STEM characterization on silica nanowires with new mesopore structures by space-confined self-assembly within nano-scale channels†

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Received (in Cambridge, UK) 12th November 2007, Accepted 17th December 2007
First published as an Advance Article on the web 23rd January 2008
DOI: 10.1039/b717461f

"Critical" channel diameters were found (below which space confinement takes effect, leading to more uniform and ordered mesopore structures) in the study of evaporation-induced co-assembly of triblock-copolymer (P123) and silica molecular precursors (TEOS, tetraethyl orthosilicate) by employing channels in anodized aluminum oxide (AAO, 13–200 nm channel diameter) and in track-etched polycarbonate (EPC, 10–80 nm channel diameter) and for the first time we have observed a new mesopore structure (*i.e.*, packed hollow spheres) in silica nanowires formed in AAO channels with diameters from 30 to 80 nm.

Ordered mesoporous silica nanomaterials are of particular interests for both fundamental study of nanostructures and a wide range of applications such as catalysis, adsorption, molecular separation, and as templates for producing other types of inorganic nanomaterials.[1,2] Since the discovery of Mobile Crystalline Materials 41 (MCM-41) in 1992,[3] extensive research has been focused on the synthesis of ordered and orientated mesoporous materials *via* organic–inorganic self-assembly.[4–12] The current studies on ordered mesoporous wires by organic–inorganic hybrid self-assembly were mainly targeted at inner channels of relatively large diameters of anodized aluminum oxide membrane (AAO) (120–200 nm)[5–8] and track-etched polycarbonate (EPC) (400 nm).[9] Two major intra-wire mesoporous structures by AAO channel confinement or no confinement were reported. These include: (1) the long axes of the cylindrical mesopores aligned with those of the AAO channels (columnar orientation), and (2) the cylindrical mesopores aligned in the axial direction to form a ring (circular orientation). Liang and Susha, by employing relatively large EPC channels of 400 nm, produced mesoporous wires of $(PEO)_{20}(PPO)_{70}(PEO)_{20}$ (P123)–silica hybrid.[9] However, there have not been any studies on self-assembled nanowires, space-confined within EPC channels in the range of 10–80 nm. Wu *et al.*[12] recently reported on P123-silica hybrid self-assembled nanowires, space-confined within the narrower AAO channels (10–80 nm). Their experiments and computer simulation on intra-wire mesoporous structures showed that the silica nanowires (above 30 nm) exhibited coiled cylindrical geometry, and transformed to a spherical cage-like geometry (silica nanowires with diameter below 30 nm).

In this communication, we report scanning transmission electron microscopy (STEM) characterization results on new intra-wire mesoporous structures in silica nanowires by space-confined evaporation-induced self-assembly of mixed block-copolymer (P123) and inorganic precursor (tetraethyl orthosilicate, TEOS) within AAO and EPC channels (with diameters between 10 and 200 nm). The space-confined, self-assembled nanowires within relatively smaller nano-scale channels (10–80 nm) of EPC are studied and reported for the first time. A new intra-wire structure (packed hollow spheres) exists in silica nanowires, formed in AAO channels with diameters from 30 to 80 nm. We show that space confinement at the nanoscale can result in more uniform and ordered nanostructures in the silica nanowires. A "critical size" of the channel diameter (30 nm for AAO and 50 nm for EPC) exists, below which uniform and ordered intra-wire mesopore structures can be formed. However, above the critical size, mixed mesophases occur in the wire.

The substrate disc consisted of parallel mesopore channels, Fig. 1. The diameter of these channels was varied in a quite wide range from 10 to 200 nm. The precursor solutions were prepared as follows: TEOS was pre-hydrolyzed in diluted hydrochloric acid (pH 2) and ethanol solution for 10 min. Tri-block copolymer, P123, which was initially dissolved in ethanol, was added to the acidic TEOS solution. The mixture was stirred for 3 h at room temperature ($\sim$22 °C). The mass ratio of the final precursor solution was kept at 2.6 TEOS : 0.6875 P123 : 1.35 HCl solution (pH 2) : 5 EtOH. The precursor solution was loaded into AAO or EPC channels by vacuum impregnation with substrate disc submerged in the solution for 1 h at room temperature, and the loaded AAO or EPC membrane was subsequently air-dried in ambient condition overnight. As a result, hybrid P123-silica wires formed inside the substrate channels. The loaded specimen was then calcined to remove the P123 template and EPC substrates. The

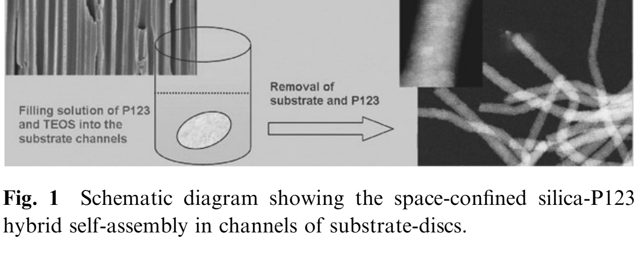

Fig. 1 Schematic diagram showing the space-confined silica-P123 hybrid self-assembly in channels of substrate-discs.

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† Electronic supplementary information (ESI) available: Experimental section. See DOI: 10.1039/b717461f

AAO substrate was completely dissolved in 5 M HCl at 60 °C for 1 h to obtain freely dispersed wires.

This paper reports our initial findings using EPC channels as a nanoscale confinement "tool". Mixed mesophases (2D hexagonal, lamellar, worm-like, and amorphous) could co-exist in silica nanowires in the 80 nm-EPC channels, however, more than half of the mesostructures assumed a "worm-like" structure, as shown in Fig. 2(a). A more uniform intra-wire mesoporous structure with pseudo-hexagonal pattern exists in the 50, 30 and 10 nm-EPC channels (Fig. 2(b), (c) and (d)), with pore diameters 5.8 ± 1 nm, determined from the STEM images by online software, ImageJ. In contrast to the wall features of nanowires obtained from AAO channels (see later), the outside walls of silica wires obtained from EPC substrate are not smooth and pits are observed. As shown in Fig. 2, the pore structure exhibits more uniform and ordered morphology as they preferentially form in the narrower EPC channels (50, 30 and 10 nm), indicating a pronounced EPC channel confinement on the mesophase formation in nanowires. Few mixed mesophases were observed in wires with diameter less than 50 nm.

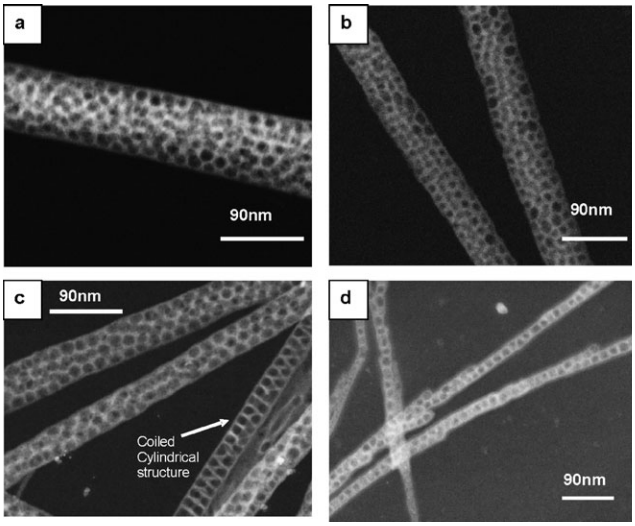

Fig. 3 Representative STEM images (*Z*-contrast mode) of side-views of mesoporous silica wires formed in AAO channels with labeled diameter (a) 73 nm; (b) 55 nm; (c) 35 nm; (d) 13 nm.

Fig. 3 shows STEM images of silica nanowires in the AAO substrate channels. In contrast to the case in EPC channels, the nanowires in the AAO channels exhibit a uniform "hollow spheres" structure. For channel diameters of 73 nm (Fig. 3(a)) and 55 nm (Fig. 3(b)), the pore structures tend to be less ordered. As the channel diameter is reduced to 35 nm, a so-called "coiled cylindrical" structure[12] is observed (see Fig. 3(c), for a single helix structure). Note that some of the nanowires in Fig. 3(c) have only three rows of pores along the wire direction. Further reduction of the channel diameter to 13 nm (Fig. 3(d)) resulted in a pore structure with only one row of "hollow spheres" in the silica nanowires. The average pore diameter in wires obtained from the AAO channels below the "critical size" is 10.7 nm, which is much larger than the pore diameter (5.8 nm) in the wires obtained from the EPC. Due to channel space confinement, only one row of mesopores (∼10.7 nm diameter) is allowed to organize in 13 nm AAO channels.

A "channel wall effect" on the mesophase ordering was experimentally observed in the wires obtained from 200 nm-AAO substrate. As can be seen in Fig. 4(a), the mesopore structure is preferentially more ordered in the vicinity of the channel wall and becomes slightly disordered in the interior of the nanowire. This might be due to the preferential concentration of block-copolymer P123 in the vicinity of the AAO wall surface, indicating the possible mechanism that mesophase ordering starts from the wall and grows further into the interior. This suggests a similar growth mechanism of the ordering as in the formation of mesostructured spherical nanoparticles from evaporation-induced self-assembly without nano-confinement.[13] Fig. 4(b) shows a STEM image of a

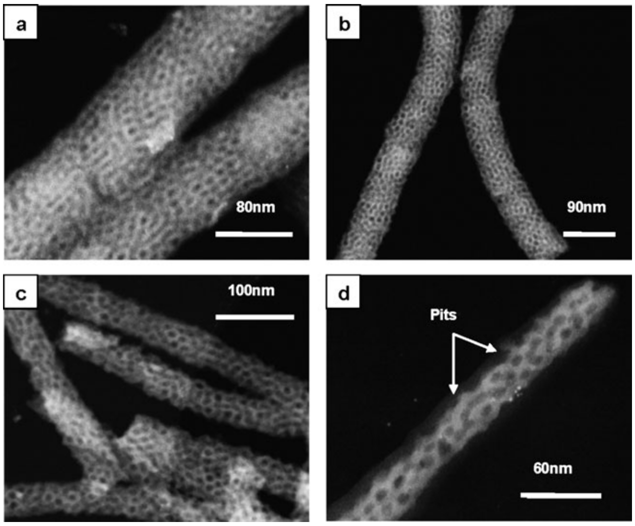

Fig. 2 Representative STEM images (*Z*-contrast mode) of side-views of mesoporous silica wires formed in EPC channels with labeled diameter (a) 80 nm; (b) 50 nm; (c) 30 nm; (d) 10 nm.

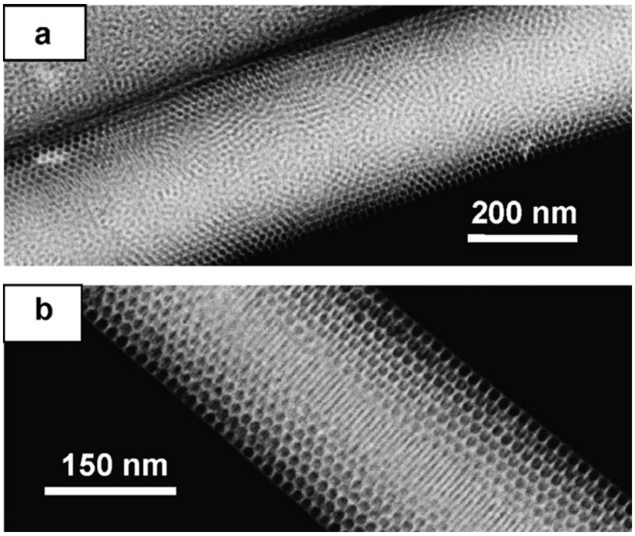

Fig. 4 The STEM image (*Z*-contrast mode) of silica wires formed in 200 nm AAO channels: (a) so-called edge-more-ordered intra-wire structure; (b) completely ordered mesostructure.

completely ordered 2D hexagonal mesostructure within a silica nanowire, which contains a circular channel structure (*i.e.*, concentric rings of cylinders with diameter of 10.6 nm).

In conclusion, new mesopore structures (*i.e.*, worm-like pseudo-hexagonal patterns and packed hollow spheres) within silica nanowires have been observed for the first time due to space-confined, self-assembly inside the channels of substrate AAO (with diameter from 30 to 80 nm) and EPC (with diameter from 10 to 80 nm). These structures exhibit distinctively different features from all previously reported STEM characterized experimental results in literature. In the P123-silica system, the final inorganic nanostructure is determined by the cooperative molecular self-assembly processes of the structure-directing agent (P123), the space confinement, and the type of substrate. For silica nanowires in both AAO and EPC channels, uniform and ordered structures are obtained only for channel sizes below a critical value. Above the critical channel size, more disordered and mixed mesophase structures co-exist.

This work is supported by the Division of Materials Science (KC 02 03 01 0), Office of Science, the US Department of Energy and also sponsored in part by the Assistant Secretary for energy Efficiency and Renewable Energy, Office of Transportation Technologies, as part of the High Temperature Materials Laboratory, managed by UT-Battelle, LLC, for the US Department of Energy under contract DE-AC05-00OR22725.

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