## Nanowires and Nanotubes

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## "Four Birds with One Stone": Synthesis of Nanostructures of ZnTe, Te, ZnAl<sub>2</sub>O<sub>4</sub>, and Te/ZnAl<sub>2</sub>O<sub>4</sub> from a Single-Source Precursor\*\*

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One-dimensional nanostructures have received much attention owing to their distinct properties and potential applications in nanoscale electronics and optoelectronics.<sup>[1]</sup> The use of porous templates containing aligned nanochannels<sup>[2,3]</sup> is a versatile method to fabricate arrays of aligned nanowires, predominantly by electrochemical<sup>[4]</sup> and chemical deposition.<sup>[5]</sup> However, it still remains a challenge to extend the range of functional target materials that can be formed as nanowires with low defect density and high aspect ratios. Recently, template-assisted thermolysis of single-source precursors inside nanopores and macropores has been exploited to form nanowires, nanotubes, and microtubes.<sup>[6,7]</sup> Regarding suitable types of single-source precursors, arylchalcogenolates of Group 12 and 14 metals were found to be a versatile class of compounds with similar molecular architecture and thermal properties, which have been employed to generate II/VI and IV/VI compound semiconductors.<sup>[7,8]</sup>

Herein, we show that arylchalcogenolates and selfordered porous alumina templates<sup>[9,10]</sup> represent a construction kit for the synthesis of single-crystalline nanowires of different types of target materials with varying morphology. Dependent on the conditions applied,  $[Zn(TePh)_2(tmeda)]^{[11]}$ (tmeda = N, N, N', N'-tetramethylethylenediamine) yields single-crystalline nanowires of zinc telluride (ZnTe), core/ shell structures composed of tellurium/zinc spinel (Te/ ZnAl<sub>2</sub>O<sub>4</sub>), pure tellurium nanowires, or nanotubes of zinc spinel (ZnAl<sub>2</sub>O<sub>4</sub>).

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ZnTe is one of the most important II/VI-type compound semiconductors, a class of materials that is of considerable interest for potential applications in the fields of sensor technology<sup>[12]</sup> and light-emitting diodes.<sup>[13]</sup> Trigonal elemental tellurium crystallizes in a noncentrosymmetric space group and shows several interesting properties, for instance, photoconductivity,<sup>[14a]</sup> thermoelectricity,<sup>[14b]</sup> and piezoelectricity.<sup>[14c]</sup> The zinc spinel ZnAl<sub>2</sub>O<sub>4</sub> is widely used as a catalyst for cracking, dehydration, hydrogenation, and dehydrogenation.<sup>[15]</sup> For core–shell nanostructures such as the tellurium wires with a zinc spinel shell described here, applications as photoconducting cables with a transparent, insulating, and chemically robust shell can well be imagined.

In a general synthetic procedure for the preparation of the nanostructures, a solution of  $[Zn(TePh)_2(tmeda)]^{[11]}$  (5 wt% in chloroform) was added dropwise onto ordered porous alumina with a pore diameter of 25 nm under ambient conditions. After the solvent had evaporated, the templates with the precursor inside the pores were heated to 280 °C and kept at this temperature for two hours. Then, the samples were heated to 500 °C, annealed at this temperature for 24 or 48 hours, and slowly cooled to room temperature.

When samples wetted in this manner were annealed in vacuum for 48 hours at 500 °C, ZnTe nanowires were obtained, which could be released by etching the templates with aqueous KOH. Figure 1 a shows a representative trans-



**Figure 1.** a) TEM image and SAED pattern (inset, zone axis  $[1\bar{1}2]$ ) of a single-crystalline ZnTe nanowire. b) Bottom part of the wire at higher magnification. c) HRTEM image of a ZnTe nanowire showing (111) lattice planes (d=3.48 Å).

mission electron microscopy (TEM) image of a ZnTe nanowire with a diameter, *D*, of 25 nm corresponding to the diameter of the template pores and an aspect ratio (length/ diameter) of about 120. Figure 1b shows a detail at higher magnification. The selected area electron diffraction (SAED) pattern (Figure 1 a, inset) of a segment of the ZnTe nanowire evidences the single-crystalline nature as it contains only indexed Bragg reflections. The high-resolution (HR) TEM image of a ZnTe nanowire (Figure 1 c) shows the (111) lattice planes (d = 3.48 Å) of cubic ZnTe (space group  $F\bar{4}3m$ ).<sup>[16]</sup> We assume that the formation of the ZnTe nanowires occurs according to the well-known degradation mechanism of [Zn(TePh)<sub>2</sub>(tmeda)].<sup>[11a]</sup>

When the wetted samples were not annealed in vacuum, but in air for 24 hours at 500 °C, single-crystalline tellurium nanowires (D=25 nm) surrounded by a polycrystalline



**Figure 2.** HRTEM image of a Te/ZnAl<sub>2</sub>O<sub>4</sub> core/shell structure. The lattice fringes of the tellurium core correspond to the (101) planes (d = 3.1 Å).

40 nm, which is larger than that of the template pores. This larger diameter indicates that the pore walls act as chemical reactants in the formation of the core/shell wires. The single-crystalline tellurium core can be seen in the HRTEM image (Figure 2). The distance between the lattice planes of the tellurium core was found to be 3.1 Å, which corresponds to the *d* value of the (101) lattice planes.

The chemical composition of released core/shell nanowires was analyzed by energy-dispersive X-ray spectroscopy (EDX; Figure 3). Exclusively strong tellurium peaks and a weak oxygen peak are found in the spectrum measured on a wire segment where the  $ZnAl_2O_4$  shell had peeled off (the copper peak originates from the TEM grid onto which the wires had been deposited; Figure 3a). This observation indicates that the core consists of pure tellurium, possibly covered by a thin oxide layer. A segment consisting only of the ZnAl<sub>2</sub>O<sub>4</sub> shell was selected for a second EDX scan (Figure 3b). The signals of aluminum, zinc, and oxygen can be seen in the spectrum, whereas no tellurium could be detected. The Zn/Al/O ratio of 1:1.9:3.7 deduced from the EDX spectrum is in accordance with the composition of ZnAl<sub>2</sub>O<sub>4</sub>. A third EDX spectrum was measured on an intact core/shell segment (Figure 3c). Here, the peaks of zinc, aluminum, oxygen, and tellurium can be seen. All EDX spectra indicate that the nanowires consist of a  $ZnAl_2O_4$  shell with a tellurium core

We suggest the following mechanism for the formation of the Te/ZnAl<sub>2</sub>O<sub>4</sub> core/shell nanowires. After thermolysis of [Zn(TePh)<sub>2</sub>(tmeda)], the telluride in the initially formed ZnTe is oxidized, thereby resulting in the formation of ZnO and elemental tellurium within the pores. Freshly formed, active ZnO reacts with the alumina template, as previously

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**Figure 3.** Chemical composition analysis of Te/ZnAl<sub>2</sub>O<sub>4</sub> nanowires by EDX spectroscopy. a) EDX point spectrum of a pure tellurium nanowire measured at the location indicated in (d). b) EDX point spectrum of a pure ZnAl<sub>2</sub>O<sub>4</sub> shell measured at the location indicated in (d). c) EDX point spectrum of a Te/ZnAl<sub>2</sub>O<sub>4</sub> core/shell structure measured at the location indicated in (d). d) TEM image of the investigated nanowire segments.

reported by Wang and Wu,<sup>[17]</sup> to form the polycrystalline ZnAl<sub>2</sub>O<sub>4</sub> shell. The formation of the compact and singlecrystalline tellurium core is greatly facilitated by the fact that elemental tellurium, with a melting point of 452 °C,<sup>[18]</sup> is formed in its liquid state at the annealing temperature of 500 °C. A slow cooling process following the annealing step leads to the formation of single-crystalline tellurium structures inside the spinel shell.

Sonification of the core/shell structures resulted in the removal of the  $ZnAl_2O_4$  crystallites, and the liberated single-crystalline tellurium nanowires can be obtained (Figure 4). The SAED patterns of these samples (Figure 4, inset) show only Bragg reflections that can be assigned to trigonal tellurium (space group  $P3_121$ ).<sup>[19]</sup> This finding gives evidence for the single-crystalline nature of the tellurium wires and the lack of relevant structural disorder in these products.

Not only could the core without the shell be obtained, but also the shell without the core could be isolated by etching of the tellurium core with aqueous KOH at 90 °C for four hours. A TEM image of the isolated shells is seen in Figure 5 a. The corresponding SAED pattern (Figure 5b) contains ring patterns corresponding to the (220), (311), (400), (511), and (440) reflections of ZnAl<sub>2</sub>O<sub>4</sub> (spinel, space group Fd3m),<sup>[20]</sup> thus indicating that the shell consists of polycrystalline ZnAl<sub>2</sub>O<sub>4</sub>.



*Figure 4.* Released single-crystalline tellurium nanowire (D=25 nm) and its indexed SAED pattern (inset, zone axis [ $\overline{1}13$ ]).



Figure 5. a) TEM image of  $ZnAl_2O_4$  nanotubes and b) SAED pattern showing their polycrystallinity.

To investigate whether or not  $ZnAl_2O_4$  nanotubes also form in the absence of tellurium, we infiltrated alumina templates with a dilute solution of  $ZnCl_2$  (5 wt %) in THF and applied the same protocol as in case of the thermolysis of  $[Zn(TePh)_2(tmeda)]$ . However, no  $ZnAl_2O_4$  nanotubes were obtained, thus indicating that the slower formation of ZnO from the tellurolate precursor and the ZnTe intermediate is crucial.

In conclusion, we have shown that proper variation of the conditions under which the template-assisted thermolysis of  $[Zn(TePh)_2(tmeda)]$  is performed yields single-crystalline nanowires of ZnTe or of a tellurium core in a ZnAl<sub>2</sub>O<sub>4</sub> shell. Interestingly, nanotubes of ZnAl<sub>2</sub>O<sub>4</sub> and isolated nano-

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wires of tellurium can be prepared after selective removal of either the core or the shell.

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