JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

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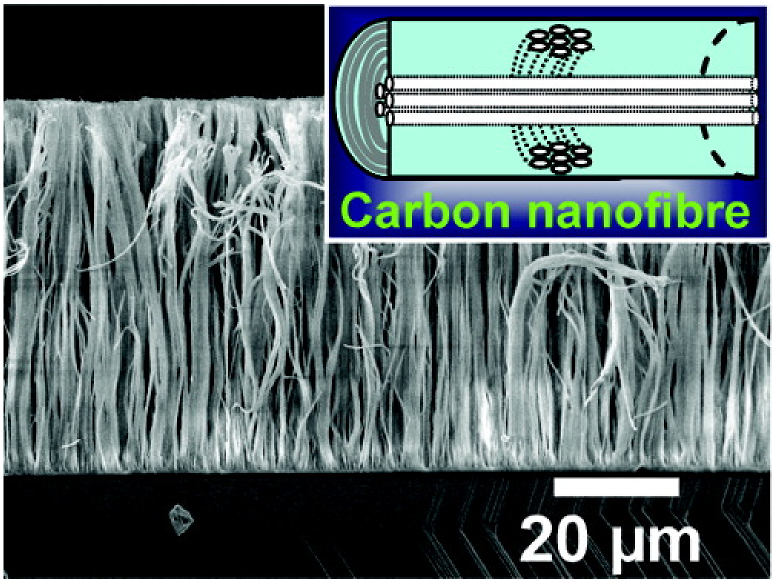
J. Am. Chem. Soc., **2007**, 129 (44), 13388-13389• DOI: 10.1021/ja0752843 • Publication Date (Web): 16 October 2007



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Direct Fabrication of Well-Aligned Free-Standing Mesoporous Carbon Nanofiber Arrays on Silicon Substrates

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Since the discovery of carbon nanotubes[1] and fullerenes,[2] nanostructured carbons have received much attention as potential materials for a range of applications, including nanoelectronics, hydrogen storage, and chemical sensors.[3] Recently, this diversity of applications has been expanded with the synthesis of mesoporous carbons which have been shown to be advantageous as materials for a variety of catalytic reactions,[3] as electrodes,[4] and as molds for the exotemplating of metal oxides.[5] Recently, one-dimensional (1D) mesoporous carbon materials have been prepared within the channels of anodic aluminum oxide (AAO) membranes by a sol−gel self-assembly method[6] and supercritical fluid deposition techniques.[7] However, a greater challenge is to find a facile method for fabricating well-aligned free-standing arrays of mesoporous nanowires or nanotubes on a substrate after the dissolution of the AAO membrane. Herein, we report for the first time the preparation of well-aligned free-standing mesoporous carbon nanofiber arrays on silicon wafers, prepared by a simple, confined, self-assembly process within the pores of AAO membranes.

The preparation of the precursor sol is similar to a previously published procedure.[8] A soluble, low molecular weight phenolic resin, synthesized from the reaction of phenol with formaldehyde, was used as the carbon source. The triblock copolymer, Pluronic F127 ($EO_{106}PO_{70}EO_{106}$, $M_{av} = 12600$), was used as the structural directing agent for generating the mesoporous phases. For the preparation of arrays of mesoporous carbon nanofibers on silicon wafers, a glass tube with a diameter of approximately 18 mm was first fixed onto the surface of the silicon wafer using mounting wax (Allied High Tech Products, Inc. 71−10040). A piece of an AAO membrane (Whatman, Anodisc 13, 200 nm) together with 0.3 mL of the above precursor sol was then put into the tube. The sol infiltrated the pores of the AAO membrane and was transformed into a gel during the aging process, at room temperature and at 60 °C. The AAO membrane which firmly adheres to the silicon wafer was subsequently calcined at 600 °C in a N_2 atmosphere for approximately 3 h to decompose the surfactant molecules and carbonize the mesoporous walls. The alumina membranes could be easily removed by treatment with a 6 M HCl solution.

Figure 1a and 1b show the scanning electron microscope (SEM) images of the resulting arrays of mesostructured carbon nanofibers embedded within the pores of AAO membranes. Usually, the release of 1D nanostructures by dissolving the AAO membranes leads to an entanglement of these nanostructures (see the Supporting Information), which would limit their applications in areas where controlled assembly is essential. Supercritical carbon dioxide (sc-CO_2), which has successfully been used to prepare free-standing CdS nanowires[9] and arrays of titania nanotubes[10] was utilized to prevent entanglement of the nanofibers, by reducing the liquid−gas interface during the drying process after dissolving the AAO membranes. A top-view SEM image of free-standing arrays of mesoporous carbon nanofibers on a silicon wafer clearly shows that the sc-CO_2 drying process minimizes entanglement of these 1D carbon structures (Figure 1c and the Supporting Information). The carbon nanofibers obtained had a diameter of approximately 200 nm, resembling the size of the pores in the alumina membranes. As shown in Figure 1d, the longitudinal dimension of these nanofibers was around 60 μm, comparable to the thickness of the templating membranes, indicating that the space within the pores was thoroughly filled by the nanofibers.

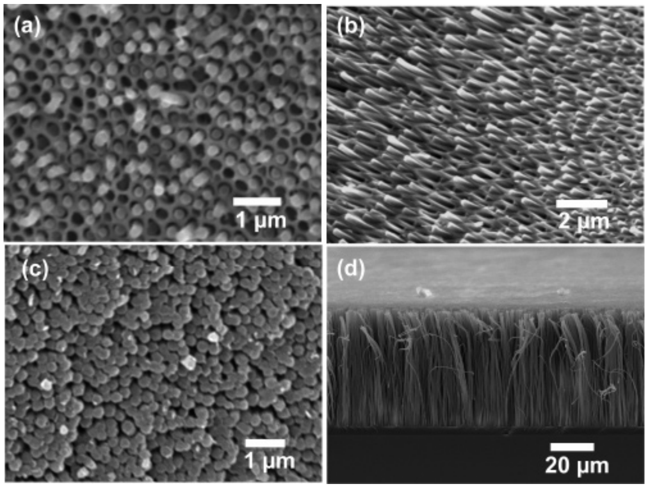

Figure 1. Scanning electron microscope images of arrays of mesoporous carbon nanofibers after being calcined at 600 °C for 3 h: (a) top and (b) side views of mesoporous carbon nanofiber arrays within the pores of AAO membranes; (c) top and (d) side views of nanofiber arrays prepared on a silicon wafer by a supercritical CO_2 drying process following the dissolving of AAO membrane.

The well-ordered mesoporous structure of the carbon nanofibers was confirmed by transmission electron microscopy (TEM) (Figure 2). Figure 2a and 2b present the typical side-view TEM images of the carbon nanofibers, released by dissolving the AAO membranes in a HCl solution, and clearly show the hexagonal arrangement of porous channels at the edges of the nanofibers. The mean diameter of the mesopores in the carbon nanofibers was approximately 5 nm. The pore-to-pore distance was around 12 nm, which is in good agreement with the value of FDU-15,[8] a mesoporous carbon material prepared by the same structural directing agent, F127. The diameters of these carbon nanofibers were in the range between 150 and 220 nm, which is consistent with the pore dimension of the commercial AAO membranes used. The saw-shaped edges of some of the nanofibers vividly reflect the inner surface morphology of the channels in the AAO membranes (see the Supporting Information). Figure 2c−e shows the plan-view TEM images of carbon nanofibers within the pores of AAO membranes observed in the direction perpendicular to the membrane surface. Circular

10.1021/ja0752843 CCC: $37.00

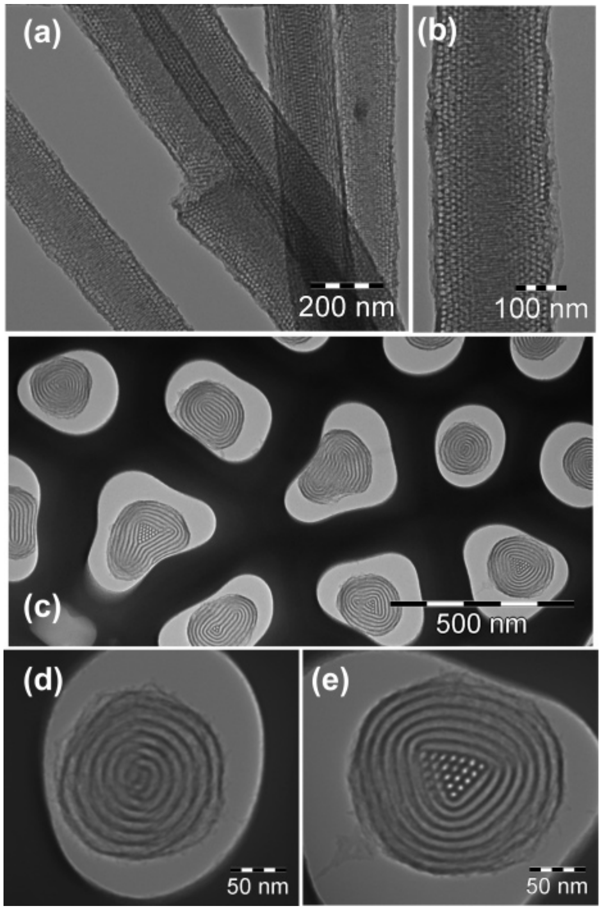

Figure 2. Transmission electron microscopy images of mesoporous carbon nanofibers after being calcined at 600 °C for 3 h (a) and (b) side views of the carbon nanofibers showing the circular hexagonal-ordered mesoporous structuresl; (c−e) plan views of the mesoporous carbon nanofibers which are confined within the pores of AAO membranes.

mesoporous channels were found concentrically coiled around the axis of the carbon fibers, which are similar to that reported for mesostructured titania[10] and silica nanorods and nanowires.[11−14]

From side-view TEM observations, all of the carbon nanofibers have the hexagonal-arranged mesochannels coiled perpendicularly to the longitudinal axis of the fibers. Top-view TEM images reveal that columnar oriented mesochannels actually exist at the center of some of the carbon nanofibers. These columnar mesochannels, wrapped by circular mesochannels, are aligned parallel to the longitudinal axis of the fibers. It should be noted that columnar oriented mesochannels are only formed in relatively big triangular-shaped AAO pores, while circular mesostructures are formed in smaller ones. The surface interaction of the alumina pore walls with the precursor sol is probably responsible for the formation of both circular and columnar oriented mesochannels. The channels of the AAO membranes have a relatively high surface energy. While as a low-melting organic substance, the precursor sol has low surface energy.[15] The precursor sol can therefore evenly wet or spread out over the inner-pore surface of the AAO membranes. The phenolic oligomers formed from the reactions of formaldehyde and phenol contain a large number of hydroxyl groups, which allow them to hydrogen bond with the hydrophilic blocks of the surfactant molecules and the terminal hydroxyl group, or bridged oxygen atoms, on the inner surface of the AAO channels. Thus, an initial meso-ring is formed. Driven by the reduction in surface energy, as proposed by Marlow et al.,[16] a confined self-assembly process occurs starting from the alumina pore wall to the pore center, and concentric rings with decreasing radii form during the aging periods. As a result, circular mesochannels are formed concentrically coiled around the axis of the carbon fiber. However, for the larger triangular-shaped AAO pores, the confining effect of the channel walls decreases dramatically toward the center of the pores and columnar oriented mesochannels form at the center of the carbon fibers after about seven meso-rings have formed.

In summary, using nonionic triblock copolymer F127 as a soft template and AAO membranes as hard templates, well-aligned free-standing arrays of mesoporous carbon nanofibers have been fabricated on silicon wafers for the first time. TEM observations showed that hexagonal-arranged circular mesochannels locate at the edge of the carbon nanofibers and columnar oriented meso-channels, wrapped by the circular mesochannels, form at the center of certain nanofibers. The surface interaction with the alumina pore walls is probably responsible for the formation of both circular and columnar oriented mesochannels. These ordered arrays of carbon nanofibers prepared on silicon substrates will possibly provide a wider range of nanoscale applications, such as interconnects, sensors, and electrodes. The measurement of their electrical properties is currently underway.

Acknowledgment. We gratefully acknowledge the financial support from Science Foundation Ireland (Grant No. 03/IN3/I375).

Supporting Information Available: Detailed preparation and supercritical CO_2 treatment, low magnification SEM images of carbon nanofiber arrays with and without supercritical CO_2 treatment, low magnification TEM image and nitrogen sorption of carbon nanofibers. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA0752843