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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 exo-templating of metal oxides[5]. Recently, one-dimensional (1 D) mesoporous carbon materials have been prepared within the channels of anodic aluminium 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 nanofibre 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 nanofibres 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 ºC. The AAO membrane which firmly adheres to the silicon wafer was subsequently calcined at 600 ºC in a N_2 atmosphere for approximately 3 hours 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.

Fig. 1a and 1b show the scanning electron microscope (SEM) images of the resulting arrays of mesostructured carbon nanofibres embedded within the pores of AAO membranes. Usually, the release of 1 D 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 nanofibres, 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 nanofibres on a silicon wafer clearly shows that the sc-CO_2 drying process minimizes entanglement of these 1D carbon structures (Fig. 1c and the supporting information). The carbon nanofibres obtained had a diameter of approximately 200 nm, resembling the size of the pores in the alumina membranes. As shown in Fig. 1d, the longitudinal dimension of these nanofibres was around 60 µm, comparable to the thickness of the templating membranes, indicating that the space within the pores was thoroughly filled by the nanofibres.

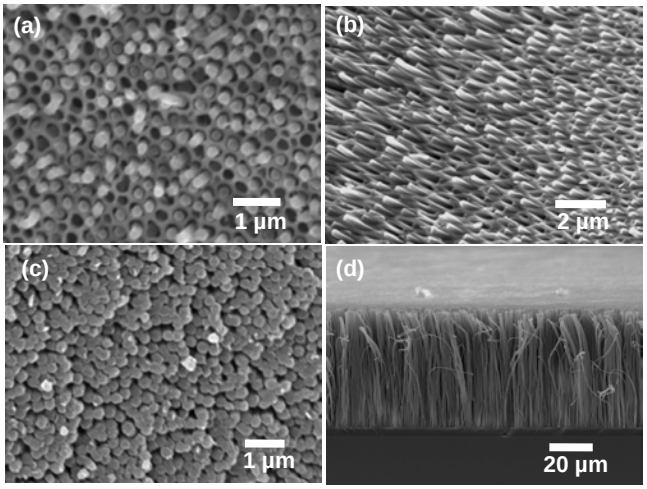


Figure 1 Scanning electron microscope images of arrays of mesoporous carbon nanofibres after being calcined at 600 ºC for 3 hours. (a) top and (b) side views of mesoporous carbon nanofibre arrays within the pores of AAO membranes, (c) Top and (d) side views of nanofibre arrays prepared on a silicon wafer by a supercritical CO_2 drying process following the dissolving of AAO membrane.

The well-ordered mesoporous structure of the carbon nanofibres were confirmed by transmission electron microscopy (TEM) (Fig. 2). Fig 2a and 2b present the typical side-view TEM images of the carbon nanofibres, released by dissolving the AAO membranes in a HCl solution, and clearly show the hexagonal arrangement of porous channels at the edges of the nanofibres. The mean diameter of the mesopores in the carbon nanofibres were 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 materials prepared by the same structural directing agent, F127. The diameters of these carbon nanofibres were in the range between 150-220 nm, which is

consistent with the pore dimension of the commercial AAO membranes used. The saw-shaped edges of some of the nanofibres vividly reflect the inner surface morphology of the channels in the AAO membranes (see the supporting information). Fig. 2c-e shows the plan-view TEM images of carbon nanofibres within the pores of AAO membranes observed in the direction perpendicular to the membrane surface. Circular mesoporous channels were found concentrically coiled around the axis of the carbon fibers, which is similar to that reported for mesostructured titania[10] and silica nanorods and nanowires.[11-14]

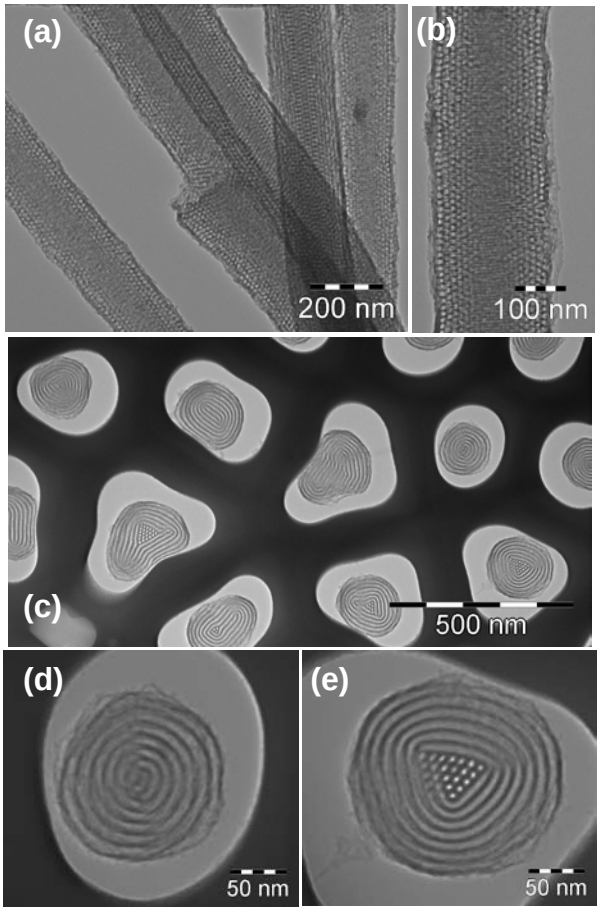


Figure 2 Transmission electron microscopy images of mesoporous carbon nanofibres after being calcined at 600 ºC for 3 hours (a) and (b) side views of the carbon nanofibres showing the circular hexagonal-ordered mesoporous structures. (c-e) plan views of the mesoporous carbon nanofibres which are confined within the pores of AAO membranes.

From side-view TEM observations, all of the carbon nanofibres have the hexagonal-arranged mesochannels coiled perpendicularly to the longitudinal axis of the fibres. Top-view TEM images reveal that columnar oriented mesochannels actually exist at the centre of some of the carbon nanofibres. These columnar mesochannels, wrapped by circular mesochannels, are aligned parallel to the longitudinal axis of the fibres. 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 centre 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 fibre. 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 at the centre of the carbon fibres after about seven meso-rings have formed.

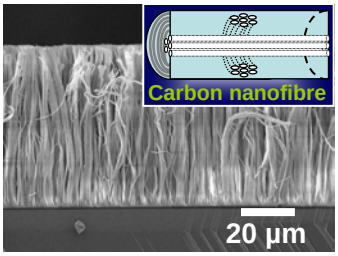
In summary, using non-ionic triblock copolymer F127 as a soft template and AAO membranes as hard templates, well-aligned free-standing arrays of mesoporous carbon nanofibres have been fabricated on silicon wafers for the first time. TEM observations showed that hexagonal-arranged circular mesochannels locate at the edge of the carbon nanofibres and columnar oriented mesochannels, wrapped by the circular mesochannels, form at the centre of certain nanofibres. 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 nanofibres 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.

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Supporting information available: Detailed preparation and supercritical CO_2 treatment, low magnification SEM images of carbon nanofibre arrays with and without supercritical CO_2 treatment, low magnification TEM image and nitrogen sorption of carbon nanofibres (PDF). These material is available free of charge via the Internet at http://pubs.acs.org.

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Using nonionic triblock copolymer F127 as a soft template and AAO membranes as hard templates, well-aligned free-standing mesoporous carbon nanofibre arrays have been fabricated on silicon wafer through a confined self-assembly process. Hexagonally arranged circular mesochannels locate at the edge of the carbon nanofibres and some well-ordered columnar oriented mesochannels are wrapped by circular mesochannels at the centre of the nanofibres. The surface interaction with the alumina pore walls is probably responsible for the formation of both circular and columnar oriented mesochannels.