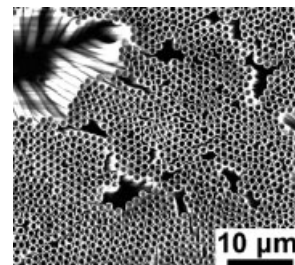


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Reactive Templates: Doing Chemistry with Pore Walls**

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The preparation of one-dimensional nanostructures and microstructures by means of inert, shape-defining molds, such as anodic aluminum oxide and macroporous silicon, is a well established and intensively investigated methodology. Up to now, however, little effort has been made to rationally explore the intrinsic reactivity of these commonly used template materials. This is astounding since reactive templates may pave the way for new synthetic routes to tubes and wires not accessible otherwise that consist of complex functional materials or exhibit core/shell morphology. Here we summarize recent advances regarding this emerging approach with special emphasis on self-ordered anodic aluminum oxide whose pore walls consists of an amorphous, highly reactive alumina scaffold.

1. Introduction

Solid nanowires and nanotubes combine the properties of the functional materials they consist of, such as metals, oxides, and semiconductors, with those imposed by the anisotropy of a one-dimensional (1D) geometry.^[1] A well-established and widely used approach to their synthesis is based on porous templates.^[2] Porous templates are laterally extended membranes or films, sometimes connected with an underlying substrate, which contain arrays of aligned nanopores with diameters tunable from a few tens of nm up to the micrometer range, and with aspect ratios (length divided by the diameter) up to several 1000.^[3] Nanowires or nanotubes are formed by deposition of a target material, or a precursor thereof, into the

nanopores, for example by electrodeposition^[4] or electroless deposition.^[5] Template systems such as nanoporous anodic aluminum oxide (AAO) produced by anodization of aluminum,^[6–9] and macroporous silicon^[10] are normally used as inert, shape-defining molds to fabricate assemblies of 1D nanostructures as replicas of their parent nanopore arrays.^[11] The pore walls of AAO, which is by far the most common template system, are amorphous and contain water, electrolyte anions and positively charged defects,^[7,12] whereas other templates, such as macroporous silicon, are prone to oxidation.

It is astounding that little effort has been made to exploit the potential associated with intrinsically *reactive* instead of inert templates beyond surface modifications, e.g., by reacting hydroxyl-terminated pore walls with silane coupling agents, or the selective wet-chemical etching of the templates to release the nanostructures prepared inside their pores.

2. Results and Discussion

To the best of our knowledge, only a few works deal with conversions involving the pore walls of porous templates as reactants.^[13–17] For example, Wang and Wu reported the formation of arrays of zinc aluminate (ZnAl_2O_4) nanotubes by reacting AAO and Zn formed by in-situ reduction of ZnO with H_2 .^[13] Thermal oxidation of macroporous silicon coupled with lithium-catalyzed crystallization of the amorphous silica

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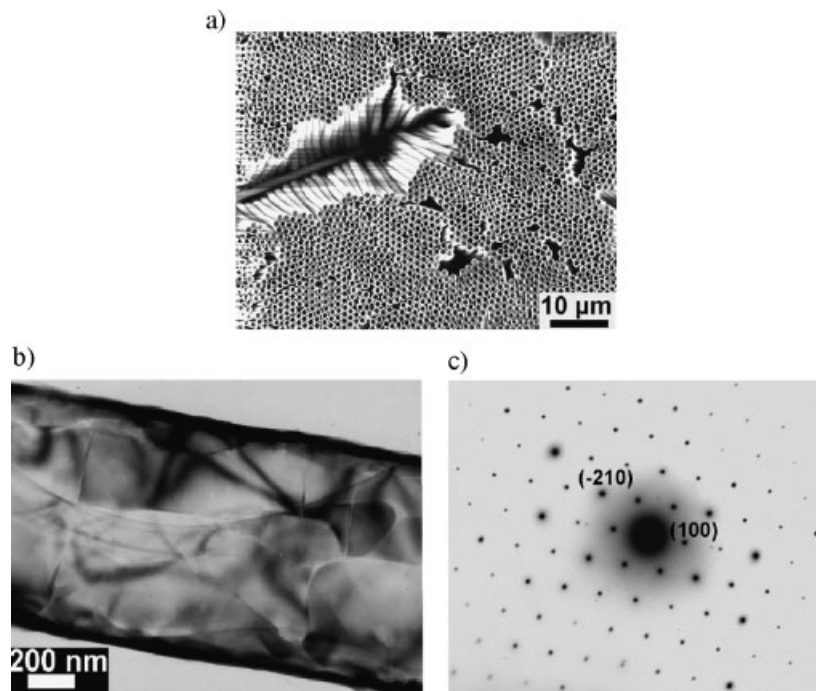


Figure 1. Quartz microtubes obtained by thermal oxidation and simultaneous lithium-catalyzed crystallization of macroporous silicon. a) Scanning electron microscopy image of aligned microtubes protruding from macroporous silicon partially removed by etching with aqueous KOH solution. b) Transmission electron microscopy (TEM) image of a single-crystalline segment of a quartz microtube and c) corresponding selected area electron diffraction (SAED) pattern.

thus formed yields crystalline silica tubes covering the pore walls of the macroporous silicon, which can be released by etching the silicon with aqueous KOH solutions (Fig. 1a). They consist of large single-crystalline segments.^[17] The formation of the different polymorphs can be controlled by the process temperature. In the range from 600 °C^[18] to 1050 °C predominantly quartz forms (Fig. 1b and c). Because of the pronounced piezoelectric properties of quartz,^[19] tubes consisting of this silica polymorph are potential building blocks for miniaturized sensors and actuators in micro-electromechanical systems.

We have attempted to put the concept of reactive templates in a more systematic context. The question arises whether it is possible to create a modular assembly system consisting of a limited number of easily accessible single-source precursors with similar, well-defined degradation properties and reactive templates. Such a modular system will enable access to a broad range of target materials by (i) reacting one and the same precursor with different template systems, or (ii) by reacting a given precursor/template system under systematically varied conditions (temperature profile, inert or oxidizing atmosphere). Thermolysis of aryl chalcogenolates, a versatile precursor platform, commonly yields the corresponding compound semiconductors. For example, SnSe is the primary thermolytic product of the precursor Sn(SePh)₄.^[20] However, inside reactive templates with corresponding redox properties, the intermediate oxidation state of Sn(II) allows further

reduction or oxidation to be carried out.^[15] In self-ordered AAO with a pore diameter of 25 nm (anodized in aqueous sulfuric acid), a complete oxidation of the SnSe is indeed observed, leading to the formation of single-crystalline SnO₂ nanowires (Fig. 2a and b). If, however, macroporous silicon with a pore diameter of 1 μm is used as a template, the SnSe can be reduced to elemental Sn, which is a liquid at the reaction temperature of 600 °C. Slow cooling therefore yields largely single-crystalline Sn microtubes (Fig. 2c and d).

It is also possible to obtain different target materials from one and the same precursor/template system by variation of the process conditions.^[16] For example, vacuum thermolysis of Zn(TePh)₂·TMEDA inside self-ordered AAO with a pore diameter of 25 nm (anodized in aqueous sulfuric acid) yields single-crystalline nanowires consisting of the primary thermolysis product ZnTe (Fig. 3a) under conditions where the template is inert. In air, single-crystalline tellurium nanowires with a diameter of 25 nm surrounded by a polycrystalline ZnAl₂O₄ shell with a thickness of 8 nm were obtained. Apparently, after thermolysis of Zn(TePh)₂·TMEDA, the initially formed ZnTe reacts with ambient oxygen, resulting in the formation of ZnO and elemental tellurium within the pores. Freshly formed active ZnO reacts with the AAO template, as reported by Wang and Wu,^[13] to form the polycrystalline ZnAl₂O₄ shell. By selective etching or vigorous sonification, respectively, ZnAl₂O₄ nanotubes (Fig. 3b and c) and Te nanowires (Fig. 3d) are obtained.

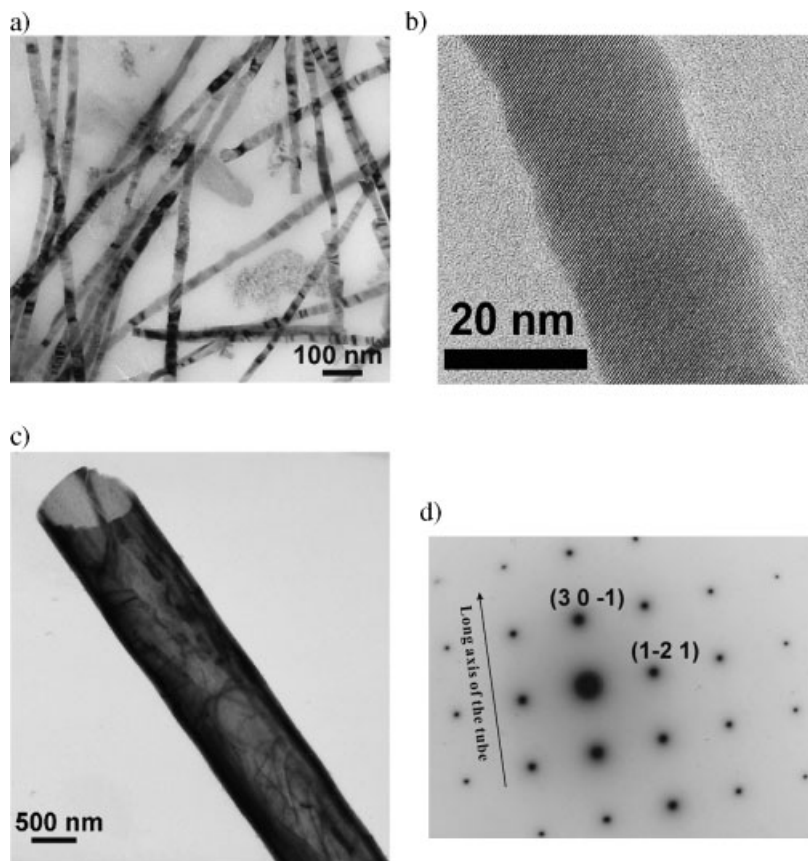


Figure 2. Different target materials by reacting Sn(SePh)₄ in templates with different redox properties. a) Large field view TEM image of SnO₂ nanowires and b) high-resolution TEM image of a single SnO₂ nanowire synthesized with AAO showing {110} lattice fringes of SnO₂. c) TEM image of a segment of a Sn microtube synthesized with macroporous Si and d) SAED pattern of a Sn microtube segment.

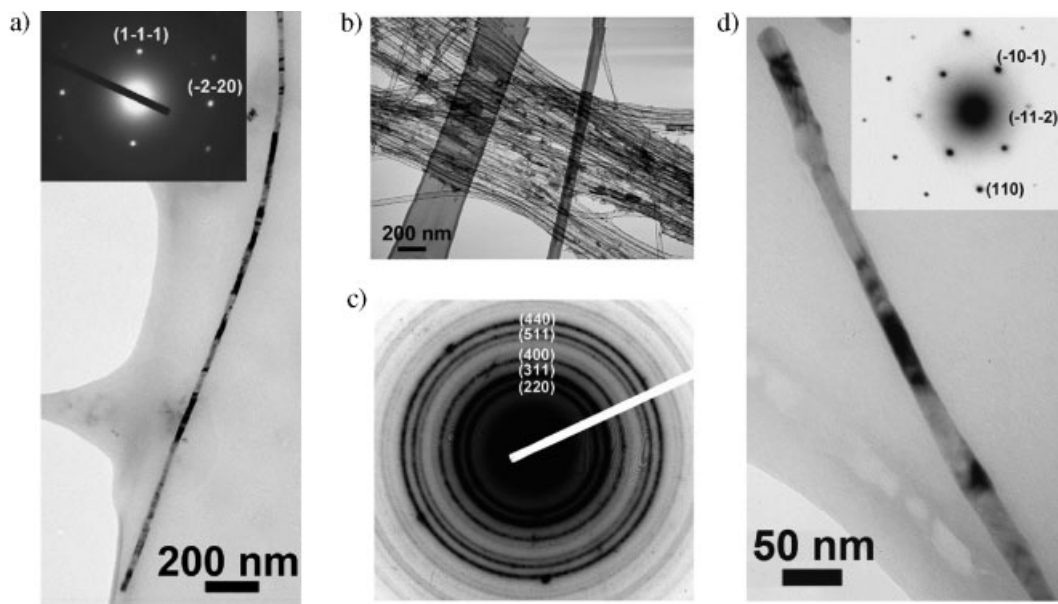


Figure 3. Different target materials by reacting the precursor/template system Zn(TePh)₂ · TMEDA/AAO under different conditions. a) Single-crystalline ZnTe nanowire (inset: corresponding SAED pattern); b) ZnAl₂O₄ nanotubes; c) SAED pattern of (c); d) single-crystalline Te nanowire (inset: corresponding SAED pattern).

3. Conclusion

Whereas the chemical properties of some template systems, such as macroporous silicon, are rather straightforward, other template families, first and foremost AAO, exhibit a complex reactivity that is not understood in detail and may involve redox processes as well as acid-base-chemistry. During anodization, electrolyte anions and positively charged defects are incorporated into the alumina scaffold. Moreover, the distributions of these contaminations across the pore walls are inhomogeneous.^[21] Therefore, isotropic etching steps performed to widen the pores of as-anodized, self-ordered AAO with an initial porosity of 10% or below will affect the reactivity of the pore walls. In turn, it is an intriguing perspective to tailor the chemical properties of AAO already during their fabrication by proper selection of the anodization conditions. The rational exploitation of the intrinsic reactivity of porous templates is still in its infancy. However, this emerging methodology may pave the way for new types of syntheses of both porous and one-dimensional nanostructures.

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