

Synthetic control of ordered and disordered arrays of carbon nanofibers from SBA-15 silica templates†

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Received (in Cambridge, UK) 17th April 2003, Accepted 22nd May 2003

First published as an Advance Article on the web 18th June 2003

A novel synthetic control method for the generation of carbon replicas successfully produces either highly ordered networks of carbon nanofibers with uniform mesopores or disordered carbon nanofibers.

The synthesis of nanostructured carbon materials has recently been of great interest mainly due to their various new characters. The replication of uniformly ordered porous carbon materials has been tuned through the use of sacrificial inorganic porous templates such as zeolites¹ or colloidal crystalline aggregates of silica spheres.² Recently, the synthesis of a new class of ordered mesoporous carbon was reported that had been templated from cubic³ and from hexagonal⁴ silica mesostructures. Spherical porous carbon capsules with hollow macroporous cores and mesoporous shells have also been reported.⁵ In the above cited references, as-synthesized mesoporous silicas were first calcined to remove surfactant molecules prior to the incorporation of carbon precursor. Unfortunately, calcination usually resulted in partial lattice collapse or shrinkage even in well-prepared mesoframeworks.⁶ However, a recent report described a direct synthesis using as-synthesized MCM-48 silica as a template.⁷ The use of this as-synthesized MCM-48 led to the formation of high quality mesoporous carbon with much thicker walls and consequently a greater mechanical strength than the carbon materials prepared from the corresponding calcined templates with their shrunken pore framework.[†]

In this paper we would like to report a novel synthetic control method that can be used for generating either highly ordered carbon nanofiber networks or disordered carbon nanofibers from SBA-15 silica. In this work, a mesoporous SBA-15 silica was synthesized at the relatively low temperature of 308 K and then pretreated in three different ways prior to the carbon replication process. For the first template, the as-synthesized SBA-15 was left untreated and designated AS15T. For the second template, the AS15T was washed with 0.1 M HCl–EtOH two or three times to remove the surfactant molecules. Thermogravimetric analysis indicated that about 90% of the surfactant had been removed. This HCl–EtOH-washed sample was then designated AWS15T. For the third type of template, the AWS15T was then calcined in air at 523, 823, or 1023 K for about 7 h to remove the remaining surfactant. The calcined templates were denoted as CS15T(523), CS15T(823) and CS15T(1023), respectively. Detailed synthetic procedures for the SBA-15 silica hosts and carbon replicas are presented in the supplementary data.[†]

Fig. 1 illustrates the powder X-ray diffraction (XRD) patterns of the silica templates and the corresponding carbon replicas, respectively. The powder XRD patterns exhibited primarily a very intense (100) diffraction peak centered at $2\theta = 0.94, 1.00, 1.06, 1.12$ and 1.18 for the silica templates with increasingly harsh treatments, respectively, along with weaker (110) and (200) reflections characteristic of a 2D hexagonal ($p6mm$) structure. The powder XRD patterns of the carbon replicas AS15T-C and AWS15T-C were similar to those of their corresponding host templates, AS15T and AWS15T, with the

main intense (100) reflection slightly shifted to $2\theta = 1.00$ and 1.06 . In the case of CS15T(523)-C the powder XRD pattern showed a lower and broader (100) reflection with the maximum shifted to $2\theta = 1.09$, but still largely maintained the reflections characteristic of a 2D hexagonal structure. However, for CS15T(823)-C and CS15T(1023)-C the reflections were even more broadened with much lower intensity, indicating the loss of the ordered lattice structures of the carbon replicas.

Fig. 2 shows the transmission electron microscopy (TEM) images of the synthesized carbon replicas. The AS15T-C and AWS15T-C (Fig. 2a) exhibited highly ordered arrays of nanofibers evenly separated by void channels. On the other hand, CS15T(823)-C and CS15T(1023)-C appeared to be largely disordered arrays of loose carbon nanofibers with a few clusters. These carbon fibers had a uniform wall thickness of ~ 4.0 nm and high aspect ratios of several hundred and more (Fig.

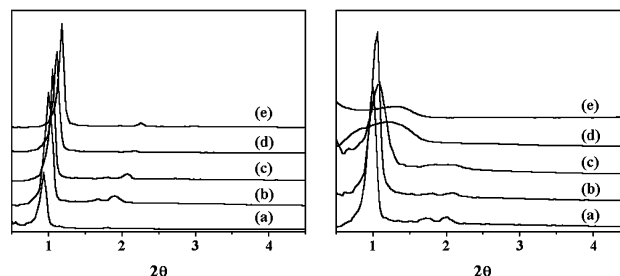


Fig. 1 Powder X-ray diffraction patterns using Cu K α radiation of the host silica templates (left), (a) AS15T, (b) AWS15T, (c) CS15T(523), (d) CS15T(823), and (e) CS15T(1023) and their corresponding carbon replicas (right), (a) AS15T-C, (b) AWS15T-C, (c) CS15T(523)-C, (d) CS15T(823)-C, and (e) CS15T(1023)-C, respectively.

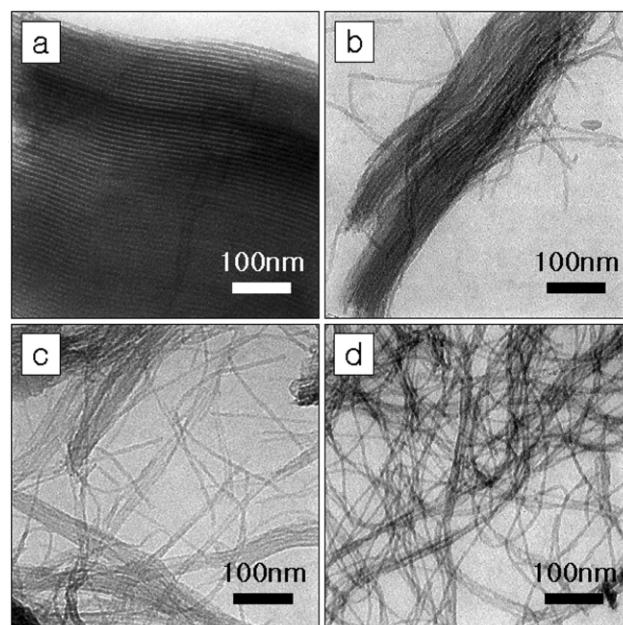


Fig. 2 Transmission electron microscopy images of (a) AWS15T-C, (b) CS15T(523)-C, (c) CS15T(823)-C, and (d) CS15T(1023)-C.

[†] Electronic supplementary information (ESI) available: Fig. S1: synthetic scheme for carbonization; Fig. S2: N₂ isotherms; Fig. S3: experimental section and TGA data. See <http://www.rsc.org/suppdata/cc/b3/b304227h/>

Table 1 Structural parameters of the silica hosts and the corresponding nanostructured carbons prepared in this work

Sample name	<i>d</i> spacing/nm	Unit cell parameter a_0^a /nm	BET surface area/m ² g ⁻¹	Total pore volume/ml g ⁻¹	Pore size ^b /nm	Wall thickness/nm
AS15T	9.39	10.84			~ 7.94 ^c	~ 2.90 ^c
AWS15T	8.83	10.20	733	0.78	7.22	2.98
CS15T(523)	8.34	9.63	681	0.86	6.27	3.36
CS15T(823)	7.88	9.10	597	0.67	5.63	3.47
CS15T(1023)	7.48	8.64	361	0.42	5.06	3.58
AS15T-C	8.83	10.20	634	0.51	3.60	
AWS15T-C	8.33	9.62	707	0.69	3.58	
CS15T(523)-C	8.10	9.35	542	0.49	3.64	
CS15T(823)-C	6.64	7.67	470	0.41		
CS15T(1023)-C			241	0.36		

^a XRD unit cell parameter equal to $a_0 = 2 \times d(100)/3^{\frac{1}{2}}$. ^b Maximum value of the BJH pore size distribution peak was deduced from the adsorption branch of the N₂ isotherm. ^c The wall thickness of AS15T was estimated from that of AWS15T since both are uncalcined.

2c and Fig. 2d). CS15T(523)-C showed a structure with intermediate order but with most parts still in order (Fig. 2b). Therefore, it was possible to control the extent of disorder of the carbon fibers by controlling calcination temperature. The silica hosts calcined at 623 K or higher produced largely disordered arrays of loose carbon nanofibers. A reasonable explanation for this is that the carbon nanostructure shown in Fig. 2a possessed interconnecting cross-links which held the nanofibers together in orderly fashion whereas in Fig. 2c and 2d these cross-links had been lost.

A related replication study for SBA-15 also afforded an ordered CMK-3 carbon material or carbon wires, depending on the calcination temperature.^{4a} However, in this previous work the SBA-15 templates were synthesized at a higher temperature of 373 K (vs. 308 K in the present work) and calcined prior to the addition of the carbon precursor. Also, the calcination temperature required to obtain a loose carbon structure was much higher (above 1243 K) than in the present work (above 623 K), and no TEM images of the loose carbon structures were provided. Another merit of the present work is that the polymer template removal from SBA-15 prior to the infiltration of a carbon precursor is not necessary or even undesirable. In this respect, the present approach is more interesting and practically more important. The carefully controlled pretreatment conditions used in this study also helped to reveal a distinctive structural feature of the SBA-15 framework. MCM-41, which has a similar hexagonal structure, produced only disordered loose carbon nanofibers under the mild pretreatment conditions that were used for SBA-15,⁸ demonstrating that MCM-41 does not possess the interconnecting side-channels found in SBA-15. Based upon the powder XRD data and the observed TEM images, the AS15T-C and AWS15T-C maintained the order of their host silica templates but CS15T(823)-C and CS15T(1023)-C did not. The shift to higher 2θ values in the powder XRD patterns of the calcined silica templates compared to the un-calcined samples may well be related to pore shrinkage during the calcination process. Similar pore shrinkage has been reported for MCM-48.⁷ Furthermore, this shrinkage process could also affect the size of the micropore side-channels which interconnect the main channels of the SBA-15 framework. If this were to happen, the interconnecting micropores might be so reduced in size that they could not any longer accept enough of the carbon precursor to establish viable cross-links between the carbon nanofibers. Thus, breakage of these fragile interconnecting carbon spacers would result in the loose carbon nanofibers shown in the TEM images.

Typical nitrogen isotherms at 77 K were measured for the samples. The AS15T-C, AWS15T-C and CS15T(523)-C exhibited a type IV isotherm characteristic of mesoporous solids according to the IUPAC nomenclature. BET surface areas were reduced for the calcined silica templates compared to the un-calcined ASW15T probably due to pore shrinkage. The CS15T(523)-C as well as AS15T-C and AWS15T-C showed narrow pore size distribution centered at about 3.60 nm. However, the CS15T(823)-C and CS15T(1023)-C exhibited

very broad pore size distribution curves. These data are in good agreement with the results of the powder XRD patterns and TEM images. Table 1 summarizes the structural parameters of the SBA-15 templates and their corresponding carbons prepared in this work. The unit cell parameters for the host silica templates and the corresponding carbon replicas consistently decreased with increasing harshness of the treatment conditions (see Table 1). Likewise, the pore sizes of the silica templates decreased. However, the decrease of the pore size is likely to be accompanied by the increase of the wall thickness as the unit cell dimension decreases. These effects ultimately resulted in thinner walls in the carbon replicas obtained from the calcined templates. Any interconnecting carbon cross-links would also be expected to weaken concomitant with the decrease in wall thickness in the carbon materials and thereby increase the chance of breakage resulting in the loose carbon nanofibers shown in Fig. 2c and 2d.

In summary, a novel synthetic control method has been applied to generate either highly ordered networks of carbon nanofibers with uniform mesopores or disordered carbon nanofibers. This control was accomplished through different methods of pretreatment of an as-synthesized silica host at relatively low reaction temperatures. In this study, the use of either as-synthesized or HCl-EtOH washed silica hosts resulted in highly ordered carbon networks. On the other hand, this work also represents an efficient synthesis route for loose carbon nanofibers by using a controlled calcination process for SBA-15. These carbon nanofibers had a uniform wall thickness of ~ 4.0 nm and high aspect ratios and thus would be expected to have many new potential applications.

The authors thank the Ministry of Science and Technology of Korea for the Nano R&D program and the Korean Basic Science Institute in Taejon for TEM images.

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