Formation of Titania/Silica Hybrid Nanowires Containing Linear Mesocage Arrays by Evaporation-Induced Block-Copolymer Self-Assembly and Atomic Layer Deposition**

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Mesoporous materials are currently being investigated as versatile support and template structures for a broad range of applications in the fields of catalysis,^[1] electronics,^[2] storage, filtration,^[3] nanobiotechnology,^[4] and drug delivery.^[5] Their preparation by the self-assembly of structure-directing soft templates, such as surfactants^[6,7] and block copolymers, has been intensively investigated, and di- and triblock copolymers containing poly(ethylene oxide) blocks have been used to produce mesoporous structures with various morphologies and adjustable pore sizes ranging from a few nanometers to a few tens of nanometers.^[8-12]

Nanoporous hard templates, such as self-ordered porous alumina,^[13] contain arrays of aligned nanochannels with uniform diameters in the range from about 25 to 400 nm and lengths of up to several hundreds of micrometers. Such templates have been used to form nanowires and nanotubes from a variety of materials.^[14] The exploitation of templated self-assembly processes, such as mesophase formation,^[15] crystallization,^[16] liquid/liquid decomposition,^[17] and the microphase separation of block copolymers inside nanoporous hard templates, allows the rational generation of onedimensional nanostructures that exhibit specific mesoscopic fine structures, which, in turn, determine their properties. In the case of block copolymers, bulk-like morphologies form in pores with diameters larger than 100-200 nm.[18,19] Mesoporous silica nanowires are thus accessible by a hierarchical templating process involving the self-assembly of a blockcopolymer soft template inside a nanoporous hard tem-

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Only a few reports deal with approaches to the preparation of silica nanowires containing linear arrays of mesocages based on the use of Pluronic-type block-copolymer templates, even though such nanowires represent an interesting platform for various applications ranging from drug delivery to sensor technology to the still-challenging fabrication of linear arrays of functional nanoparticles.^[23] Herein we report the preparation of silica/titania hybrid nanowires that consist of a silica core containing linear arrays of mesocages and a titania shell by hierarchical self-assembly of block-copolymer soft templates inside nanoporous hard templates involving evaporation-induced self-assembly (EISA)^[7,10] and subsequent atomic layer deposition (ALD).^[24] The combination of EISA and ALD is a versatile modular assembly system that allows the internal mesoscopic fine structure and the properties of the outer nanowire surface to be tailored independently. The ALD step, for example, could improve the biocompatibility of mesoporous nanowires loaded with drugs.

The synthesis of the silica/titania hybrid nanowires is shown schematically in Figure 1. The mesoporous silica cores were obtained with polystyrene-block-poly(ethylene oxide) (PS-b-PEO) soft templates and tetraethyl orthosilicate (TEOS) as the silica source. Homogeneous precursor solutions containing TEOS, PS-b-PEO, 0.1M HCl, ethanol, and toluene (weight ratio 1:0.2-0.5:0.1-0.3:40-60:0-15) were prepared as described elsewhere^[10,12] and infiltrated into nanoporous alumina hard templates with pore diameters of 35 or 60 nm (Figure 1 a). Evaporation of the volatile solvents (ethanol and toluene) resulted in the onset of a microphase separation where the polar component PEO segregates to the oxidic pore walls and encases the hydrophobic phase containing the PS blocks. The silica source (TEOS) selectively segregates into the PEO-rich phase. The PS phase selfassembles into a regular array of domains having the form of slightly elongated spheres dispersed in a PEO/TEOS matrix (Figure 1b). After gelation at room temperature for 24 h and then at 110°C for 24 h, the PS-b-PEO soft template was removed by calcination at 550°C for 6 h (Figure 1 c). The silica nanowires thus obtained, which were released from the hard template by a wet-chemical etching step with aqueous



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Figure 1. Diagram showing the preparation of titania/silica hybrid nanowires containing linear mesocage arrays by hierarchical templating. a) A homogeneous precursor solution containing PS-b-PEO as a soft template is infiltrated into a self-ordered porous alumina hard template. b) Evaporation of ethanol induces the formation of spherical PS domains in a PEO/TEOS matrix by EISA. c) Gelation and calcination yield silica nanowires containing linear arrays of spherical mesocages. d) The silica nanowires are released by wet-chemical etching of the hard template and e) coated with titania by ALD.

phosphoric acid (Figure 1d), were found to contain linear arrays of elongated spherical mesocages.

Figure 2a shows a representative transmission electron microscopy (TEM) image of released silica nanowires (length: 9.5 μ m; diameter: 25–30 nm). These nanowires were prepared with symmetric PS(9500)-*b*-PEO(9500)^[25] as a soft template and a hard template with a pore diameter of 35 nm and a pore depth of 10 μ m. The diameters of these silica nanowires are slightly smaller than those of the nanopores in the hard template owing to shrinkage during the calcination step. The nanowires contain highly regular, linear arrays of mesocages with a period of about 25 nm. These mesocages are elongated, extending about 15 nm in the direction of the fiber axis and about 20 nm in the transversal direction (Figure 2b).

The morphology of the silica nanowires can be adjusted by varying the pore diameter of the hard template and the composition of the precursor solutions. Figure 3 a shows silica nanowires (diameter: 50 nm) containing two rows of spherical mesocages with a diameter of about 15 nm which were obtained with asymmetric PS(9500)-b-PEO(18000) as a soft template and a hard template having a pore diameter of 60 nm. The size of the hydrophobic domains in sols containing amphiphilic block copolymers, such as PS-b-PEO, can be tuned by the addition of organic co-solvents, such as toluene, to the precursor solution.^[9] This organic co-solvent enriches the nonpolar PS domains, which therefore swell. Consequently, the use of precursor solutions (weight ratio TEOS/ PS-b-PEO/0.1M HCl/ethanol = 1:0.5:0.25:40) containing 20 wt% toluene yielded silica nanowires with larger mesocages than those prepared under the same conditions but without addition of toluene. For example, the use of precursor solutions containing PS(9500)-b-PEO(18000) and toluene in



Figure 2. TEM images of released silica nanowires containing a single row of mesocages obtained with PS(9500)-*b*-PEO(9500) as the soft template and a porous alumina hard template (pore diameter: 35 nm; pore depth: 10 μ m): a) low magnification; b) high magnification.

a hard template with a pore diameter of 60 nm resulted in the formation of mesocages with a size of about 40 nm (Figure 3b) compared to about 15 nm without toluene (Figure 3a). The silica nanowires thus obtained with a diameter of about 50 nm contain only a single mesocage row because of the increased size of the mesocages. The arrangement of these mesocages is less regular and their size distribution is apparently broader than in the case of silica nanowires prepared from toluene-free precursor solutions. Possible reasons for this finding may be the occurrence of changes in the EISA process and a change in the volume ratio between the polar and nonpolar phases, which may lead to changes in the equilibrium microphase structure of the sol.

Released mesoporous silica nanowires were further functionalized in an ALD step to coat their outer surface with a thin titania layer (Figure 1e). ALD is a versatile approach for the fabrication of thin films on various substrates, it involves successive two-step deposition cycles



Figure 3. Morphology tuning with PS(9500)-*b*-PEO(18000) as the soft template and porous alumina hard templates with a pore diameter of 60 nm: a) TEM image of silica nanowires containing two rows of mesocages; b) silica nanowires containing a single row of mesocages with a size of about 40 nm obtained by adding 20 wt% toluene to the precursor solution. The inset in b) shows a high-magnification image of two adjacent nanowires.

with intermediate purging steps. In the first step the sample is exposed to the vapor of a first, reactive precursor so that a layer of the precursor molecules is bound to the substrate surface. Residual precursor molecules are then removed by purging. A second gaseous precursor converts the first one into the target compound in the second step. The overall thickness of the deposited layer can be adjusted by changing the number of successive deposition cycles and gives a precision on the subnanometer scale. Thin inorganic films have been deposited by ALD on a variety of organic, biological, and inorganic nanostructures, such as nanospheres,^[26] nanowires,^[27] and plant viruses.^[28]

Figure 4a shows a TEM image of mesoporous silica/ titania hybrid nanowires coated with an approximately 15nm-thick outer titania layer. The mesoporous silica cores were prepared with a precursor solution containing PS(9500)b-PEO(18000) as a soft template (weight ratio TEOS/PS-b-PEO/0.1M HCl/ethanol/toluene = 1:0.5:0.25:50:10) in a hard template with a pore diameter of 35 nm. The cores were subjected to 200 ALD cycles with tetraisopropyl titanate



Figure 4. Titania/silica hybrid nanowires: a) TEM image; b) EDX spectrum of a single nanowire.

 $Ti(OiPr)_4$ and water as precursors.^[28,29] The presence of titania was confirmed by analytical TEM investigations. As expected, the characteristic peaks for Ti, O, and Si appear in the energy-dispersive X-ray (EDX) spectrum recorded from a single hybrid nanowire (Figure 4b). The carbon and copper peaks are due to the TEM grid onto which the nanowires were deposited.

In summary, we have demonstrated that evaporationinduced self-assembly of a block-copolymer soft template inside a nanoporous hard template yields silica nanowires containing linear arrays of mesocages. Combining this hierarchical self-assembly process with atomic layer deposition allows the internal mesoscopic fine structure of the nanowires and the chemical properties of their outer surface to be tailored independently.

Experimental Section

The precursor solutions were prepared according to protocols similar to those reported elsewhere^[10,12] by mixing TEOS (Alfa Aesar), PS-*b*-PEO (Polymer Source Inc., Canada), 0.1M HCl, ethanol, and toluene (weight ratio TEOS/PS-*b*-PEO/0.1M HCl/ethanol/toluene = 1:0.2–0.5:0.1–0.3:40–60:0-15). To increase the size of the mesocages, symmetric PS(9500)-*b*-PEO(9500) was dissolved in an ethanol/toluene mixture (weight ratio 5:1), then 0.1M HCl and TEOS were added (weight ratio TEOS/PS-*b*-PEO/0.1M HCl/solvent mixture = 1:0.4:0.2:50). The porous alumina templates were immersed in the

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precursor solutions, and gelation was performed at room temperature and at 110 °C for 24 h each. The samples were heated to 550 °C at a rate of $1.0 \,\mathrm{K\,min^{-1}}$ and calcined at this temperature for 6 h. The silica nanowires thus obtained were released by a wet-chemical etching step with 10 wt % aqueous H₃PO₄ for 8 h. The resulting suspension was washed with deionized water in five subsequent centrifugation steps. For the ALD coating (Savannah 100 ALD reactor from Cambridge Nanotech Inc.), the silica nanowires were placed on TEM grids coated with holey carbon films and processed at 80 °C. The Ti(O*i*Pr)₄ was heated to 60 °C during the process. The purging time was set to 120 s to ensure complete removal of water adsorbed to the chamber walls. Transmission electron microscopy was performed with a TEM JEOL 1010 apparatus and EDX measurements with a TEM JEOL 2010.

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