

Preparation of Oriented Mesoporous Carbon Nano-Filaments within the Pores of Anodic Alumina Membranes

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Ordered mesoporous materials (OMMs) of silicates and aluminosilicates were first prepared from liquid crystal templates by researchers at the Mobil Oil Corporation.¹ Since their discovery, considerable research effort has been devoted to controlling the mesostructure, composition, pore size, surface area, and morphology of these materials for use as catalyst supports, nanoreactors for chemical reactions, and hosts for nanostructured materials.² Recently, the compositional diversity of OMMs has been expanded with the synthesis of mesoporous carbons, which have been shown to be advantageous as materials for a variety of catalytic reactions, as electrodes, and as molds for the exo-templating of metal oxides.³ Further benefits of OMMs could be realized if the mesostructured domains within these materials could be preferentially aligned into ordered regions. Recently, a number of research groups^{4,5} have successfully demonstrated that arrays of OMMs with unique and tunable mesophase structures can be prepared within the confined channels of anodic alumina membranes (AAMs). A noticeable advantage of these composites over mesoporous powders and films is that they are assembled in the form of macroscopic membranes which can be easily handled and manipulated. Additionally, these materials are hierarchically ordered, first in the ordered arrangement of channels in the AAMs and second in the assembly of the mesophase counterparts within these channels. Until now, no carbon-based analogues of these mesophase structures have been reported, although the formation of carbon-based nanostructures within the pores of AAMs has been achieved.⁶ Being carbon based, such structures offer significant benefits ranging from electrical conductivity to enhanced chemical functionality and stability over their silica mesophase analogues.

In this communication, we report for the first time the synthesis of ordered mesoporous carbons with unique mesophase structures by replication of Fe-containing silica-based mesoporous nano-filaments prepared in the channels of AAMs. The preparation of these materials relies on the impregnation of channels within AAMs with solutions containing silica oligomers, originating from the hydrolysis and condensation of tetraethyl orthosilicate (TEOS), a triblock copolymer surfactant (Pluronic 123, BASF), and Fe(NO)₃·9H₂O. These solutions are similar to those recently used for the preparation of Fe-containing mesoporous thin films (MTFs) employed to grow carbon nanotubes (see Supporting Information).⁷ Upon evaporation of the solvent from the solution, silica/surfactant/Fe nanocomposites assemble within the channels of the AAMs, and after prolonged drying, extended mesophase structures are formed. Well shaped nanoscopic filaments with tubular morphologies are seen protruding from the channels of the AAMs (see Supporting Information). Energy-dispersive X-ray (EDX) analysis

taken along the length of the membrane thickness showed similar Si/Al and Fe/Al weight ratios, suggesting continuous embedment of the silica/surfactant/Fe nano-filaments inside the channels of the AAMs (see Supporting Information). After calcination of the silicate mixture in the channels of the AAM at 550 °C in flowing air, and subsequent hydrogen reduction at 750 °C, the Fe-containing mesoporous silica hosts were further used as templates for the incorporation of carbon using a supercritical fluid (SCF) deposition technique from a xylene/CO₂ mixture. The experimental setup for the SCF inclusion method is given elsewhere.⁸ Pure carbon replicas were obtained by dissolving the alumina/silica hosts in HF (see Supporting Information).

The mesophase structure of the composite membranes was investigated by grazing-incidence small-angle X-ray scattering (GI-SAXS) and transmission electron microscopy (TEM) as described in the Supporting Information. Four well-resolved diffraction spots were recorded in the GI-SAXS pattern of the as-deposited and calcined silica/template/Fe nitrate composite membranes (see Supporting Information). This diffraction pattern can be identified as coming from a local hexagonal arrangement of "circular" mesopores that are parallel to the membrane surface. A detailed discussion of the GI-SAXS patterns obtained from pure silica mesoporous filaments in AAMs is given in a separate report.⁵ The hexagonally ordered mesophase structure is directly observed in the TEM images, taken perpendicular to the long axis of the nano-filament after dissolution of the membrane (Figure 1a). At the same time, these filaments show circular, concentric mesophase channels when imaged perpendicular to the membrane surface (Figure 1c). Additionally, mesopores are also observed to be oriented parallel to the long axis of the channels in the AAMs, as shown in Figure 1b. The mesopores are also arranged in a hexagonal geometry (Figure 1d). The two distinct arrangements of mesopores can be seen in neighboring channels of the AAMs, although in some cases, twinned structures (the two mesophase orientations in the same channel of the AAMs) were also observed. The orientation of the mesopores with respect to the long axis of the AAM channels can be tuned by adjusting the silica/template ratio, relative humidity during the deposition, and the ionic strength (salt content) in the deposition mixtures. A detailed discussion of these effects is given in a separate report.⁵

The second step in our synthetic procedure is the inclusion of carbon inside the pores of the Fe-containing mesoporous silica filaments deposited in the channels of the AAMs. Our inclusion process is based on a modified SCF deposition technique⁸ utilizing xylene as the carbon-based precursor. We believe the carbon deposition results from the enhanced contact afforded through the increased diffusion of the xylene molecules in the SCF and the catalytically active Fe sites on the silica surface.

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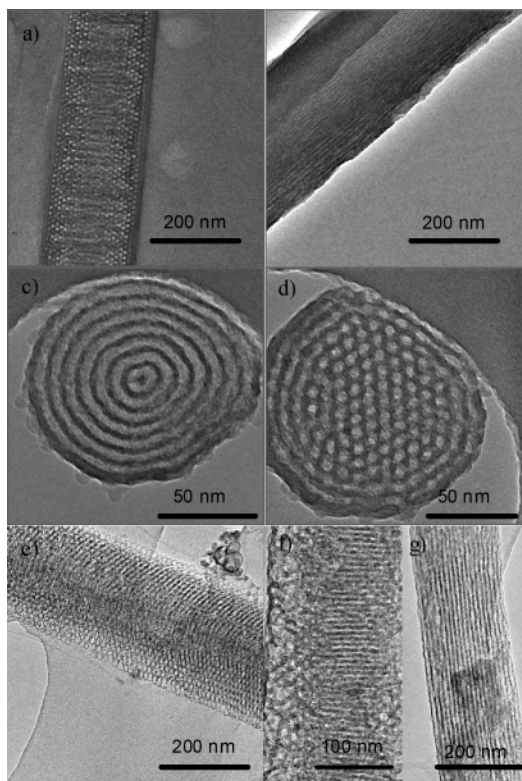


Figure 1. TEM images of the Fe-containing silica mesostructured nano-filaments with (a) circular and (b) columnar channels; (c) and (d) are the corresponding TEM images of the filaments inside the pores of an AAM, and TEM images of isolated carbon replicas with (e) and (f) circular, and (g) columnar mesopores.

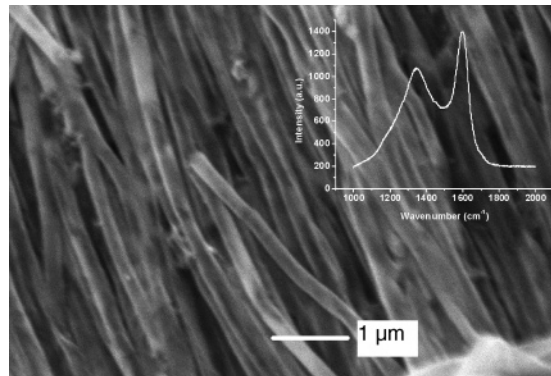


Figure 2. SEM image of the carbon nano-filaments after dissolving the alumina/silica template (inset: corresponding Raman spectrum).

After inclusion of carbon, the samples were treated in concentrated HF to remove the silica/alumina template. EDX analysis of the pure carbon material after HF treatment confirmed the absence of Si, Al, and Fe (see Supporting Information). Figure 2 shows the SEM image of the carbon filaments obtained after dissolving the silica and alumina hosts. Macroscopic pieces of the carbon structures can be extracted containing well aligned, carbon nano-filaments with diameters corresponding to the channel dimensions of the AAM hosts. The lengths of the carbon filaments typically exceeded tens of micrometers. At the same time, a full replication of the two orientations of the mesoporous silica host is obtained. For example, Figure 1e and f shows carbon replicas with a hexagonal arrangement of mesopores running in the direction perpendicular to the long axis of the nano-filament. These structures are replications of the circular mesophase channels shown in Figure 1a and c and are composed of carbon nanotubes that are following the curvature

of the host channel system. The second arrangement of mesopores gives rise to carbon replicas with channels running along the filament length (Figure 1g). Taking into account that the silica host is composed of tubular channels, the replicated carbon material also consists of “columnar” carbon nanotubes bundled in a filament. We suggest that the intact structure of the nano-filaments results from the presence of interconnecting microspores typically observed for Pluronic 123-templated mesoporous silicas.

The inset in Figure 2 shows a Raman spectrum from the carbon filaments prepared in this work. A Raman-active E_{2g} mode at 1596 cm^{-1} , characteristic of graphitic sheets, was recorded for our carbon filaments. This sharp well-defined G-band confirms the presence of sp^2 carbon-type structures present within the tube wall framework.⁹ The appearance of a further broad Raman signal at 1350 cm^{-1} indicates a certain degree of disorder in the carbon filaments.^{9a} There are multiple causes for this disorder which include deformation of the tube walls during HF treatment and replication of the silica structure, as well as the inability of the Fe catalyst to completely convert non-organized or glassy carbon to graphitic structures.

In summary, mesoporous carbon nano-filaments were prepared as replicas from Fe-containing silica mesostructures deposited inside the channels of AAM. Due to the confinement imposed by the channels of the AAMs, rather unusual mesophase structures showing circular and columnar mesoscopic channels were formed that were replicated, using SCF deposition technique, as pure carbon analogues after removal of the templating hosts. The carbon nano-filaments obtained were assembled in the form of macroscopic membranes and may find applications as innovative materials for high surface area carbon electrodes, catalyst supports, and further templates for more elaborate metallic nanostructures. Our results may offer some new insights into the structure control of carbon nanomaterials, which at present is proving to be an illusive endeavor, particularly in the case of carbon nanotubes.

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Supporting Information Available: The experimental procedures, GI-SAXS patterns, SEM and EDX results are available. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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