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## Direct Synthesis of Mesoporous Carbon Microwires and Nanowires

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Ordered mesoporous materials[1,2] combine a large specific surface area with well-defined pore geometry and have been used in energy storage, energy conversion, separation, and catalysis.[3] Their synthesis is based on the self-assembly of block copolymers and surfactants. Whereas the mesopore arrays thus formed may show a well-developed local order, the control over shape and arrangement of the mesoporous entities on a macroscopic scale remains a challenge. A strategy that addresses these problems involves the synthesis of mesoporous silica nanowires inside the pores of porous alumina,[4,5] thus adapting an established method for the preparation of one-dimensional nanostructures based on the use of porous templates.[6] It is highly desirable to apply this concept to amorphous mesoporous carbon,[3,7−9] which exhibits superior resistance to acids and bases, excellent heat resistance, and high intrinsic electrical conductivity compared to mesoporous silica. Potential applications for hybrid membranes consisting of mesoporous carbon within porous alumina include size-selective electrosorption, electrosynthesis of nanostructures, catalysis, separation, and storage. Moreover, released mesoporous carbon microwires and nanowires may be used as lightweight functional filler material that allows tuning of the mechanical and electrical properties of nanocomposites.

Rodriguez et al. prepared tubular mesoporous carbon structures by infiltration of block copolymer/carbohydrate solutions into porous alumina.[10] Disordered powders of amorphous mesoporous carbon nanorods were obtained as replicas of solution-grown mesoporous silica nanorods serv-

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ing as sacrificial templates.[11] Cott et al. obtained mesoporous carbon nanowires by a procedure involving the preparation of Fe-containing mesoporous silica inside porous alumina, subsequent reduction with hydrogen at 750 °C, incorporation of carbon using a supercritical fluid deposition technique from a xylene/$CO_2$ mixture, and removal of both the alumina template and the sacrificial silica template by etching with hydrofluoric acid.[12] Therefore, hybrid membranes containing mesoporous carbon inside a porous alumina matrix are not accessible by this approach. No simple, robust, and direct preparation procedure that circumvents the use of sacrificial scaffolds is available yet. Moreover, the preparation of hybrid membranes consisting of porous alumina containing mesoporous carbon must be performed at low temperatures for two reasons. First, self-ordered porous alumina[13] is commonly supported by an aluminum substrate (melting point of Al: 660 °C). It stabilizes the alumina membrane mechanically and facilitates infiltration as well as the cleaning of the membrane surface after carbonization before it is removed by a selective etching step. Second, the inset of crystallization in the initially amorphous alumina membranes at elevated temperatures causes mechanical stress and eventually the collapse of the pore structure.

We report the direct template-based synthesis of mesoporous carbon microwires and nanowires by solvent-free infiltration of a precursor mixture for mesoporous carbon into porous alumina and carbonization at a moderate temperature of 500 °C. The procedure described below yields alumina membranes with areas of several square centimeters containing mesoporous amorphous carbon that retain their mechanical stability. We adapted a procedure for the synthesis of mesoporous carbon previously reported by some of us[9] that involves the use of a precursor consisting of inexpensive, commercially available components: the triblock copolymer Pluronic F127 ($EO_{106}PO_{70}EO_{106}$; EO = ethylene oxide; PO = propylene oxide) as a structure-directing agent and phloroglucinol as a carbon source. A solution containing F127, phloroglucinol, formaldehyde, and traces of HCl in an ethanol/water mixture was stirred at room temperature until a separation into an upper water/ethanol phase and a lower polymer-rich phase occurred. We centrifuged the mixture and removed the supernatant solvents. The polymer-rich phase was further dried under ambient conditions for ∼30 min and then spread onto self-ordered porous alumina with pore diameters of 400 and 60 nm.[13] The liquid but viscous polymer-rich phase had a honeylike consistency and readily infiltrated the pores. The removal of the solvents prior to the infiltration step circumvents the occurrence of macroscopic phase separation and hydrodynamic instabilities occurring upon evaporation of the solvent from the pores. The phloroglucinol segregates to the poly(ethylene oxide) (PEO) microdomains because it forms hydrogen-bonding networks with the PEO blocks. To fixate the microphase structure, the phloroglucinol molecules were cross-linked with formaldehyde during curing steps at room temperature and at 80 °C. Carbonization at 500 °C converts the PEO microdomains into amorphous carbon. At this temperature, the alumina matrix remains intact. The mesoporous carbon microwires and nanowires thus obtained are largely free of defects and have high aspect ratios (length/diameter) corresponding to those of the template pores. The absence of solvents may result in the minimization of the inevitable shrinkage of the microwires and nanowires during the pyrolytic removal of the organic materials. In general, the

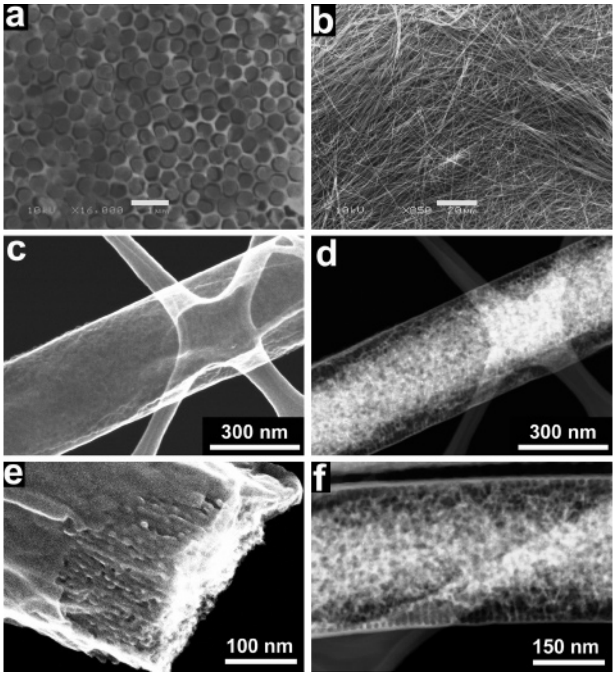

**Figure 1.** Mesoporous carbon microwires with a diameter of 400 nm. (a) SEM image of the surface of porous alumina containing microwires (scale bar 1 μm); (b) SEM image of released microwires at low magnification (scale bar 20 μm); (c) SE image showing a microwire segment; (d) DF-TEM image of the area shown in (c); (e) SE image of a fractured mesoporous carbon microwire; (f) DF-TEM image of a detail of a microwire segment at high magnification.

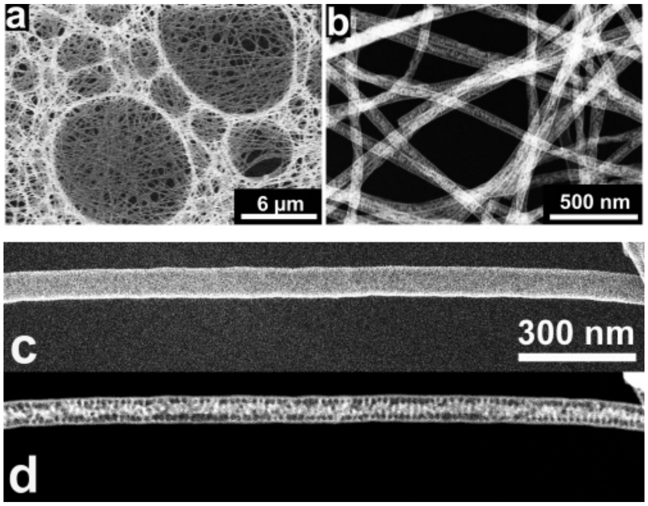

**Figure 2.** Mesoporous carbon nanowires with a diameter of 60 nm. (a) SE image of released nanowires deposited onto a copper grid coated with a holey carbon film (bright areas) at low magnification; (b) DF-TEM image of released nanowires; (c) SE image showing a nanowire segment at high magnification; (d) DF-TEM image of the area shown in (c).

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high surface energy[14] of interfaces consisting of oxides such as alumina or silica results in strong adhesion of the material inside the pores to the pore walls, resulting in shrinkage toward the pore walls. Consequently, mesoporous silica microrods inside macroporous silicon with pore walls consisting of silica prepared by conventional procedures, which involve the infiltration of a sol solution, had cylindrical hollow spaces in their centers.[4c] Mesoporous carbon wires prepared by solvent-free infiltration do not show such defects. This is a prerequisite for the functionality of porous alumina/mesoporous carbon hybrid membranes.

Figure 1a shows a scanning electron microscopy (SEM) image of the surface of a porous alumina template (pore diameter 400 nm) after the carbonization. Inside the pores, the carbon microwires can clearly be seen. Even though some damage occurred in the course of the mechanical cleaning of the template surface, it is obvious that the pores are evenly filled with mesoporous carbon. We could easily release the mesoporous carbon microwires by etching the template with aqueous KOH solution. Their length typically amounts to several tens of micrometers even though they were centrifuged and sonificated several times, indicating their high mechanical stability (Figure 1b). Their diameter of ~400 nm corresponds to that of the template pores.

We probed the morphology of the carbon microwires by secondary electron (SE) imaging and dark field transmission electron microscopy (DF-TEM). SE imaging revealed that the outer walls of the carbon microwires are smooth (Figure 1c). The DF-TEM image of the area seen in Figure 1c evidences the presence of an internal mesoporous fine structure (Figure 1d), which we could also detect in SE images (Figure 1e). The outermost carbon shell of the fractured carbon microwire shown in Figure 1e partially peeled off. In the areas thus uncovered, features with a characteristic size of ~10 nm, apparently formed by self-assembly of the precursor, are seen. The presence of an outermost, void-free carbon layer with a thickness of a few nanometers surrounding the mesoporous interior of the carbon microwires indicates that the PEO blocks preferentially segregate to the walls of the template pores. The diameter of the microwires is much larger than the period of ~10 nm in bulk mesoporous carbon prepared under similar conditions. Thus, no geometric confinement influences the structure formation in the template pores, and a bulklike morphology characterized by a bicontinuous network of mesoporous carbon and air channels[9] forms the core of the carbon microwires. This morphology type is of considerable practical use as it combines high specific surface area with good accessibility of the surface. However, in the proximity of the walls of the carbon microtubes, helical mesopores apparently occur whose arrangement is governed by the geometry of the interface (Figure 1f).

Self-assembly of block copolymers inside pores with diameters below ~100 nm leads to microphase structures different from those of the corresponding bulk systems.[5,15] Mesoporous carbon nanowires obtained from porous alumina with a pore diameter of ~60 nm have lengths of a few tens of micrometers after their release involving several centrifugation and sonification steps (Figure 2a). Their diameter corresponds to that of the template pores. DF-TEM investigations revealed that the 60 nm carbon nanowires contain helical mesopores (Figure 2b). Thus, their morphology corresponds to that previously reported for mesoporous silica nanowires with a similar diameter.[5] Images c and d of Figure 2 show SE and DF-TEM images of the same segment of a mesoporous carbon nanowire. Its outer surface consists of a smooth carbon layer (Figure 2c) that surrounds a helical hollow space with a pitch of ~15 nm (Figure 2d).

We have reported a direct and solvent-free approach to the synthesis of mesoporous carbon nanowires and microwires with high aspect ratios and low defect density. Porous alumina membranes containing mesoporous carbon as well as released mesoporous carbon nanowires and microwires are accessible. Such materials may be promising components for miniaturized devices or nanocomposites.

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**Supporting Information Available:** Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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