The discovery that layered transition metal dichalcogenide (TMD) materials such as WS$_2$[1] and MoS$_2$[2] can form nanotubes and other inorganic fullerene-type structures has generated considerable interest in the study and synthesis of nanomaterials consisting of two-dimensional (2D), layered structures.[3–5] One unique property of TMD nanomaterials includes superior tribological behavior,[6] other applications include use as solid lubricants,[7] catalysts for hydrosulfurization,[8] and hydrogen-storage devices.[9] Control over the nanoscale architecture could also greatly accelerate investigations of finite size effects on complex electronic properties such as superconductivity and charge-density wave (CDW) behavior. For example, tantalum disulfide (TaS$_2$) displays three polytypes where Ta atoms are covalently bonded between two layers of S atoms in trigonal prismatic (2H), octahedral (1T), or mixed (6R) coordinations.[10] Investigations of structure–property relationships of TaS$_2$ nanomaterials have been limited, however, because they can neither be produced in high yield nor with control over the crystalline structure.

Tubular TaS$_2$ nanomaterials have been synthesized by the hydrogen reduction of TaS$_3$ precursors[11] but the crystal structure could not be determined because of sample degradation under the electron beam. Other nanostructures of TaS$_2$ include fullerene-like TaS$_2$ nanoparticles produced by a gas-phase reaction[12] and TaS$_2$ nanoplates formed by laser ablation[13] or from molecular precursors.[14] 2H-TaS$_2$ nanowires synthesized from elemental Ta and S by chemical vapor transport exhibited a superconductivity transition temperature ($T_c = 3.4$ K) higher than that of bulk 2H-TaS$_2$ (0.8 K).[15] Recently, we demonstrated synthetic control over the size, shape, and polytype of surface-patterned TaS$_2$ nanostructures by converting nanopatterned tantalum oxide (Ta$_2$O$_5$) to TaS$_2$ using a gas-phase reaction.[14]

Here we report how large quantities of crystalline TaS$_2$ multi-walled nanotubes can be synthesized starting from Ta$_2$O$_5$ nanotube templates. We achieved control over the length, diameter, and the number of TaS$_2$ layers within the nanotube. Our template-based approach produced a high yield of structurally uniform nanotubes, which opens up possibilities for potential scalable applications. Also, we observed that the electronic properties were different from the bulk, where the $T_c$ of the TaS$_2$ nanotubes was elevated, and the CDW transition temperature ($T_{CDW}$) was suppressed.

Figure 1a depicts the scheme for converting Ta$_2$O$_5$ nanotubes to multi-walled TaS$_2$ nanotubes. First, large-area arrays ($\approx 3.5 \times 10^{10}$ tubes cm$^{-2}$) of amorphous Ta$_2$O$_5$...
nanotubes (Figure 1b) were grown by the electrochemical anodization of a 300-μm-thick Ta film (Aldrich, 99.9%) in a room-temperature solution of HF:H₂SO₄ (2 mL 48% HF, 50 mL 85% H₂SO₄) at 30 V for 10 min. Ta₂O₅ nanotubes were washed repeatedly with deionized water to remove all traces of H₂SO₄ and then vacuum filtered. Transmission electron microscopy (TEM, JEOL JEM-2100F, 200 kV) revealed that Ta₂O₅ nanotubes synthesized under these conditions were 10–13 μm long, 60–70 nm in diameter, and 15–20 nm in wall thickness (Figure 1c). The dried samples were placed in a 13° quartz tube furnace for sulfidization and heated at a rate of 2 °C min⁻¹ to 625 °C under 16 sccm of 99.5% H₂S(g). The reaction time controls the number of TaS₂ layers formed within the nanotube. A 24 h reaction time was enough to convert the Ta₂O₅ nanotubes completely into multi-walled TaS₂ nanotubes. The furnace was then cooled to ambient temperature, and a black powder was obtained (Figure 1d).

Glancing-angle X-ray diffraction (GA-XRD) patterns (Rigaku ATX-G, 18 kW Cu source) of the sample were consistent with 2H-TaS₂ (PDF 01-080-0685), with lattice parameters a = 3.314 Å, b = 3.314 Å, c = 12.097 Å (Figure 2a). TEM images show that fully converted tubes had approximately 25 layers of TaS₂ stacked along the c-axis (Figure 2b). The electron-diffraction patterns show prominent rings that correspond to randomly oriented (101) and (106) planes of TaS₂ along the length of the nanotube (Figure 2c). The intense (002) spots aligned perpendicular to the nanotube axis corresponded to the c-axis spacing between the layers, which was calculated to be 6.07 ± 0.03 Å. This result is in good agreement with the interlayer spacing of 2H-TaS₂ (6.05 Å) and further supports that the TaS₂ nanotube polytype was 2H.

Unlike other synthetic approaches, our method allows nanotubes to be formed with varying numbers of TaS₂ layers depending simply on the reaction time. We synthesized TaS₂ nanotubes at three different conversion times (1 h, 4 h, and 12 h) to gain insight into the reaction mechanism. GA-XRD patterns of the intermediate times showed that as the conversion time increased from 1 h to 12 h, the initially amorphous Ta₂O₅ nanotube template exhibited highly crystalline Ta₂O₅ peaks at 4 h, which were then gradually replaced by the characteristic (002), (100), and (106) TaS₂ peaks at 12 h and 24 h as the sulfidization reaction progressed (Figure 3). This increase in peak intensity corresponds to the growing number of TaS₂ layers along the c-axis as the conversion time increased.

Figure 2. Structural characterization of TaS₂ nanotubes after 24 h reaction. a) GA-XRD spectra. b) TEM image of a single nanotube. c) Electron diffraction pattern of a single nanotube using a 1.4-μm-radius illumination disc.

Figure 3. GA-XRD spectra of TaS₂ nanotubes at different conversion times in H₂S(g). After 12 h, there is still some residual yet crystalline Ta₂O₅, which is most likely in the center of the nanotube.
TEM images confirmed that the average number of metal disulfide layers depended on the reaction time. After 1 h, <5 TaS$_2$ layers formed on the interior and exterior surfaces of the amorphous Ta$_2$O$_5$ nanotube. The layers were discontinuous and did not connect along the entire length of the nanotube (Figure 4a). After 4 h of conversion, more TaS$_2$ layers were formed (10–15) and started to connect along the length of the nanotube (Figure 4b). Electron diffraction patterns were indexed to (002), (101), and (106) TaS$_2$, as well as (002) Ta$_2$O$_5$, which indicated the presence of unreacted oxide. At 12 h of conversion, TaS$_2$ layers continued to form along the c-axis (Figure 4c). The relative intensity of the (002) Ta$_2$O$_5$ feature in the 12 h electron diffraction pattern decreased because of the conversion of Ta$_2$O$_5$ to TaS$_2$. After 24 h, the entire Ta$_2$O$_5$ wall was converted to layers of TaS$_2$ (25±5), resulting in the multilayered structure of the nanotubes (Figure 2b). The (002) Ta$_2$O$_5$ ring was undetectable in the 24 h electron diffraction pattern. The reaction time-dependent TEM images suggest a diffusion-controlled process that progresses from both the interior and exterior of the nanotube towards the center. This mechanism is consistent with the residual Ta$_2$O$_5$ present in the 24-h nanotubes in the GA-XRD spectrum (Figure 2a).

Superconductivity and CDW behavior have been observed to be competing mechanisms in bulk layered dichalcogenides such as Cu$_x$TiSe$_2$[17] and NbSe$_2$[18] NbSe$_2$ nanotubes have been shown to be superconducting at low temperatures,[19] and calculations have predicted that NbS$_2$ nanotubes will exhibit superconducting behavior different to that of the bulk.[20] Our template-based method offers an ideal approach to design a model system for studying the effects of nanoscale structure on electronic properties in reduced dimensions. Bulk 2H-TaS$_2$ is known to be superconducting below $T_c = 0.8$ K[10] and to exhibit an incommensurate CDW transition around $T_{CDW} = 75$ K.[10] TaS$_2$ nanowires and nanobelts have shown an elevated $T_c$,[15,21] however, there are no reports on measurements of both $T_c$ and $T_{CDW}$ for the same TaS$_2$ nanomaterial, and no investigations on how the electronic properties depend on the finite number of TaS$_2$ layers. We used a superconducting quantum interference device (SQUID) to characterize the electronic behavior of 4 h and 24 h nanotubes. Zero-field-cooled (ZFC) measurements at low field ($H = 10$ Oe) revealed a $T_c$ of 2.3 K and 2.8 K, respectively (Figure 5), which is higher than bulk $T_c$. ZFC measurements at high field ($H = 500$ Oe) showed a strong peak at 63 K for 24 h tubes, which is less than bulk $T_{CDW}$, while the 4 h nanotubes did not exhibit any features (Figure 5, inset). One possible reason for the low signal of 4 h tubes could be the low quantities of TaS$_2$ in partially converted tubes.

Figure 4. TEM images and electron diffraction patterns (insets) of TaS$_2$ nanotubes converted for a) 1 h, b) 4 h, c) 12 h. White arrows indicate inner TaS$_2$ walls and black arrows indicate outer TaS$_2$ walls.

Figure 5. Superconductivity measurements of TaS$_2$ measurements at low field ($H = 10$ Oe). Inset: CDW measurements at high field ($H = 500$ Oe).
In summary, we have demonstrated a simple method to synthesize multi-walled 2H-TaS₂ nanotubes in high yield from Ta₂O₅ nanotube templates with control over the length, diameter, and the number of TaS₂ layers. These nanotubes exhibit superconductivity and CDW behavior different from bulk TaS₂. We anticipate that this template-based method can be readily applied to synthesize other TMD nanotubes from the appropriate precursors, and advance the study of TMD materials in reduced dimensions.

**Keywords:**
- chalcogenides
- nanotubes
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- tantalum sulfide
- templates


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