Synthesis and characterisation of ordered arrays of mesoporous carbon nanofibres†

Kaixue Wang,[ab] Pavels Birjukovs,[c] Donats Erts,[bc] Richard Phelan,[ab] Michael A. Morris,[ab] Haoshen Zhou[d] and Justin D. Holmes[*ab]

A facile and reproducible one-step pathway has been developed for preparing ordered arrays of mesoporous carbon nanostructures within the pores of anodized aluminium oxide (AAO) membranes, through the confined self-assembly of phenol/formaldehyde resol and amphiphilic copolymer templates. The morphology of the mesoporous carbon nanostructures can be controlled by varying the copolymer surfactant, the quantity of the resol–surfactant precursor sol used and the amount of phenol–formaldehyde resol introduced into the resol–surfactant sol. One-dimensional (1-D) carbon nanostructures, such as carbon fibres with a core–shell structure and carbon ribbons with circular mesopores running parallel to the longitudinal axis of the ribbons, have been successfully prepared. More importantly, the orientation of the mesoporous channels within these 1-D carbon nanostructures can be tuned by changing the mean pore diameter of the AAO membranes and the surfactants used in their preparation. The conductive properties of these vertically aligned mesoporous carbon nanofibres within the AAO membranes have been characterised by conductive atomic force microscopy (C-AFM).

Introduction

Carbon materials, with properties such as remarkable chemical stability, excellent heat resistance and intrinsic electrical conductivity, have attracted considerable attention in the fields of hydrogen storage, energy conversion, transistor and sensors, especially after the discovery of carbon nanotubes and fullerenes.[1–7] Recently, researchers have extended the preparation of carbon nanostructures to form periodic mesoporous carbon. In addition to the intrinsic properties of carbon-based materials, mesoporous carbon has a variety of promising properties, including high specific surface area and easily accessed pore channels derived from their well-ordered porous structure.[8–11] Many applications of mesoporous carbon will benefit from the ordered alignment of 1-D structures, such as nanofibres and nanotubes, with controllable pore channel arrangements on the mesoscale. One simple and practical way to prepare 1-D mesoporous carbon is to employ a hard template, with well-ordered regular channels, such as anodised aluminium oxide (AAO) membranes. AAO membranes can be prepared by a simple anodic oxidation process of Al foils in an acidic solution.[12,13] The unique properties of AAO membranes, such as well-defined columnar pore channels that can be readily accessed by electrochemical or sol–gel processes, make them very promising hosts for the preparation of 1-D nanomaterials. For example, well-ordered arrays of mesoporous silica nanowires and titania nanotubes have been prepared within the channels of AAO membranes.[14–21] In particular, Yang and co-workers reported the preparation of mesoporous silica nanotubes and nanofibres through a sol–gel process,[14] where the orientation of the hexagonal mesochannels could be tuned by changing the concentration of the surfactant template, by adjusting the relative humidity and by selecting AAO membranes with different pore dimensions. Recently, mesoporous titania nanotubes have been synthesised within the channels of AAO membranes.[21] The dimensions of these nanotubes could be manipulated by changing the pore diameter of the alumina membranes and varying the viscosity of the starting sol.

Despite the success that has been achieved in synthesising 1-D mesoporous silica and titania structures, little progress has been made in the preparation of 1-D mesoporous carbon materials. There are only a few literatures reports on the successful preparation of 1-D mesoporous carbon materials and in most of these cases the processing steps involved are complicated, time-consuming and usually employ 1-D mesoporous silica fibres as hard templates.[22] Recently, several groups reported the preparation of highly ordered mesoporous carbons based on an organic–organic self-assembly of triblock copolymers with soluble low formula weight polymer precursors.[23–26] The successful synthesis of mesoporous carbon from a precursor sol makes the fabrication of well-aligned 1-D mesoporous carbons within the pores of AAO membranes, through a simple evaporation-induced self-assembly (EISA) process, possible. Recently, a direct and solvent-free approach has been reported for the synthesis of mesoporous carbon nanowires using AAO membranes as hard templates.[27–29] Using an ethanolic solution of

[a]Department of Chemistry and the Tyndall National Institute, University College Cork, Cork, Ireland. E-mail: j.holmes@ucc.ie; Fax: +353 (0)21-4274097; Tel: +353 (0)21-4903608
[b]Centre for Research on Adaptive Nanostructures and Nanodevices (CRANN), Trinity College Dublin, Dublin 2, Ireland
[c]Institute of Chemical Physics, University of Latvia, Riga, Latvia
[d]Energy Technology Research Institute, AIST Tsukuba, Central 2, Ibaraki, 305-8568, Japan
† Electronic supplementary information (ESI) available: Low-magnification TEM images of the carbon nanofibres and fibre bundle released from the AAO membrane. See DOI: 10.1039/b817156d

the Pluronic copolymer surfactant F127 ($EO_{106}PO_{70}EO_{106}$, M_{av} = 12 600) and phenolic resol, mesoporous carbon nanofibres have been prepared within the pores of AAO membranes.[27] After dissolving away the AAO templates, well-aligned arrays of carbon nanofibres could be fabricated on the surface of silicon wafers through a supercritical CO_2 drying process. Mesoporous carbon nanofibres with a core–shell structure have also been prepared through this sol–gel process.[29] However, rational manipulation of the morphology of the 1-D carbon nanostructures on the macro-scale and deliberate control of the pore orientation in the meso-scale remain a challenge.

Herein, we report a one-step method for preparing highly ordered mesoporous carbon nanostructures, with defined structures, within the pores of AAO membranes using triblock copolymer surfactants–phenolic resol ethanolic solutions. The morphology of the 1-D mesoporous carbons could be controlled by tuning the resol-to-surfactant ratio of the initial precursor mixtures or the amount of the surfactant–resol ethanolic precursor sol used. More importantly, the orientation of the mesoporous channels of these 1-D carbon materials can be controlled by choosing different surfactants and AAO membranes with various pore dimensions.

Experimental

The preparation of the phenol–formaldehyde resol and the precursor sol

The phenol–formaldehyde resol was prepared from the reaction of phenol with formaldehyde in a base-catalysed process following a previously reported procedure.[26] In a typical procedure, 0.61 g of phenol was melted at 40–42 °C in a flask and mixed with 0.13 g of 20 wt% sodium hydroxide aqueous solution under stirring. After 10 min, 1.05 g of formalin (37 wt% formaldehyde) was added dropwise below 50 °C to the mixture. Upon further stirring for 1 h at 70–75 °C, the mixture was cooled to room temperature. The pH of the solution was adjusted with 0.6 M HCl solution until it reached a value of 7.0, and water was removed by vacuum evaporation below 50 °C. The final product was dissolved in 5 mL of ethanol.

The precursor sol contain the above prepared resol which works as the carbon source and a variety of amphiphilic surfactants, such as F127, P123 ($EO_{20}PO_{70}EO_{20}$, Pluronic, M_{av} = 5800) and cationic surfactant, cetyltrimethylammonium bromide (CTAB), as structural directing agents. In a typical preparation, 1.0 g of F127 was dissolved in 20.0 g of ethanol. Then 5.0 g of the resol precursor solution in ethanol was added. After stirring for 10 min a homogeneous solution was obtained.

The preparation of arrays of mesoporous carbon nanofibres in AAO membranes

A glass tube with an inner diameter of about 18 mm was attached onto the surface of a silicon wafer by mounting wax. A piece of AAO membrane together with 0.3 mL of the precursor sol was put into the tube (Scheme 1). The sol infiltrates the pores of the AAO membrane and changes into a gel during the aging process, at room temperature and at 60 °C. After drying, the AAO membrane which firmly adheres to the silicon wafer was calcined at 600 °C in a N_2 atmosphere for approximately 3 h to
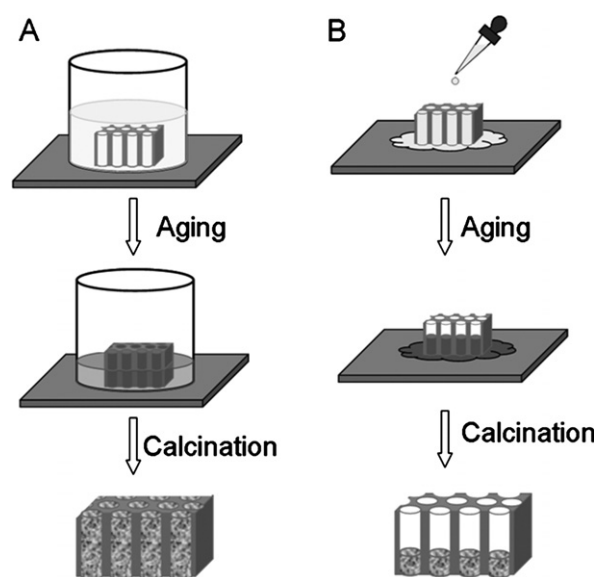
Scheme 1 Schematic illustration of the carbon nanostructures formed inside the AAO pores by using (a) the in-sol gelation method and (b) the popular soak–dry method.

decompose the surfactant molecules and carbonise the mesoporous walls.

Characterisation

The morphology of the arrays of carbon nanofibres was characterised by scanning electron microscopy (SEM) performed on a JEOL JSM-5510 scanning microscope and a field-emission scanning microscope (FESEM; Carl Zeiss Gemini Supra) operating at 10 kV. Transmission electron microscopy (TEM) images were recorded using a JEOL 2000E microscope operated at 200 kV. Samples for TEM were prepared by the following method: 1) the AAO membranes were dissolved in 6 M HCl solution to release the embedded mesoporous carbon fibres; 2) top views were prepared by dimple grinding followed by Ar ion polishing. A commercial atomic force microscope (AFM) (MFP-3D-BIO™, Asylum Research) in contact mode was used for topography and current mapping. Conductive Pt/Ti-coated silicon AFM tips (Olympus AC240TM) were used in all experiments.

Results and discussion

Influence of the precursor sol on morphology

The 1-D mesoporous carbon nanostructures were prepared by a dual-template method *via* a simple one-step sol–gel process. Amphiphilic triblock copolymers, poly(ethylene oxide)-*block*-poly(propylene oxide)-*block*-poly(ethylene oxide) were used as soft-templates to direct the formation of the ordered mesoporous structure within the 1-D carbon nanostructures during the EISA process. Commercial AAO membranes with pores of approximately 200 nm in diameter were used as hard templates to shape the precursor sol or gel into 1-D nanostructures during the aging and calcination process. The precursor sol containing a soluble

low molecular-weight phenol–formaldehyde resol, and amphiphilic surfactant molecules were first prepared following the procedure described previously.[27] The method used here for the confined self-assembly of the ordered mesoporous carbon nanostructures within the channels of AAO membranes is depicted in Scheme 1. First, a glass tube with an inner diameter of approximately 18 mm was attached onto the surface of a silicon wafer or glass slide by mounting wax. Then, a certain amount of the precursor sol together with a piece of AAO membrane was put into the tube, followed by aging and calcination. The glass tube, attached to the substrate, prevents the spread of the sol onto the surface of the substrates and was essential to ensure complete filling of the AAO pores with the precursor sol. This feature makes this in-tube gelation method a simple and reproducible way to prepare 1-D carbon nanostructures. Moreover, given the defined diameter of the glass tubes, the degree of filling of these AAO pores by the precursor sol can be controlled by varying the amount of the sol used. Actually, the amount of the precursor sol not only influences the degree of filling of the AAO pore channels, but also influences the morphology of the carbon nanostructures prepared.

Fig. 1 shows the SEM images of carbon nanostructures prepared from various amounts of precursor sol. The top-view SEM images show that only approximately half of the AAO pores were occupied by the carbon nanofibres for the samples prepared with the precursor sol less than 0.1 mL (Fig. 1a). During the high temperature calcination process, the nanostructures formed within the AAO pores were subjected to a dramatic shrinkage both along and perpendicular to the axis of the pore channels. The carbon nanostructures occupy only part of the pore channel, which is similar to that reported by Yamaguchi et al. where a filtration method was applied.[16] As a result, only short fine carbon nanofibres were obtained. Nearly 100% of the AAO pores were occupied by the carbon nanofibres when more than 0.3 mL of the precursor sol was introduced into the glass tubes. Fig. 1b clearly shows that well-shaped carbon nanofibres protrude from the openings of the AAO membranes. Our previous results also suggest that the carbon nanofibres prepared with 0.3 mL of the precursor sol were running throughout the entire channels of the AAO membranes.[27]

TEM images of the released carbon nanostructures prepared with various amounts of the precursor sol further confirmed the presence of mesoporous fibre-like nanostructures (Fig. 2). Side- and top-view TEM images shows that no obvious mesoporous ordering was observed for the carbon nanofibres prepared with
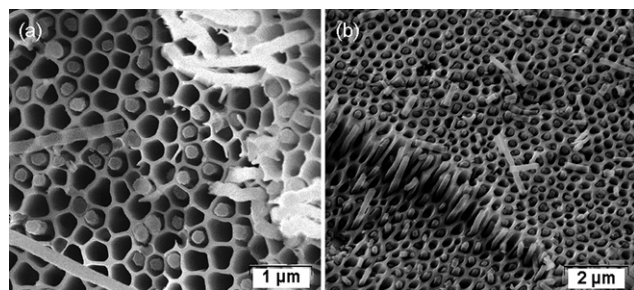

Fig. 1 Representative top-view SEM images of carbon nanofibres prepared with (a) 0.1 and (b) 0.3 mL of the precursor sol.
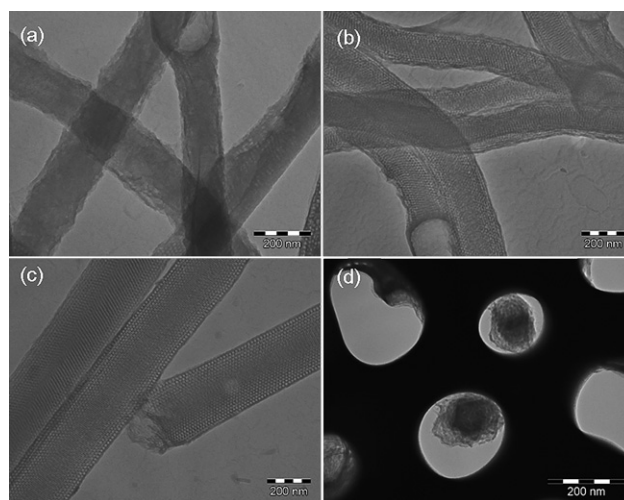

Fig. 2 TEM images of the released carbon nanofibres prepared with (a) 0.07, (b) 0.1 and (c) 0.3 mL of the precursor sol and (d) top-view of (a) embedded within the AAO pores.

a precursor sol with a volume less than 0.1 mL (Fig. 2a and 2d). When a precursor sol volume of more than 0.1 mL was used, hexagonally arranged mesoporous channels at the edge of the carbon nanofibres were produced, as shown in the TEM images. The mean pore diameter of these carbon nanostructures, employing F127 as a structural directing agent, was approximately 5 nm. The pore-to-pore distance between the mesopores was approximately 12 nm, which is in good agreement with the mesopore spacing in FDU-15,[26] a mesoporous carbon material prepared using F127. The diameter of the carbon nanofibres prepared were in the size range between 150 and 220 nm, which is consistent with the pore dimension of the commercial AAO membranes used.

Influence of the phenol–formaldehyde resol on morphology

The formation of the mesoporous carbon structures is based on the cooperative self-assembly among the surfactant molecules and the organic phenol–formaldehyde resol. Therefore, the quantity of resol added to the precursor sol plays an important role in the preparation of these mesoporous nanostructures. Keeping other synthesis parameters constant, the amount of phenol–formaldehyde resol was varied to investigate the impact on the morphology and structure of the carbon nanomaterials produced (Table 1). Typically, 0.5–4.0 g of the phenol–formaldehyde resol ethanolic solution, where 1 g of the resol ethanolic solution contains 0.12 g of phenol and 0.078 g of formaldehyde, was added to 4 mL of the ethanolic solution, containing 0.2 g of F127, to form homogenous resol–surfactant precursor sols. Together with AAO membranes, 0.3 mL of the above resol–surfactant precursor sols were added to glass tubes, which were attached to silicon wafers. Fig. 3 shows the SEM images of the carbon nanostructures released from the AAO membranes. When a small quantity of the phenol–formaldehyde resol ethanolic solution, for example 0.5 g, was used, a core–shell structure was prepared (Fig. 3a). This core–shell structure was confirmed by TEM, as shown in Fig. 4a. The cores of the nanostructures were wrapped by a thin layer of carbon shells. A similar

This journal is © The Royal Society of Chemistry 2009

J. Mater. Chem., 2009, **19**, 1331–1338 | 1333

Table 1 Influence of the phenol–formaldehyde resol and surfactants on morphology of the resultant carbon nanostructures

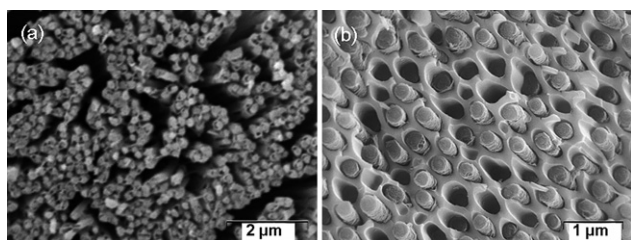| phenol–formaldehyde resol/g	Surfactants	Morphology
0.5	0.2 g F127	Mesoporous core–shell structure
1.0	0.2 g F127	Mesoporous nanofibres
> 3.0	0.2 g F127	Mesoporous nanofibres with bubble-like macropores
10.0	1.0 g P123	Nanoribbons with deformed mesochannels
10.0	1.0 g CTAB	Nanofibres with bubble-like macropores

Fig. 3 SEM images show the influence of the amount of the phenol–formaldehyde resol added to the precursor sol on the morphology of the carbon nanostructures prepared. (a) core–shell and (b) fibre-like carbon structures prepared with 0.5 g and 3.0 g of the phenol–formaldehyde resol ethanol solution, respectively.
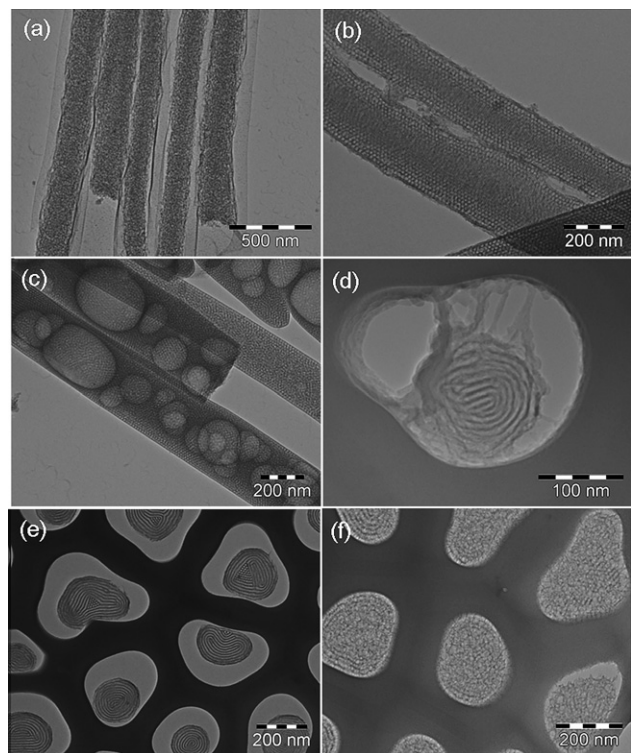

Fig. 4 Side-view TEM images of carbon structures prepared by using (a) 0.5, (b) 1.0, and (c) 3.0 g of the phenol–formaldehyde resol ethanol solution. (d), (e) and (f) top-view TEM images of (a), (b) and (c), respectively.

core–shell structure prepared within the channels of the AAO membranes using a F127–phenolic resol ethanol solution has already been reported by Cao and co-workers,[29] where the shells were composed of ordered mesopores, which can be easily destroyed to release the relatively solid mesoporous carbon cores by ultrasonic treatment. When more than 1.0 g of the phenol–formaldehyde resol ethanolic solution is added to the sol mixture, the morphology of the carbon nanostructures changes significantly. SEM images, shown in Fig. 3(b), show that only nanofibres were fabricated when the quantity of the resol solution was greater than 1.0 g.

Fig. 4 shows side-view TEM images of carbon nanostructures released by dissolving the AAO membranes in a 6 M HCl solution and top-view images for samples prepared by dimple grinding and subsequent Ar ion polishing. Compared to the results reported by Cao *et al.*,[29] no distinct mesopores were observed in the semi-transparent shells, and no obvious mesoporous ordering was observed in the core-shell structures prepared (Fig. 4a and 4d). By increasing the amount of the phenol–formaldehyde resol to the resol–surfactant precursor sol, mesoporous carbon nanofibres were prepared. As shown in the side-view TEM image (Fig. 4b), the carbon nanostructures prepared with more than 1.0 g of the resol solution exhibit well-ordered hexagonally arranged porous channels at the edge of the nanostructures, as reported in our previous work.[27] However, when even more resol solution, over 3.0 g, was incorporated in the self-assembly process, a hierarchical porous structure with both bubble-like macropores and well-ordered mesopores was fabricated (Fig. 4c and 4f). TEM image shows that the bubble-like macropores exist only at one end of the nanofibres (see ESI† for details). From the top-view TEM observations, all of the AAO pore channels were fully occupied by the mesoporous carbon nanofibres, even after calcination at 600 °C. Large quantities of phenol–formaldehyde resol may take part in the self-assembly process leading to relatively dense pore walls that would resist the volume shrinkage during the aging and calcination processes and result in blocked AAO pore channels. The blockage of AAO pore channels by the carbon nanofibres would prevent the small air bubbles from escaping from the channels, which could be trapped within the channels with the addition of the precursor sol or formed during gelation processes. As a result, various sized bubble-like macropores were formed.

The impact of the surfactants on morphology

The amphiphilic structural directing agents play an important role in the formation of the mesoporous structures. A variety of mesoporous structures ranging from 1-D hexagonal and 2-D lamellar to 3-D cubic frameworks can be prepared from mixtures of resol and different surfactant templates through an EISA process.[30–32] In addition to the F127 surfactant, the triblock copolymer surfactant P123 and the cationic surfactant cetyltrimethylammonium bromide (CTAB), were investigated as structural directing agents for the formation of carbon nanostructures (Table 1).

The preparation procedure for the carbon nanostructures using P123 and CTAB as structural directing agents is similar to that described above. In a typical synthesis, 1.0 g of P123 or CTAB was dissolved in 20.0 mL of ethanol, followed by the

addition of 10.0 g of the phenol–formaldehyde resol ethanolic solution. When P123 was used as the surfactant, ribbon-like carbon materials were obtained as shown by the TEM image in Fig. 5. All of the carbon nanoribbons have circular mesochannels running parallel to their longitude axis. The carbon layers of the mesochannels were wrapped together concentrically in a similar way to multi-walled carbon nanotubes. An anisotropic shrinkage of these carbon nanostructures occurred during the high temperature calcination process which lead to the formation of carbon nanoribbons with deformed mesochannels, as shown in the plan-view TEM images (Fig. 5c).

The cationic surfactant CTAB has been widely used in the preparation of mesoporous silica materials, such as the M41S family.[31] However, instead of well-ordered mesoporous structures, carbon nanofibres with bubble-like macropores were fabricated when CTAB was employed as a structural directing agent (Fig. 6). As outlined by Huo et al.,[32] the synthesis of mesostructures using cationic surfactants involves the electrostatic interaction of the cationic head group with anionic framework species. For the phenol–formaldehyde resol, no anions will form under neutral conditions and consequently the cationic surfactant might not be involved in the templating processes during gelation. As a result, no well-ordered mesoporous structures are generated.

The impact of pore dimensions on mesoporous carbon formation

In our experiments, the AAO membranes act as hard templates for the fabrication of the carbon nanostructures and the
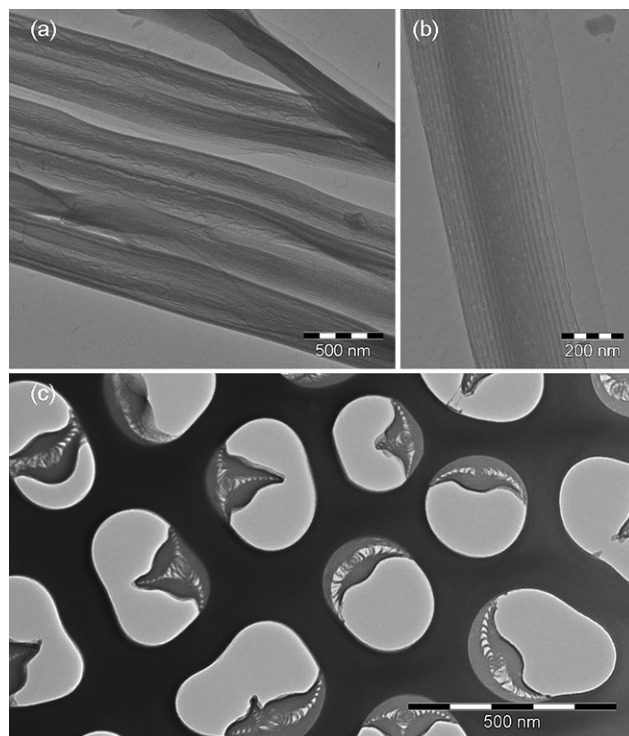

Fig. 5 Side-view (a) and (b), and top-view (c) TEM images of mesoporous carbon nanoribbons prepared by using P123 as a structural directing agent, showing the circular mesochannels running parallel to the longitude axis of the ribbons.
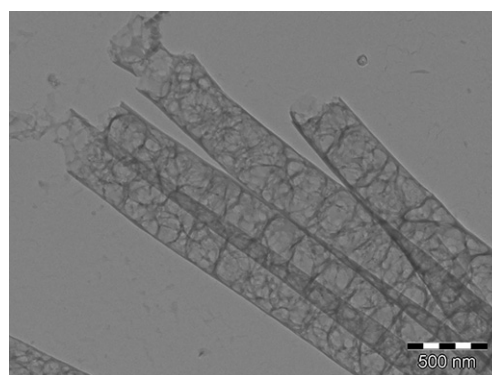

Fig. 6 TEM image of carbon structures prepared by using CTAB as a structural directing agent.

dimensions and properties of the AAO channels influence the morphology of the carbon nanostructures prepared. Y-branched carbon nanofibres and nanofibres with saw-shaped edges, as observed in the TEM images, can be obtained from commercial AAO membranes (see ESI† for details), which reflects the inner surface morphology of the porous channels. In fact, the diameter and shape of the AAO pores and the properties of the inner surface of the pore walls not only define the morphology of the 1-D carbon nanostructures, but also influence the mesoporous frameworks formed.

Using the non-ionic triblock copolymer F127 as a soft template, well-aligned mesoporous carbon nanofibres can be fabricated with the pore channels of commercial AAO membranes through a confined self-assembly process as shown in Fig. 4 and as outlined ref. 25. From the side-view TEM observations, the carbon nanofibres have hexagonally arranged circular mesochannels concentrically coiled around the longitudinal axis of the fibres, consistent with the mesoporous structure of silica and titania nanowires or nanotubes prepared within the pores of the AAO membranes. However, in some relatively large triangular-shaped AAO pores, columnar oriented mesochannels actually exist at the centre of the carbon nanofibres. As shown in the top-view TEM images (Fig. 4e), these columnar mesochannels, wrapped by circular mesochannels, are aligned parallel to the longitudinal axis of the fibres. Thus, the size and shape of the AAO pores have a significant impact on the orientation of the mesochannels. The formation of these mesoporous carbon structures is assumed to occur through the confined self-assembly of resol and surfactant molecules within the limited void space of the AAO pore channels. Due to the difference in surface energy, the precursor sol can evenly wet or spread out over the inner-pore surface of the AAO membranes. Thus, the void space within the AAO membrane is completely occupied by the precursor sol, or the relatively condensed gel formed during the gelation process.

Hydroxyl groups of the phenol–formaldehyde oligomers formed from the reactions of formaldehyde and the phenol will hydrogen bond with the hydrophilic blocks of the surfactant molecules and the terminal hydroxyl groups or bridged oxygen atoms on the inner surface of the AAO channels to form the initial meso-rings. Driven by the reduction in surface energy, a confined self-assembly process occurs starting from the alumina pore wall to the pore centre and concentric rings with
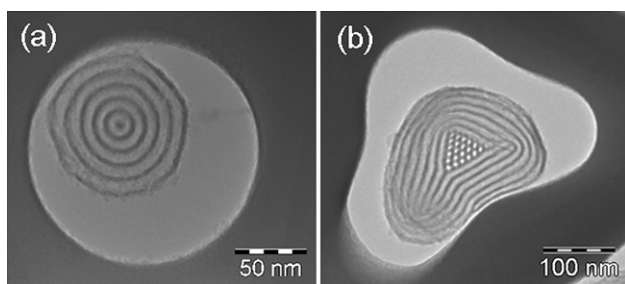
This journal is © The Royal Society of Chemistry 2009

J. Mater. Chem., 2009, **19**, 1331–1338 | **1335**

Fig. 7 Top-view TEM images of mesoporous carbon nanofibres showing the influence of the size and shape of the AAO pores on the arrangement of the mesochannels.

decreasing radii form during the aging process. As a result, circular mesoporous channels form concentric coils around the axis of the carbon fibres in some relatively small and regular AAO pores (Fig. 7a). However, for the larger triangular-shaped AAO pores, the confining effect of the channel walls decreases dramatically towards the centre of the pores and columnar oriented mesochannels form in the centre of the carbon fibres after about seven meso-rings have formed. The triangular alignment of the columnar channels at the centre of the fibres clearly reflects the influence of pore size and pore shape on the formation of the mesoporous carbons (Fig. 7b). The distance from the vertexes of the triangle AAO pore to its centre is much

longer compared to the sides, and thus the confining effect from the vertexes on the self-assembly of the resol and surfactant molecules is weaker. Columnar channels prefer to form in the same direction as the vertexes of AAO pores. As a result, the columnar channels stack into triangular shapes, with vertexes pointing to the corresponding vertexes of the AAO pores at the centre of the carbon nanofibres. The contraction of the carbon nanofibres, perpendicular to their axes, results from peeling of the nanofibres from the inner surface of AAO channels during high temperature calcination. This peeling effect, leads to the formation of voids between the fibres and the walls of the AAO channels.

The confined assembly of silica-surfactant composite meso-structures within the porous channels of AAO membranes has been studied by Stucky and co-workers.[17] The smaller pore diameter of the AAO membranes employed, less than 75 nm, produced a greater confining effect on the mesoporous silica materials compared to the commercial membranes used in our study. Thus, only coiled cylindrical or spherical cage-like meso-pores could be prepared by Stucky et al.[18] due to the strong confining effect.

Conductive properties of the mesoporous carbon nanofibres

Conductive atomic force microscopy (C-AFM) was used to characterise the conductive properties of the mesoporous carbon nanofibres and to test if the nanofibres ran continuously through
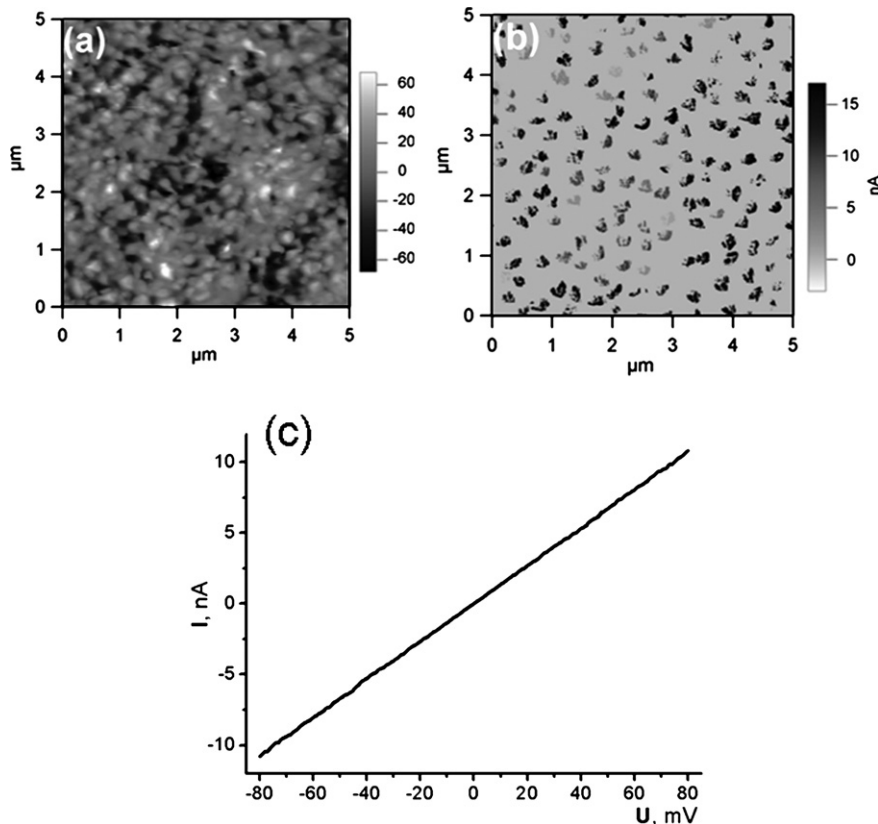

Fig. 8 (a) AFM image of the surface of AAO membrane embedded with the carbon nanofibres after mechanical polishing and chemical etching. (b) C-AFM current map of the area shown in (a) at 150 mV and (c) the linear *I–V* curve acquired from a single carbon nanofibre.

the full length of pores in the AAO membranes. C-AFM has proven to be suitable for measuring the electrical transport properties of individual germanium nanowires within AAO pores.[33] Both surfaces of the AAO membranes were mechanically polished in order to remove the layers of residual growth products and to avoid electrical contacts between the nanowires through this layer. One side of the AAO membrane, used for macrocontact deposition, was treated with 9% H_3PO_4 for 30 min in order to partially remove the AAO membrane and to expose the ends of the nanowires. The contact area and the contact resistance have previously been found to decrease after surface treatment with H_3PO_4.[28] A current map of individual mesoporous carbon nanofibres, prepared from the F127 surfactant, within an AAO membrane measured at 150 mV is shown in Fig. 8. The areas of high current density, as shown in Fig. 8b, correspond well with the protrusions in the topographic image of the nanofibres displayed in Fig. 8a. As shown in the current map, almost all of the nanofibers are conductive and are continuous throughout the length of the membrane, approximately 60 μm. The current–voltage (*I–V*) curve acquired from a single carbon nanofibre exhibits linear characteristics (Fig. 8c), indicating the ohmic nature of the contact. The resistivity for a single nanofibres was in the range 0.014–0.028 Ωm. The true resistivity of the nanofibres may be even lower as contact resistance has not been accounted for in these measurements. The resistivity values of these mesoporous nanofibres are nearly three orders of magnitude lower than that of poly(methyl methacrylate) and multiwalled carbon nanotube (MWCNT) nanocomposite fibers, approximately 18.9 Ωm, with the concentration of the MWCNTs of 2%.[34] Due to their excellent electrical conductivity and high porosity, there well-aligned mesoporous nanofibers offer potential applications in the fields of biosensors, anode materials for high performance lithium ion batteries, and nanoelectronic devices.

Conclusion

A simple and reproducible one-step preparation method has been developed for growing 1-D mesoporous carbon nanostructures within the pores of AAO membranes. Using amphiphilic surfactants as soft-templates and AAO membranes as hard templates, well-aligned mesoporous carbon nanostructure arrays have been fabricated. The morphology of the mesoporous carbon nanostructures has been controlled by choosing various copolymer surfactants, varying the amount of the resol–surfactant precursor sol and the amount of resol introduced into the sol. The dimension of the AAO channels plays an important role in defining the mesoporous structures of the carbon materials by influencing the confined self-assembly of resol and surfactant molecules. The orientation of the mesoporous channels in these 1-D carbon materials can be tuned by simply selecting AAO membranes with various pore sizes and choosing different surfactants. The conductive properties of the mesoporous carbon nanofibres have been characterised by C-AFM. The resistivity for a single nanofibres based on a mean value obtained for a group of nanofibres is in the range 0.014–0.028 Ωm. The diversity of structures and morphologies, and good electrical conductivity may offer the prepared carbon nanomaterials very promising applications in the fields of biosensors, anode

materials for high performance lithium ion batteries, and nanoelectronic devices.

Acknowledgements

References

1 S. Iijima, *Nature*, 1991, **354**, 56.
2 H. W. Kroto, J. R. Heath, S. C. Obrien, R. F. Curl and R. E. Smalley, *Nature*, 1985, **318**, 162.
3 C. Liu, Y. Y. Fan, M. Liu, H. T. Cong, H. M. Cheng and M. S. Dresselhaus, *Science*, 1999, **286**, 1127.
4 A. Bachtold, P. Hadley, T. Nakanishi and C. Dekker, *Science*, 2001, **294**, 1317.
5 J. Kong, N. R. Franklin, C. W. Zhou, M. G. Chapline, S. Peng, K. J. Cho and H. J. Dai, *Science*, 2000, **287**, 622.
6 R. H. Baughman, A. A. Zakhidov and W. A. de Heer, *Science*, 2002, **297**, 787.
7 A. C. Dillon, K. M. Jones, T. A. Bekkedahl, C. H. Kiang, D. S. Bethune and M. J. Heben, *Nature*, 1997, **386**, 377.
8 J. Lee, S. Yoon, T. Hyeon, S. M. Oh and K. B. Kim, *Chem. Commun.*, 1999, 2177.
9 H. S. Zhou, S. M. Zhu, M. Hibino, I. Honma and M. Ichihara, *Adv. Mater.*, 2003, **15**, 2107.
10 J. Lee, S. Yoon, S. M. Oh, C. H. Shin and T. Hyeon, *Adv. Mater.*, 2000, **12**, 359.
11 A. H. Lu, W. Schmidt, B. Spliethoff and F. Schuth, *Adv. Mater.*, 2003, **15**, 1602.
12 G. E. Thompson, *Thin Solid Films*, 1997, **297**, 192.
13 J. H. Yuan, F. Y. He, D. C. Sun and X. H. Xia, *Chem. Mater.*, 2004, **16**, 1841.
14 Z. L. Yang, Z. W. Niu, X. Y. Cao, Z. Z. Yang, Y. F. Lu, Z. B. Hu and C. C. Han, *Angew. Chem., Int. Ed.*, 2003, **42**, 4201.
15 B. Yao, D. Fleming, M. A. Morris and S. E. Lawrence, *Chem. Mater.*, 2004, **16**, 4851.
16 A. Yamaguchi, F. Uejo, T. Yoda, T. Uchida, Y. Tanamura, T. Yamashita and N. Teramae, *Nat. Mater.*, 2004, **3**, 337.
17 Y. Y. Wu, G. S. Cheng, K. Katsov, S. W. Sides, J. F. Wang, J. Tang, G. H. Fredrickson, M. Moskovits and G. D. Stucky, *Nat. Mater.*, 2004, **3**, 816.
18 G. Kickelbick, *Small*, 2005, **1**, 168.
19 D. H. Wang, R. Kou, Z. L. Yang, J. B. He, Z. Z. Yang and Y. F. Lu, *Chem. Commun.*, 2005, 166.
20 B. Platschek, N. Petkov and T. Bein, *Angew. Chem., Int. Ed.*, 2006, **45**, 1134.
21 K. X. Wang, M. D. Wei, M. A. Morris, H. S. Zhou and J. D. Holmes, *Adv. Mater.*, 2007, **19**, 3016.
22 D. J. Cott, N. Petkov, M. A. Morris, B. Platschek, T. Bein and J. D. Holmes, *J. Am. Chem. Soc.*, 2006, **128**, 3920.
23 S. Tanaka, N. Nishiyama, Y. Egashira and K. Ueyama, *Chem. Commun.*, 2005, 2125.
24 C. D. Liang, K. L. Hong, G. A. Guiochon, J. W. Mays and S. Dai, *Angew. Chem., Int. Ed.*, 2004, **43**, 5785.
25 Y. Meng, D. Gu, F. Q. Zhang, Y. F. Shi, H. F. Yang, Z. Li, C. Z. Yu, B. Tu and D. Y. Zhao, *Angew. Chem., Int. Ed.*, 2005, **44**, 7053.
26 Y. Meng, D. Gu, F. Q. Zhang, Y. F. Shi, L. Cheng, D. Feng, Z. X. Wu, Z. X. Chen, Y. Wan, A. Stein and D. Y. Zhao, *Chem. Mater.*, 2006, **18**, 4447.
27 K. Wang, W. Zhang, R. Phelan, M. A. Morris and J. D. Holmes, *J. Am. Chem. Soc.*, 2007, **129**, 13388.
28 M. Steinhart, C. D. Liang, G. W. Lynn, U. Gösele and S. Dai, *Chem. Mater.*, 2007, **19**, 2383.
29 M. B. Zheng, J. M. Cao, X. F. Ke, G. B. Ji, Y. P. Chen, K. Shen and J. Tao, *Carbon*, 2007, **45**, 1111.
30 D. Y. Zhao, J. L. Feng, Q. S. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka and G. D. Stucky, *Science*, 1998, **279**, 548.

This journal is © The Royal Society of Chemistry 2009

J. Mater. Chem., 2009, **19**, 1331–1338 | 1337

31 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 1992, **359**, 710.

32 Q. S. Huo, D. I. Margolese, U. Ciesla, D. G. Demuth, P. Y. Feng, T. E. Gier, P. Sieger, A. Firouzi, B. F. Chmelka, F. Schuth and G. D. Stucky, *Chem. Mater.*, 1994, **6**, 1176.

33 D. Erts, B. Polyakov, B. Daly, M. A. Morris, S. Ellingboe, J. Boland and J. D. Holmes, *J. Phys. Chem. B*, 2006, **110**, 820.

34 B. Sundaray, V. Subramanian, T. S. Natarajan and K. Krishnamurthy, *Appl. Phys. Lett.*, 2006, **88**.