Hierachical mesoporous silica wires by confined assembly†

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The assembly of silicate and surfactant confined within cylindrical alumina pore channels results in circular hexagonal, concentric lamellar and other unique mesostructures.

Compared with the traditional top-down techniques, self-assembly, has been considered as one of the most promising approaches for novel material design and synthesis. Interfacial, geometric and other boundary conditions may alter such weak-interaction-driven assembly processes, providing an extra dimension to construct various nature-like hierarchical structures. For example, assembly of spheres, block copolymers, and silicate/surfactant mixtures within one-dimensional (1D) channels, respectively, creates hierarchical ordered lattice arrays,[1] aligned mesostructures compliant to the channel direction and geometry,[2] and hierarchical mesostructured silica.[3] This communication extends our recent work[4] on confined assembly of silicate and surfactant within cylindrical pore channels, demonstrating the formation of various hierarchical mesostructures through confinement-induced assembly.‡

As shown in the TEM image (Fig. 1a), a simple infiltration approach leads to the formation of uniformed mesostructured silica wires (see ESI† for procedural details). Fig. 1b shows a TEM image of the silica wires with a hexagonal mesostructure. Contrary to the reported result,[5] in which hexagonal pore channels were reportedly aligned themselves parallel along the alumina pore channels through a similar synthesis approach, the wires show ordered hexagonal pore channels without preferred orientations. Such unorientated hexagonal mesostructures are similar to the swirling hexagonal structure observed in thin films prepared using the same precursor condition that is due to low bending energy of the surfactant tubes and the inability of the liquid interface to impose long-range order during the tube assembly process.[6] Only a very small fraction of wires with parallell aligned hexagonal pore channels were observed; most of the wires contain pore channels that are curved along the alumina pore channels.
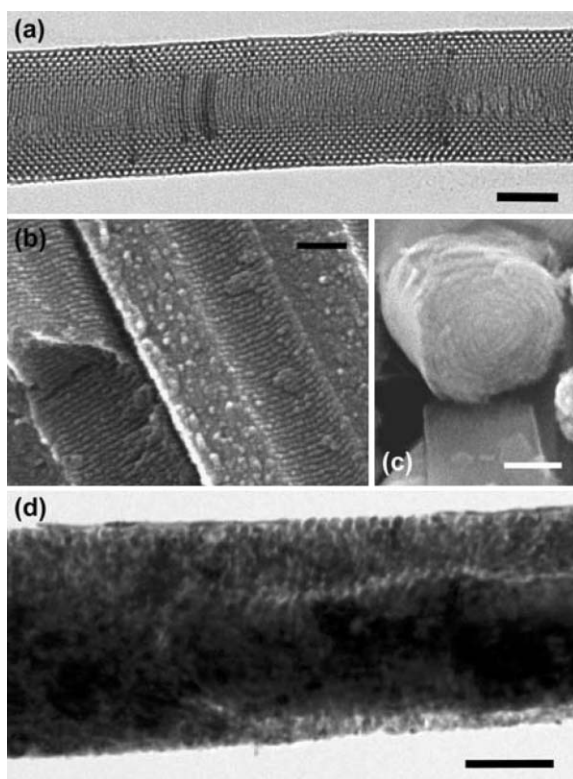
Mesostructure of the silica wires with curved hexagonal pore channels were further studied. A representative TEM image shown in Fig. 2a reveals the [001] oriented mesostructure symmetrically along the edges and a parallel tubular structure in the central region of the silica wire. This unique mesostructure is due to the confined growth of hexagonal tubes within the cylindrical pore channels and it is composed of hexagonal mesostructured pores circularly packed around the alumina pore channel. For comparison, hexagonal mesoporous silica films prepared under identical experimental conditions often contain pore channels oriented preferably along the substrates.[7] The pore-to-pore distance observed is around 8–9 nm, which is consistent with the XRD result (see ESI†, Fig. S1). Fig. 2b shows a SEM side-view image confirming the circularly curved hexagonal pore channels. Fig. 2c shows a cross-section SEM image of this structure, clearly displaying a circular structure. For further understanding, we replicated this mesostructure by electrochemically filling the pore
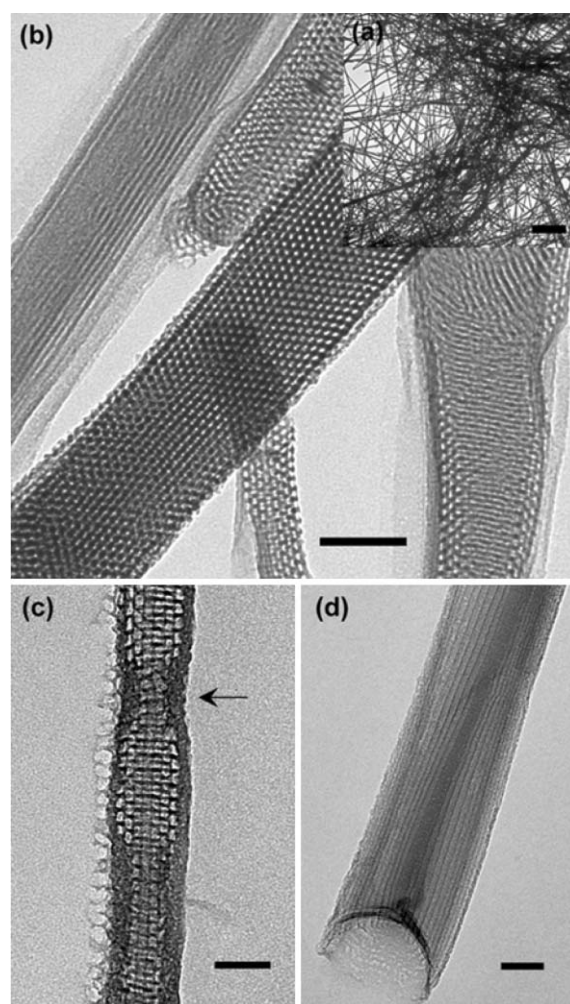
Fig. 1 TEM images of 1D mesostructured silica wires. (a) A low-magnification TEM image of the silica wires. (b) A representative TEM image showing silica wires with different oriented hexagonal structures. (c) A silica wire confined within a 70 nm alumina pore channel that may form a helical hexagonal mesostructure. (d) A silica wire with a concentric lamellar mesostructure. Scale bar is 10 μm, 100 nm, 50 nm, 100 nm, respectively.

Fig. 2 TEM and SEM images of 1D mesoporous silica wires with circular hexagonal mesostructure. (a) A TEM image of a silica wire showing the circular hexagonal mesostructure; (b) and (c), Side-view and cross-section SEM images of the silica wires; (d) A TEM image of a palladium nanowire architecture replicating the circular hexagonal mesostructure. Scale bars are 100 nm.

channels with palladium and removing the silica using HF.[7] A TEM image of the palladium replica (Fig. 2d) further proves the proposed circular hexagonal structure.

Similar confinement effects were also observed in smaller alumina pore channels. Fig. 1c shows a TEM image of hexagonal mesoporous silica confined in a 70-nm pore channel. We believe that the observed complicated mesostructure may be composed of pore channels that are helically extended along the long axis of the alumina pore channel. Note the pore channel alignment complies with shape or diameter variations of the alumina pore channels (see the arrow mark in Fig. 1c), further indicating the efficient confinement effect.

Confined assembly of silicate and a higher concentration surfactant results in the circular lamellar mesostructure shown in Fig. 1d. The mesoscale silica circular layers are coaxially oriented within the silica wire. Such a 2D concentric layered structure is similar to those of mesostructured silica particles with 3D concentric spherically layered structure.[8] The layer-to-layer distance measured from TEM is around 7–8 nm, which is also similar to those observed in the spherical layered particles. Differing from the lamellar thin films or bulks, the constraint from the cylindrical geometry prevents the constituent layered

structures from collapsing upon the surfactant removal. The mesoporous silica wires parallel aligned to the long axis of pores is of great interest for separation, hosts, and other applications.

In summary, the confined mesostructures prefer to curve themselves within the alumina pore channels in order to comply with the geometric constraint, which results in the formation of circular hexagonal, coaxial lamellar and other complicated mesostructures. The formation mechanism may involve nucleation of mesostructures on the hydroxylated alumina pore surface and their subsequent inward growth. Since the nucleation of hexagonal tubular structures often shows non-preferred orientation on amorphous oxide surface,[9] no preferred mesostructural orientation is observed in the hexagonal wires; however, the homogenous nucleation of a lamellar phase on the alumina pore surface results in the oriented concentric lamellar mesostructure. It is expected that an external field may provide the aligned nucleation that can subsequently lead to an oriented hexagonal structure. Nevertheless, this research provides insights into the nanoscale confinement effects on cooperative assembly between inorganic and organic components, which may provide new platforms for templated synthesis, separation and other applications.

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