seem to give large silica particles, which are too large to go into the mesopores of the SBA-15, and lead to formation of porous carbon outside of SBA-15 particles. Mesopores around 3.5 nm can also be varied when mesoporous silicas with different silica framework thickness are used as the templates.

In summary, the use of dual silica templates provides a simple way to synthesize OMC materials with bimodal pore distribution (∼1.5 nm and ∼3.5 nm) *via* nano-replication and nano-imprinting techniques.[28] This approach for the synthesis of OMC materials involves the creation of not only periodic mesopores but also of tunable pore system within the carbon frameworks. Moreover, this technique promises the successful preparation of bimodal porous carbons with different pore connectivity and sizes, if the mesoporous silica templates have different structures such as MCM-48, SBA-16 and MCF.[14] Owing to their properties such as high surface area, regular and tunable pore sizes and bimodal pore system, the present OMC-*x*-*y* materials may be applicable in many areas.

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