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A direct template synthesis of nanoporous carbons with high mechanical stability using as-synthesized MCM-48 hosts†

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A simple and efficient synthetic method for highly ordered nanoporous carbons with high mechanical and thermal stability has been performed through a direct template carbonization using as-synthesized MCM-48 hosts.

Porous carbons have been greatly studied as adsorbents and electrode materials,[1] and been fabricated using inorganic templates including zeolites,[2] alumina membranes,[3] opals,[4] and silica gels.[5] Recently, a new class of mesoporous carbons were synthesized through carbonization of preformed polymers filled into the void mesopores of calcined cubic[6,7] and hexagonal[8] mesostructured templates. In this case, before the carbonization, the surfactant molecules in as-synthesized templates were completely removed by the calcination process. Such processes may often cause some partial lattice collapse or shrinkage even in well-prepared mesoframeworks as observed by line broadening or signal shift in powder X-ray diffraction patterns. The process also wastes the expensive surfactants, usually organic hydrocarbons or block copolymers, which can be a good carbon source. To help to avoid these drawbacks, we report here for the first time, a simple synthetic method denoted 'a direct template synthesis' of porous carbons using as-synthesized mesostructures as templates. This method needs no calcination process, hence taking advantage of directly using intact as-synthesized hosts in the beginning. The surfactant molecules are also used as a carbon source. Thus this work can save extra labor, time and energy required for the calcination process and yet is found to be an efficient way of synthesizing high quality nanoporous carbons with great mechanical stability.

Mesoporous silica MCM-48 was prepared as reported previously.[7] As-synthesized silica MCM-48 template is denoted as AM48T in this work. For comparison purposes, some of the as-synthesized MCM-48 was washed in a HCl–EtOH solution, filtered off and dried in an oven at 423 K and subsequently calcined in air at 823 K to remove surfactant molecules. The calcined silica MCM-48 template is denoted CM48T. Each of AM48T and CM48T was transferred to a reaction flask in a dry box and dried under vacuum at 373 K for 3 h prior to introduction of the carbon precursor. Divinylbenzene (DVB) with a free radical initiator, azobisisobutyronitrile (AIBN) (DVB/AIBN mole ratio 24) was used as the carbon precursor. The carbon precursor was incorporated into the mesopores of the dried MCM-48 template and polymerized by heating at 343 K for 10 h. Although the composites in the as-synthesized form are relatively dense, DVB molecules can still enter the pores. In fact, the AM48T dried at 373 K was determined to have a total pore volume of 0.15 ml per g of both surfactant and silica. This roughly corresponds to a total pore volume of 0.30 ml per g of silica alone,[9] which is about one quarter of a total pore volume, 1.15 ml g^{-1} determined for CM48T with no surfactant. Interestingly, the amount of DVB used for AM48T was about one third the amount used for CM48T of the same volume. The resulting template/polymer composites were then carbonized under argon gas flow by heating at *ca.* 1273 K for 7 h. The resulting carbons were obtained after subsequent dissolution of the silica.[10]

Fig. 1 shows powder X-ray diffraction (XRD) patterns of the silica hosts and the resulting carbons, respectively. AM48T shows the first intense (211) XRD signal at $2\theta = 2.1°$. The calcination process used in this work caused framework shrinkage as indicated in a slight shift of the first signal to $2\theta = 2.2°$ as shown for CM48T. Two intense signals at $2\theta = 1.4$ and 2.4°, and $2\theta = 1.5$ and 2.5° were observed for AM48T-C (carbon) and for CM48T-C, respectively. The overall XRD intensity of AM48T-C (formed from both surfactant and DVB as carbon precursors) was usually better than that of CM48T-C. The first new (110) intense signal not seen in the MCM-48 host was the result of the phase transition upon removal of the silica framework,[6,7] and was also observed for mesostructured polymers templated in MCM-48.[11] Interestingly, the two intense signals of CM48T-C as compared with those of AM48T-C were found to shift to higher 2θ values by about the same $2\theta = 0.1°$ as the shift of the first (211) signal of CM48T in comparison with that of AM48T. Transmission electron microscopy (TEM) images show highly regular arrays of holes separated by walls, indicating an equal degree of structural integrity and order for the both carbons.

The values of the unit cell parameter, BET surface area, total pore volume and pore diameter are listed for all samples in Table 1. The sorption isotherm for AM48T-C is almost identical to that of CM48T-C. Interesting pore size changes were observed from morphological alterations during the replication process, in which the pores and walls of the silica host were transformed to the walls and pores in the resulting carbon network, respectively. AM48T-C has a greater unit cell dimension and slightly smaller pore size distribution as compared with those of CM48T-C. The greater unit cell (or *d* interplanar spacing) of the former stems from direct template use of the intact AM48T. The framework shrinkage observed in CM48T is considered to occur mainly in the pores, which will be filled by the carbon precursor, rather than in the silica walls, thus resulting in thin walls in the corresponding CM48T-C. The

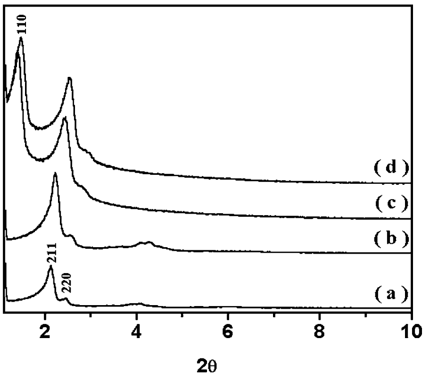

Fig. 1 Powder X-Ray diffraction patterns using Cu-Kα radiation of (a) as-synthesized MCM-48 (AM48T), (b) calcined MCM-48 (CM48T) and the resulting nanoporous carbons prepared from (c) AM48T and (d) CM48T.

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† Electronic supplementary information (ESI) available: Fig. S1: TEM images. Fig. S2: adsorption–desorption isotherms. Fig. S3: schematic for carbonization process. Fig. S4: TGA data. See http://www.rsc.org/suppdata/cc/b2/b202307p/

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smaller pore size in AM48T-C may indicate that the surfactants distributed throughout the pores indeed contribute so favorably to the carbon formation as to decrease the shrinkage of AM48T-C itself. Eventually, these two effects indicate at least 7% thicker cross-sectional wall diameter for AM48T-C as compared with that of CM48T-C, thus allowing one way of a fine-tuning for carbon wall thickness control.[12]

Thermogravimetric (TG) analysis indicated a significant weight loss in a narrow temperature range near 820–830 K for all the resulting carbons. The TG temperatures are in fairly good agreement with those for other graphitized carbons,[13] indicating that the resulting carbons may have a graphitic nature.

Carbon was also obtained from carbonization of the surfactant existing in AM48T. However, the surfactant carbon shows no XRD pattern below $2\theta = 10°$ and no particular mesostructured pattern according to TEM. However, when the surfactant molecules were removed by repeated HCl–EtOH washing from a surfactant/polyDVB composite preformed in AM48T, subsequent carbonization of the added polyDVB alone (polyDVB alone-C) led to good XRD and TEM patterns characteristic of mesostructures. Further extensive TG analyses determined the relative weights of surfactant, polymer and resultant carbons with respect to silica host, which enable the determination of their carbon contribution. The amount of polyDVB incorporated into AM48T was 0.422 g per 1.0 g silica host. This together with the surfactant (0.945 g per 1.0 g silica) leads to a total sum of 1.367 g per 1.0 g silica host in the AM48T incorporated with the polyDVB. The analyses showed the formation of 15 mg surfactant carbon from the AM48T and 122 mg for AM48T-C (composite carbon from both surfactant and DVB) and 86 mg for polyDVB alone-C, respectively, per 1.0 g silica host. This calculation indicates that AM48T-C is roughly estimated to consist of *ca.* 70–88% DVB carbon and *ca.* 30–12% surfactant carbon.

Mechanical strength was measured by monitoring XRD intensity changes after pressurizing pelletized carbons at each of the different pressures as shown in Fig. 2. The relative intensity decreases mainly at low pressures less <120 MPa and slowly decreases at higher pressures. The intensity for CM48T-C decreased more rapidly than that for AM48T-C with *ca.* 70% and *ca.* 80% of their corresponding initial intensity at 700 MPa, respectively, indicating the latter showed better mechanical stability. This may be mainly due to the difference in wall thickness. With an assumption of a cylindrical shape for the walls, simple calculations indicates at least a 14% larger cross-sectional wall area for AM48T-C as compared with that for CM48T-C. In contrast to the carbon replicas, the CM48T silica with high structural order maintained only 18% of the initial intensity after 700 MPa, which is similar to a previous work with *ca.* 20% of the initial intensity after 600 MPa.[14]

In summary, it has been demonstrated for the first time that the direct synthesis method using as-synthesized MCM-48 as template is simple and energy-saving, and yet also an efficient method for synthesizing ordered nanoporous carbons. The composite carbon formed from both surfactant and DVB showed no structural instability and defects from the heterogeneity, and together with direct use of the intact as-synthesized hosts, greatly increased its structural integrity and mechanical stability. This simple direct template synthetic method can be also easily applied to the synthesis of other types of high quality nanoporous carbons.

Table 1 Structural properties of the AM48T and CM48T silica hosts and the corresponding nanoporous AM48T-C and CM48T-C

Sample	*d* Spacing[a]/nm	Unit cell parameter, a_0[b]/nm	BET surface area/$m^2\ g^{-1}$	Total pore volume/$ml\ g^{-1}$	Pore size[c]/nm
AM48T	4.2	10.3	63	0.15	—
CM48T	3.9	9.6	1130	1.15	3.3
AM48T-C	6.3	8.9	1116	0.94	2.3
CM48T-C	5.9	8.3	1147	0.88	2.4

[a] The *d* spacings were determined from (211) and (110) reflections for the MCM-48 templates and corresponding carbon replicas, respectively. [b] XRD unit cell parameter equal to $6^{1/2} \times d(211)$ for AM48T and CM48T and equal to $2^{1/2} \times d(110)$ for AM48T-C and CM48T-C, respectively. [c] Maximum value of the BJH pore size distribution peak calculated from the adsorption branch of the N_2 isotherm.

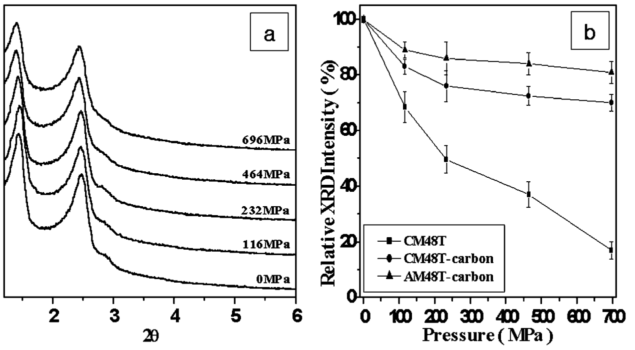

Fig. 2 (a) X-Ray diffraction patterns after pressurizing pelletized AM48T-C (*ca.*100 mg carbon and 1/2 inch diameter) for 10 min at each of the different pressures and (b) the relative XRD intensity changes of AM48T-C, CM48T-C and CM48T *vs.* pressure.

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Notes and references

1 F. Rodriguez-Reinoso, in *Introduction to Carbon Technology*, ed. H. Marsh, E. A. Heintz and F. Rodriguez-Reinoso, Universidad de Alicante, Secretariade de Pub., Alicante, 1997, p. 35.

2 Z. Ma, T. Kyotani and A. Tomita, *Chem. Commun.*, 2000, 2365.

3 T. Kyotani, L. Tsai and A. Tomita, *Chem. Mater.*, 1996, **8**, 2109; G. Che, B. B. Lakshimi, E. R. Fisher and C. R. Martin, *Nature*, 1998, **393**, 347.

4 A. A. Zakhidov, R. H. Boughman, Z. Iqbal, C. X. Cui, I. Khayrullin, S. O. Danta, L. Marti and V. G. Ralchenko, *Science*, 1998, **282**, 897.

5 J.-S. Yu, S. B. Yoon and G. S. Chae, *Carbon*, 2001, **39**, 1442; S. B. Yoon, K. Sohn, J. Y. Kim, C. H. Shin, J.-S. Yu and T. Hyeon, *Adv. Mater.*, 2002, **14**, 19.

6 (*a*) R. Ryoo, S. H. Joo and S. Jun, *J. Phys. Chem. B*, 1999, **103**, 7743; (*b*) S. H. Yoon, T. Hyeon, S. M. Oh and K. B. Kim, *Chem. Commun.*, 1999, 2177.

7 S. B. Yoon, J. Y. Kim and J.-S. Yu, *Chem. Commun.*, 2001, 559.

8 S. Jun, S. H. Joo, R. Ryoo, M. Kruk, M. Jaroniec, Z. Liu, T. Ohsun and O. Terasaki, *J. Am. Chem. Soc.*, 2000, **122**, 10712; S.-S. Kim and T. J. Pinnavaia, *Chem. Commun.*, 2001, 2418.

9 Thermogravimetric (TG) analysis indicated 0.95 g surfactant per g of silica for the AM48T dried at 373 K.

10 In our previous work,[7] silylation of mesopores of calcined silica MCM-48 with trimethylsilyl chloride was reported to be an efficient method for fabricating highly ordered mesoporous carbon. Now new optimization in synthetic conditions through extensive synthesis practices and improvements has led to our conclusion that the mesoporous carbons prepared with the calcined silica MCM-48 without silylation were also as good as those prepared from the silylated MCM-48.

11 J. Y. Kim, S. B. Yoon, F. Kooli and J. -S. Yu, *J. Mater. Chem.*, 2001, **11**, 2912.

12 Since the wall thickness is linearly dependent on the *d* interplanar spacing for both cubic and hexagonal mesostrucures (see, *J. Phys. Chem. B*, 2000, **104**, 7960; 2000, **104**, 292), we obtain a roughly 7% difference in cross-sectional wall diameter only from the *d* spacing with the assumption of the other parameters being identical for AM48T-C and CM48T-C. This difference in the wall thickness will be more when considering the slightly smaller pore size for AM48T-C.

13 A. C. Dillon, T. Gennett, K. M. Jones, J. L. Alleman, P. A. Parilla and M. J. Heben, *Adv. Mater.*, 1999, **11**, 1354.

14 M. Hartmann and C. Bischof, *J. Phys. Chem. B*, 1999, **103**, 6230.