

# Synthesis of TaS<sub>2</sub> Nanotubes From Ta<sub>2</sub>O<sub>5</sub> Nanotube Templates\*\*

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The discovery that layered transition metal dichalcogenide (TMD) materials such as WS<sub>2</sub><sup>[1]</sup> and MoS<sub>2</sub><sup>[2]</sup> 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.<sup>[3–5]</sup> One unique property of TMD nanomaterials includes superior tribological behavior;<sup>[6]</sup> other applications include use as solid lubricants,<sup>[7]</sup> catalysts for hydrosulfurization,<sup>[8]</sup> and hydrogen-storage devices.<sup>[9]</sup> 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<sub>2</sub>) 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.<sup>[10]</sup> Investigations of structure–property relationships of TaS<sub>2</sub> nanomaterials have been limited, however, because they can neither be produced in high yield nor with control over the crystalline structure.

Tubular TaS<sub>2</sub> nanomaterials have been synthesized by the hydrogen reduction of TaS<sub>3</sub> precursors<sup>[11]</sup> but the crystal structure could not be determined because of sample degradation under the electron beam. Other nanostructures of TaS<sub>2</sub> include fullerene-like TaS<sub>2</sub> nanoparticles produced by a

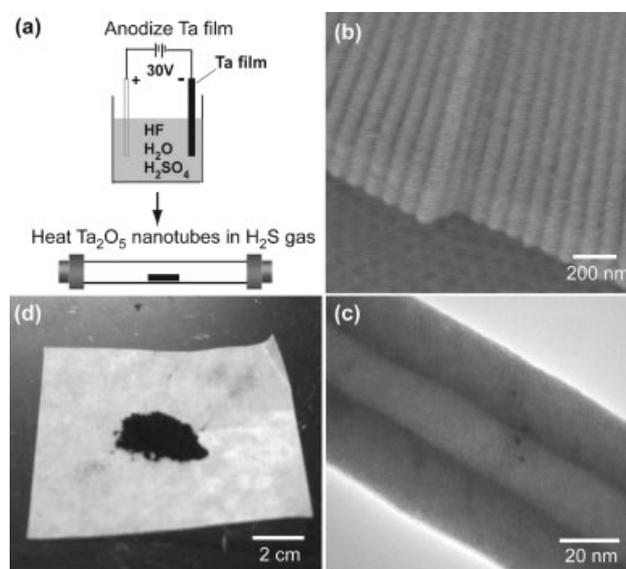
gas-phase reaction<sup>[12]</sup> and TaS<sub>2</sub> nanoplates formed by laser ablation<sup>[13]</sup> or from molecular precursors.<sup>[14]</sup> 2H-TaS<sub>2</sub> nanowires synthesized from elemental Ta and S by chemical vapor transport exhibited a superconductivity transition temperature ( $T_c = 3.4$  K) higher than that of bulk 2H-TaS<sub>2</sub> (0.8 K).<sup>[15]</sup> Recently, we demonstrated synthetic control over the size, shape, and polytype of surface-patterned TaS<sub>2</sub> nanostructures by converting nanopatterned tantalum oxide (Ta<sub>2</sub>O<sub>5</sub>) to TaS<sub>2</sub> using a gas-phase reaction.<sup>[14]</sup>

Here we report how large quantities of crystalline TaS<sub>2</sub> multi-walled nanotubes can be synthesized starting from Ta<sub>2</sub>O<sub>5</sub> nanotube templates. We achieved control over the length, diameter, and the number of TaS<sub>2</sub> 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<sub>2</sub> nanotubes was elevated, and the CDW transition temperature ( $T_{CDW}$ ) was suppressed.

Figure 1a depicts the scheme for converting Ta<sub>2</sub>O<sub>5</sub> nanotubes to multi-walled TaS<sub>2</sub> nanotubes. First, large-area arrays ( $\approx 3.5 \times 10^{10}$  tubes cm<sup>-2</sup>) of amorphous Ta<sub>2</sub>O<sub>5</sub>

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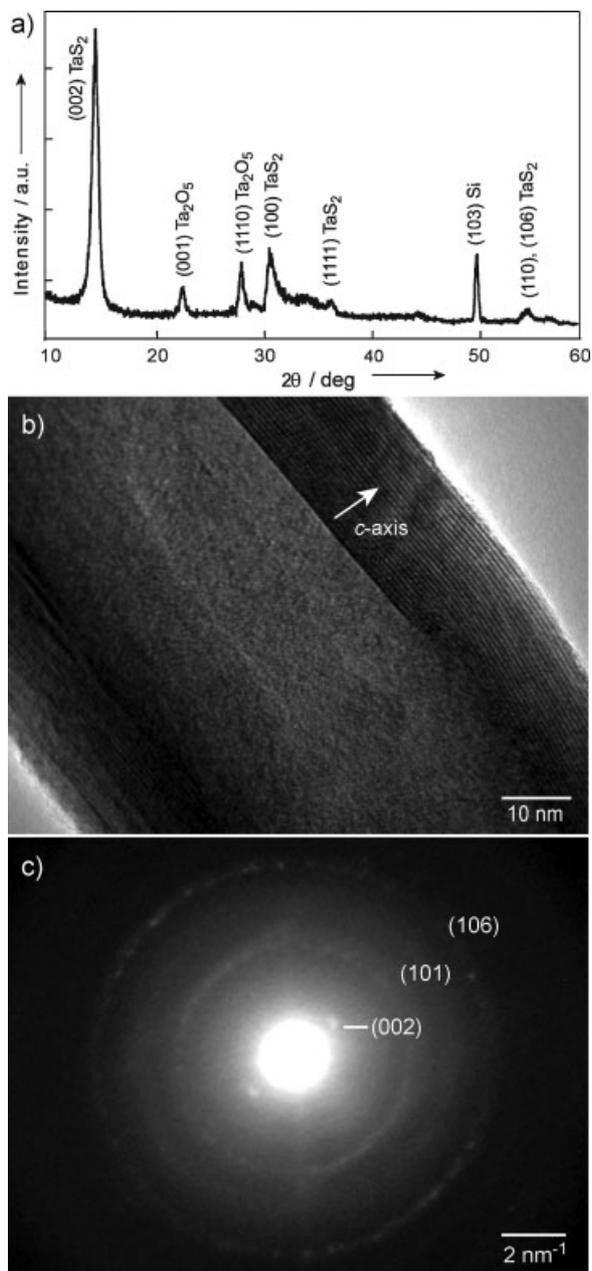
**Figure 1.** a) Scheme of chemical conversion process to synthesize TaS<sub>2</sub> nanotubes starting from Ta<sub>2</sub>O<sub>5</sub> nanotube templates. b) SEM image of Ta<sub>2</sub>O<sub>5</sub> nanotube arrays formed after anodizing the Ta film. c) TEM image of a Ta<sub>2</sub>O<sub>5</sub> nanotube. d) Photograph of bulk quantities of TaS<sub>2</sub> nanotubes.

nanotubes (Figure 1b) were grown by the electrochemical anodization of a 300- $\mu\text{m}$ -thick Ta film (Aldrich, 99.9%) in a room-temperature solution of HF:H<sub>2</sub>SO<sub>4</sub> (2 mL 48% HF, 50 mL 85% H<sub>2</sub>SO<sub>4</sub>) at 30 V for 10 min.<sup>[16]</sup> Ta<sub>2</sub>O<sub>5</sub> nanotubes were washed repeatedly with deionized water to remove all traces of H<sub>2</sub>SO<sub>4</sub> and then vacuum filtered. Transmission electron microscopy (TEM, JEOL JEM-2100F, 200 kV) revealed that Ta<sub>2</sub>O<sub>5</sub> nanotubes synthesized under these conditions were 10–13  $\mu\text{m}$  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<sup>-1</sup> to 625 °C under 16 sccm of 99.5%

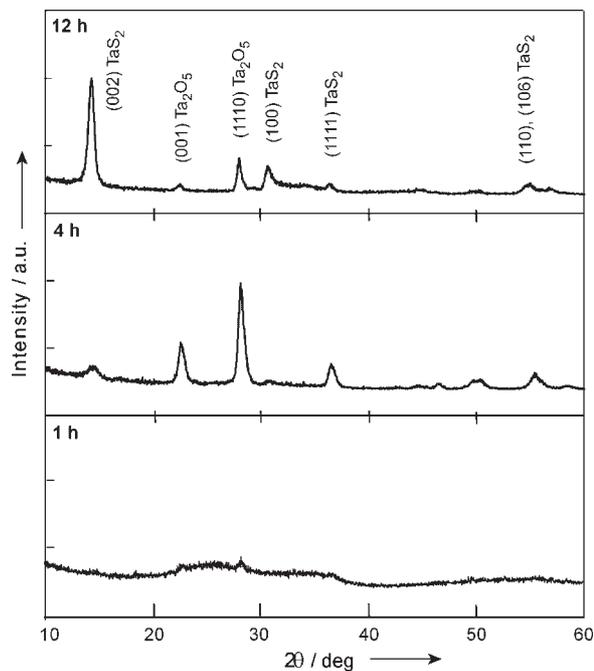
H<sub>2</sub>S(g). The reaction time controls the number of TaS<sub>2</sub> layers formed within the nanotube. A 24 h reaction time was enough to convert the Ta<sub>2</sub>O<sub>5</sub> nanotubes completely into multi-walled TaS<sub>2</sub> nanotubes. The furnace was then cooled to ambient temperature, 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-TaS<sub>2</sub> (PDF 01-080-0685), with lattice parameters  $a = 3.314 \text{ \AA}$ ,  $b = 3.314 \text{ \AA}$ ,  $c = 12.097 \text{ \AA}$  (Figure 2a). TEM images show that fully converted tubes had approximately 25 layers of TaS<sub>2</sub> stacked along the  $c$ -axis (Figure 2b). The electron-diffraction patterns show prominent rings that correspond to randomly oriented (101) and (106) planes of TaS<sub>2</sub> 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  $6.07 \pm 0.03 \text{ \AA}$ . This result is in good agreement with the interlayer spacing of 2H-TaS<sub>2</sub> ( $6.05 \text{ \AA}$ )<sup>[12]</sup> and further supports that the TaS<sub>2</sub> nanotube polytype was 2H.

Unlike other synthetic approaches, our method allows nanotubes to be formed with varying numbers of TaS<sub>2</sub> layers depending simply on the reaction time. We synthesized TaS<sub>2</sub> 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 Ta<sub>2</sub>O<sub>5</sub> nanotube template exhibited highly crystalline Ta<sub>2</sub>O<sub>5</sub> peaks at 4 h, which were then gradually replaced by the characteristic (002), (100), and (106) TaS<sub>2</sub> 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 TaS<sub>2</sub> layers along the  $c$ -axis as the conversion time increased.

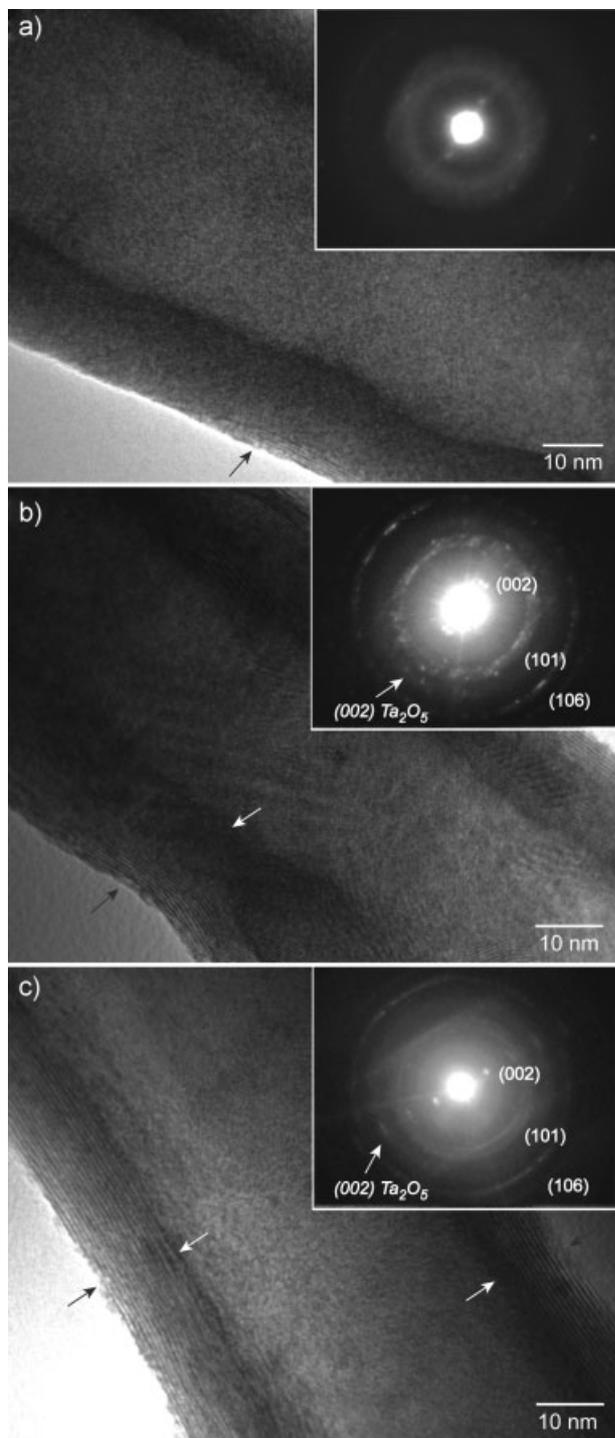


**Figure 2.** Structural characterization of TaS<sub>2</sub> nanotubes after 24 h reaction. a) GA-XRD spectra. b) TEM image of a single nanotube. c) Electron diffraction pattern of a single nanotube using a 1.4- $\mu\text{m}$ -radius illumination disc.



**Figure 3.** GA-XRD spectra of TaS<sub>2</sub> nanotubes at different conversion times in H<sub>2</sub>S(g). After 12 h, there is still some residual yet crystalline Ta<sub>2</sub>O<sub>5</sub>, which is most likely in the center of the nanotube.

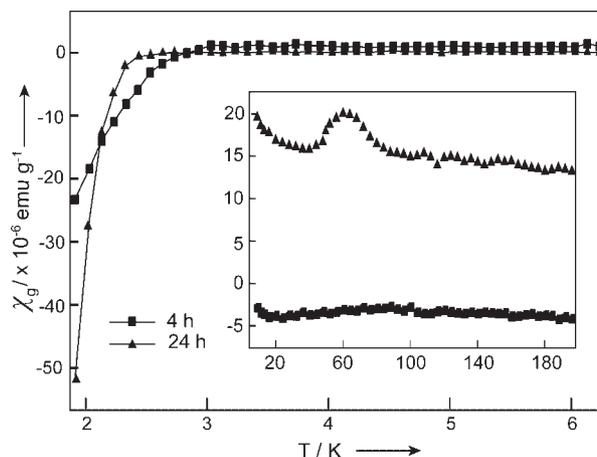
TEM images confirmed that the average number of metal disulfide layers depended on the reaction time. After 1 h, <5 TaS<sub>2</sub> layers formed on the interior and exterior surfaces of the amorphous Ta<sub>2</sub>O<sub>5</sub> nanotube. The layers were discontinuous and did not connect along the entire length of the nanotube (Figure 4a). After 4 h of conversion, more TaS<sub>2</sub> layers were formed (10–15) and started to connect along the length of the nanotube (Figure 4b). Electron diffraction patterns were



**Figure 4.** TEM images and electron diffraction patterns (insets) of TaS<sub>2</sub> nanotubes converted for a) 1 h, b) 4 h, c) 12 h. White arrows indicate inner TaS<sub>2</sub> walls and black arrows indicate outer TaS<sub>2</sub> walls.

indexed to (002), (101), and (106) TaS<sub>2</sub>, as well as (002) Ta<sub>2</sub>O<sub>5</sub>, which indicated the presence of unreacted oxide. At 12 h of conversion, TaS<sub>2</sub> layers continued to form along the *c*-axis (Figure 4c). The relative intensity of the (002) Ta<sub>2</sub>O<sub>5</sub> feature in the 12 h electron diffraction pattern decreased because of the conversion of Ta<sub>2</sub>O<sub>5</sub> to TaS<sub>2</sub>. After 24 h, the entire Ta<sub>2</sub>O<sub>5</sub> wall was converted to layers of TaS<sub>2</sub> (25 ± 5), resulting in the multilayered structure of the nanotubes (Figure 2b). The (002) Ta<sub>2</sub>O<sub>5</sub> 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<sub>2</sub>O<sub>5</sub> 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<sub>x</sub>TiSe<sub>2</sub><sup>[17]</sup> and NbSe<sub>2</sub>.<sup>[18]</sup> NbSe<sub>2</sub> nanotubes have been shown to be superconducting at low temperatures,<sup>[19]</sup> and calculations have predicted that NbS<sub>2</sub> nanotubes will exhibit superconducting behavior different to that of the bulk.<sup>[20]</sup> 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<sub>2</sub> is known to be superconducting below  $T_c = 0.8$  K<sup>[10]</sup> and to exhibit an incommensurate CDW transition around  $T_{CDW} = 75$  K.<sup>[10]</sup> TaS<sub>2</sub> nanowires and nanobelts have shown an elevated  $T_c$ .<sup>[15,21]</sup> However, there are no reports on measurements of both  $T_c$  and  $T_{CDW}$  for the same TaS<sub>2</sub> nanomaterial, and no investigations on how the electronic properties depend on the finite number of TaS<sub>2</sub> 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<sub>2</sub> in partially converted tubes.



**Figure 5.** Superconductivity measurements of TaS<sub>2</sub> 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-TaS<sub>2</sub> nanotubes in high yield from Ta<sub>2</sub>O<sub>5</sub> nanotube templates with control over the length, diameter, and the number of TaS<sub>2</sub> layers. These nanotubes exhibit superconductivity and CDW behavior different from bulk TaS<sub>2</sub>. 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 · superconductors · tantalum sulfide · templates

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