There has been considerable recent interest in the synthesis and characterization of transition-metal disulfide nanotubes. The significant breakthrough in obtaining WS$_2$ and MoS$_2$
nanotubes by Tenne and co-workers\cite{1,2} was accomplished through either the hydrosulfurization of a very thin film of tungsten or the gas–solid reaction between MoO\(_3\) (M = W, Mo) and H\(_2\)S in a reducing atmosphere at elevated temperatures (800–1000°C). Methods, such as chemical transport,\cite{3} solution routes,\cite{4} in situ heating,\cite{5} activation techniques,\cite{6} and gas–solid reactions\cite{7} can all be used to prepare MS\(_2\) nanotubes. Recently, Remskar et al.\cite{9} synthesized bundles of very long single-walled MoS\(_2\) nanotubes (9.6 Å in diameter) using a C\(_60\)-catalyzed transport reaction. Furthermore, Nath and Rao\cite{10,11} successfully prepared multiwalled transition-metal disulfide nanotubes of groups 4 and 5 through the thermal decomposition of metal trisulfides in a hydrogen atmosphere at 800–1000°C. However, in comparison with their HfS\(_2\) and ZrS\(_2\) counterparts, TiS\(_2\) nanotubes are more sensitive to electron beams,\cite{11} and details of their characterization were not made available.

Layered transition-metal dichalcogenides MS\(_2\) (such as TiS\(_2\) and MoS\(_2\)) are of great interest as they act as host lattices by reacting with a variety of guest atoms or molecules to yield intercalation compounds, in which the guest is inserted between the host layers.\cite{12} In layered MS\(_2\) materials, atoms within a layer are bound by strong covalent forces, while the individual layers are held together by van der Waals (vdW) interactions. The weak interlayer vDW interactions allow foreign atoms or molecules to be introduced between the layers through intercalation.\cite{13} Zak and co-workers\cite{14} have accomplished the intercalation of alkali metals into fullerene-like MS\(_2\) (M = W, Mo) nanoparticles, and have investigated the properties of these intercalation compounds. Their results show that the inert vDW surface of the closed nanoparticles presents a diffusion barrier for the intercalation process. Since the MS\(_2\) nanotubes are formed through the folding of layered nanoparticles, it may be imagined that hollow multiwalled nanotubes with open-ended tips are suitable materials for atomic or molecular intercalation. Here, we report the low-temperature synthesis of open-ended TiS\(_2\) nanotubes, and the subsequent intercalation of lithium into the nanotube by a solution-based chemical approach.

TiS\(_2\) nanotubes were prepared by the following procedures: Na\(_2\)S·9H\(_2\)O (> 99% purity, Aldrich) was dried under vacuum (≈10\(^{-5}\) bar) at 200°C for 24 h over P\(_2\)O\(_5\) to remove the water of crystallization. THF was refluxed for 6 h in the presence of LiAlH\(_4·8\)THF and subsequently distilled under argon. Only water-free Na\(_2\)S and THF were used in the subsequent reactions. A solution of TiCl\(_4\) (3.8 g, 20 mmol, Aldrich) in THF (150 mL) was prepared in a glove box filled with pure argon (99.999%) in the presence of an oxygen scavenger and a sodium drying agent. At 40°C, crystalline Na\(_2\)S (3.1 g, 40 mmol) was added to the above solution while stirring. The mixture was then cooled after 30 min. The dark-brown solid was filtered, and washed with THF and methanol several times to remove NaCl formed during the reaction. The powder was then transferred into a teflon-lined stainless-steel tube, which was flushed with H\(_2\) and maintained at 200°C for 6 h to obtain pure TiS\(_2\) nanotubes while removing the solvent. In a typical synthesis, about 2 g of the product was recovered. The process employed to obtain the TiS\(_2\) nanotubes can be described thus:

\begin{equation}
\text{TiCl}_4 + 2\text{Na}_2\text{S} \rightarrow \text{TiS}_2 + 4\text{NaCl}
\end{equation}

(1)

\begin{equation}
\text{TiS}_2 \rightarrow \text{TiS}_2 + \text{Na}_2\text{S} + \text{H}_2
\end{equation}

(2)

The change in standard Gibbs free energy (ΔG\(^\circ\)) of reaction (1) is about −431.5 kJ mol\(^{-1}\), which implies that the reaction strongly favors the formation of TiS\(_2\).

The as-prepared samples were characterized by scanning electron microscopy (SEM; JEOL JSM-5600 microscope), transmission electron microscopy (TEM; Philips Tcacai F20 microscope, 200 kV), energy-dispersive X-ray spectroscopy (EDXS), powder X-ray diffraction (XRD; Rigaku INT-2000 X-ray generator, CuK\(_{\alpha}\) radiation), X-ray photoelectron spectroscopy (XPS; Shimadzu Electron ESCA-3400 spectroscopy, MgK\(_{\alpha}\) radiation), and Brunauer–Emmett–Teller (BET) nitrogen sorption (Shimadzu-Micromeritics ASAP 2010 Instrument).

Characterization of the as-prepared samples suggested that the low-temperature synthesis was successful in preparing open-ended nanotubes. Figure 1 shows a characteristic SEM image of the as-prepared products. It can be seen that a large number of nanotube filaments are distributed homogeneously over a wide area, and that they are a number of micrometers in length and several tens of nanometers in diameter. A significant proportion (> 95%) of the sample exhibits a tubular structure.

![SEM image of the as-prepared TiS2 nanotubes.](image)

This low-temperature method also gave a satisfactory yield of multiwalled TiS\(_2\) nanotubes with open-ended tips, as can be observed from TEM and high-resolution TEM (HRTEM) analyses (Figure 2). A low-magnification TEM image of a typical TiS\(_2\) sample is shown in Figure 2a, from which it can be seen that the sample consists of single nanotubes and nanotube bundles. Both the single nanotubes and the nanotube bundles exhibit uniform tubular structures.
with a length of approximately 2 µm, an outer diameter of approximately 30 nm, an inner diameter of approximately 10 nm, and an interlayer spacing of approximately 0.57 nm (Figure 2b, d, e, and f). Note that the nanotube tips are open and that there is little evidence for the coexistence of an amorphous phase at the tube tips (Figure 2b and f).

The chemical composition of both the individual nanotubes and the bundles was analyzed by EDXS, and both were shown to have a Ti/S atomic ratio of 1:2. XPS analysis demonstrates that the valence of the Ti centers within the nanotubes is +4, and the peak is assigned to Ti 2p3/2 orbital in TiS2, which is characterized by a detected binding energy of 458 eV in a well-defined spin-coupled curve. Powder XRD analysis of the product confirmed that the sample was composed of the 1T-TiS2 phase in high purity, with hexagonal lattice parameters (a = b = 3.405 Å, c = 5.697 Å) that are in good agreement with those of polycrystalline TiS2 (a = b = 3.4049, c = 5.6912 Å; ICDD–JCPDS card No. 15-0853). The c value from the XRD pattern is also consistent with the interlayer spacing observed from the HRTEM images shown in Figure 2. Thus, the EDXS, XPS, and XRD measurements have unambiguously demonstrated that the tubular structures in our sample are multiwalled TiS2 nanotubes with open-ended tips.

Since multiwalled nanotubes with open-ended tips potentially have a lower diffusion barrier for the intercalation process than their closed counterparts, the introduction of lithium into the layers of the nanotubes was attempted by a solution-based approach. Lithium intercalation into TiS2 nanotubes can be described thus:

\[ \text{TiS}_2 + x \text{Li}^+ + x \text{e}^- \rightarrow \text{Li}_x\text{TiS}_2 \]

Li,TiS2 samples (x = 0.12, 0.52, and 1.0) were prepared by the chemical intercalation of TiS2 nanotubes using nBuLi and/or moisture during the measuring process. For TEM observations, the sample grid and specimen holder were prepared in the glove box and transferred to a glove bag (Cheltenham, Model X-27–27H). During the transfer of the specimen holder to the TEM chamber, special care was taken to minimize the exposure of the sample grid to the atmosphere.

XRD of the lithium-intercalated samples indicates that the nanotube structure of TiS2 is maintained after intercalation. Figure 3a shows XRD patterns for the TiS2 nanotubes before lithium intercalation, and for the resulting Li,TiS2 products. Upon intercalation, the (001) peak shifts to lower angles, which indicates an expansion of the interlayer spacing. Figure 3b shows the lattice parameters a and c obtained from the XRD for samples with different x values. It can be seen that only very slight differences were observed in the value of the lattice constant a, while the lattice spacing c is strongly correlated to the intercalated lithium quantity x. The largest interlayer spacing (6.3 Å) was observed when x = 1, which corresponds to an expansion in the c axis of approximately 10.5%. It has been previously reported that lithium intercalation in polycrystalline TiS2 leads to a single homogeneous phase with a lattice expansion of approximately 10% for the entire intercalation range, up to x = 1 in Li,TiS2. Therefore, lithium intercalation in the open-ended TiS2 nanotubes was as effective as that of their polycrystalline counterparts.

The morphology of the lithium-intercalated TiS2 nanotubes was further investigated by HRTEM. Figure 4 shows such images recorded for the Li,TiS2 sample. It was found that individual intercalated nanotubes were evenly aligned and distributed (Figure 4a). The observed interlayer spacing is about 6.3 Å, which is consistent with the XRD data shown in Figure 3. The lithium-intercalated TiS2 nanotubes are somewhat sensitive to electron-beam irradiation during HRTEM investigations. This is believed to result from lithium being

Figure 2. Representative low-magnification (a, c) and high-resolution (b, d, e, f) TEM images of multiwalled TiS2 nanotubes.
“pumped out” from the nanotubes upon irradiation, which is consistent with qualitative analysis that shows a decrease in the interlayer spacing for the intercalated TiS$_2$ nanotubes after relatively long irradiation periods (Figure 4c and d). After irradiation for 5 s, the interlayer spacing of the nanotubes is about 6.3 Å (Figure 4b), while after 40 and 60 s of intensive electron-beam irradiation, the interlayer spacing of the nanotubes decreases to approximately 6.1 (Figure 4c) and 6.0 Å (Figure 4d), respectively.

It should be emphasized that some of the walls of the intercalated TiS$_2$ nanotubes were transformed to an amorphous phase and that more defects were observed after further subjection to intense beam irradiation (Figure 4e). The inset in Figure 4e shows the electron diffraction pattern, which exhibits a hexagonal arrangement of the remaining layers and indicates the axis of the tube is the perpendicular to the $c$ axis. In addition, the halo pattern in the electron diffraction pattern reveals the strong incoherent scattering of the electron beam caused by the amorphous phase of TiS$_2$ around the tube walls. Since this beam sensitivity makes the electron-diffraction analysis difficult, further HRTEM and EDXS measurements were not carried out. Nonetheless, the present XRD and HRTEM observations confirm that the increase in basal spacing can be attributed to the intercalation of lithium. As is already known, the octahedral and tetrahedral interstitial sites in crystalline TiS$_2$ are available for the intercalation of lithium. In general, the octahedral sites are energetically more favored,[13,18] which leads to a possible maximum intercalation level of one lithium atom per formula unit. The intercalation of lithium within the vdW spacings results in the expansion of the host structure along the $c$ axis.

Figure 4. a) HRTEM image of an individual Li$_x$TiS$_2$ nanotube and charts of the interlayer spacing of the nanotubes after electron-beam irradiation of 5 (b), 40 (c), and 60 s (d) duration; e) HRTEM image of the Li$_x$TiS$_2$ nanotube shown in (a) after irradiation for 60 s (inset: the corresponding electron diffraction pattern).
In conclusion, multiwalled TiS$_2$ nanotubes with open-ended tips have been successfully synthesized through a low-temperature solution route. It is believed that this rational route can be extended for the synthesis of other similar nanotubes, by starting from the layered structures in solution. Moreover, it can be shown that such TiS$_2$ nanotubes are very effective toward lithium intercalation while maintaining a homogeneous phase, despite their extreme sensitivity to electron-beam damage. Current work is directed towards further study of the intercalation–deintercalation of alkali metals, hydrogen, and organic molecules in TiS$_2$ nanotubes. In principle, such intercalated nanotubes should allow elucidation of the mechanism of superlattice formation, high-energy storage systems, and nanophase catalytic reactions.

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