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Titanium Disulfide Nanotubes as Hydrogen-Storage Materials

Jun Chen,*,† Suo-Long Li,† Zhan-Liang Tao,† Yu-Tian Shen,‡ and Chun-Xiang Cui‡

Institute of New Energy Material Chemistry, Nankai University, Tianjin 300071, P.R. China, and School of Materials Science & Technology, Hebei University of Technology, Tianjin 300130, P.R. China

Received February 11, 2003; E-mail: chenabc@nankai.edu.cn

An economical and safe hydrogen-storage medium is a critically needed component of a hydrogen-fueled application system. Despite the interests and activities in hydrogen storage using various materials, either achieving high hydrogen-storage capacity under ambient conditions or elucidating the hydrogen-storage mechanism in so-called nanotubes remains challenging.[1] The transition-metal dichalcogenide TiS_2 has been originally of interest as insertion materials of the positive electrode of lithium batteries.[2] Atoms within a S−Ti−S sheet are bound by strong covalent forces, while individual S−Ti−S layers are held together by van der Waals interactions. This enables the introduction of foreign atoms or molecules between the layers by intercalation. On the other hand, there has been considerable research devoted to the synthesis and characterization of transition-metal disulfide nanotubes in the past decade.[3−5] Tenne and co-workers have made significant breakthrough in obtaining WS_2 and MoS_2 nanotubes through gas−solid reaction at elevated temperatures (800−1000 °C).[3] Remskar et al. have synthesized bundles of very long single-wall MoS_2 nanotubes by a C_{60}-catalyzed transport reaction.[4] Nath and Rao have successfully prepared Groups 4B and 5B transition-metal disulfide nanotubes with multiwalls through the thermal decomposition of metal trisulfides in a hydrogen atmosphere at 800−1000 °C.[5] Our previous work has shown that MoS_2 nanotubes can electrochemically store hydrogen.[6] However, are TiS_2 nanotubes appropriate for hydrogen storage? Here we report that high-purity multiwalled TiS_2 nanotubes with open-ended tips, which were obtained by a chemical transport reaction, can efficiently store 2.5 wt % hydrogen at the temperature of 25 °C and under the hydrogen pressure of 4 MPa.

Titanium metal sponge (99.9%, Aldrich Chemical Corp.), sulfur powder (99.5%), and reagent-grade iodine were utilized as starting materials. TiS_2 nanotubes were prepared by employing a chemical transport reaction, which was carried out in Vycor tubes with a size of 3.0 cm in diameter and 10 cm in length. The reaction involving a mixture of Ti and S powder in an atomic Ti:S ratio of 1:2, which was transported by iodine vapor (2−3 mg cm^{-3}) as the transport agent, was run typically for 72 h at 750 °C in an evacuated silica ampule at a pressure of 10^{-2} Pa. The transport rate increased rapidly with a small increase in iodine concentration; however, nanorods resulted when the iodine concentration substantially exceeded 4 mg cm^{-3}. The transported material, which was dark-brown in color, was subsequently washed with distilled water, dried in a vacuum (10^{-3} Pa) at 100 °C for 2 h, and then kept in a glovebox filled with high-purity argon (99.999%). Elemental analysis of the chemical transported material by inductively coupled plasma emission spectroscopy (ICP) shows that there were two elements, Ti and S, and that the atomic Ti:S ratio was 1:2, demonstrating the stoichiometry of TiS_2.

The chemical transport reaction gave a satisfactory yield (more than 95%) of multiwalled TiS_2 nanotubes with open-ended tips, as evidenced from the transmission electron microscope (TEM) images, high-resolution TEM (HRTEM) image, and X-ray diffraction (XRD) pattern shown in Figure 1. The TEM images (Figure 1, a and b) reveal that the sample contains nanotubes, whereas the HRTEM image (Figure 1c) shows that the nanotubes exhibit uniform open-ended tubular structures with an outer diameter of ∼30 nm, an inner diameter of ∼10 nm, and an interlayer spacing of ∼0.57 nm. The XRD pattern (Figure 1d) illustrates that the nanostructures are composed of nanocrystalline TiS_2 with a hexagonal structure. The unit cell parameters are determined to be $a = b = 3.4050$ Å and $c = 5.6920$ Å, in good agreement with those of bulk TiS_2 ($a = b = 3.4049$ Å and $c = 5.6912$ Å, ICDD-JCPDS card No. 15-0853).

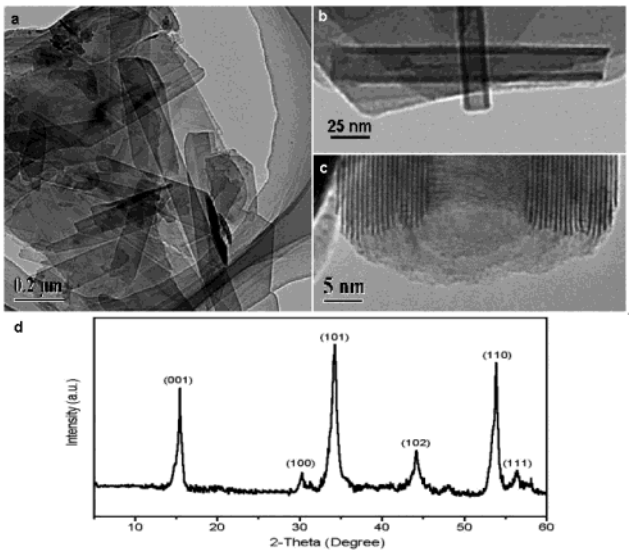

Figure 1. TEM (a, b) and HRTEM (c) images and XRD pattern (d) of the as-synthesized TiS_2 nanotubes.

The complete pressure−composition−temperature (PCT) curves of TiS_2 nanotubes at the temperatures of 25, 75, and 125 °C[7] are shown in Figure 2. At 25 °C, the atomic ratio is 2.8 when expressed as H/TiS_2, and the hydrogen concentration in TiS_2 is 2.5 wt %. An increase in temperature causes a decrease of the hydrogen content, but considerable amounts of hydrogen can be still stored reversibly in the nanotubes. The reaction rates at room temperature for both absorption and desorption are very high. For example, the complete desorption at 25 °C took only 30 min. It is emphasized that the PCT curves of TiS_2 nanotubes show no distinct plateau, but rather sloping hydrogen absorption and desorption isotherms. In such a case, it is not applicable to calculate the fundamentals related to hydride thermodynamics such as the reaction enthalpy and entropy.

Obviously, the large amounts of hydrogen storage in the TiS_2 nanotubes cannot be simply interpreted in terms of physisorption both inside the tube and in the interstitial channels, because the physisorbed hydrogen is very weakly bound and thus could not lead to such large sorption at room temperature. After a preliminary

† Institute of New Energy Material Chemistry, Nankai University.
‡ School of Materials Science & Technology, Hebei University of Technology.

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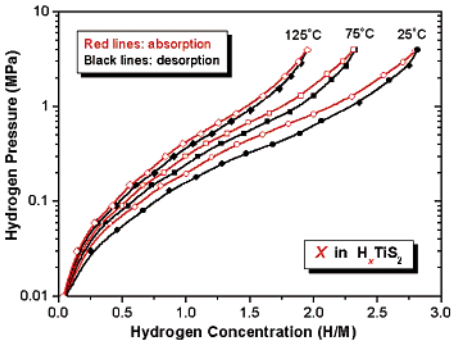

Figure 2. PCT curves for hydrogen absorption and desorption of TiS_2 nanotubes at 25, 75, and 125 °C.

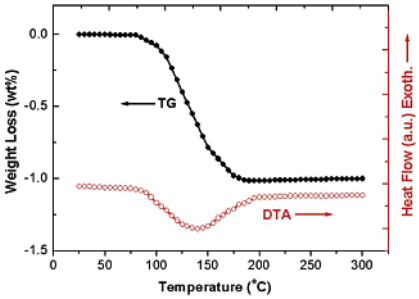

Figure 3. TG-DTA characterization of the TiS_2 nanotubes in the hydride state (at 25 °C and 4 MPa hydrogen) that was subjected to ambient pressure.

test of 20 consecutive cycles of hydrogen absorption and desorption at 25 °C, the hydrogen-storage capacity of TiS_2 nanotubes decreased by only about 2%, indicating the high reversibility in the hydrogen absorption and desorption processes. The sample in the hydride state was then subjected to ambient pressure and investigated by XRD and thermogravimetry-differential thermal analyses (TG and DTA, Figure 3), respectively. The XRD diagram shows that the sample consists merely of one phase, which was identified as the same structure as that of Figure 1d, except that the peaks [especially the (001) reflection] shift to lower diffraction angles, revealing larger lattice parameters. This can be understood due to the hydrogen absorption in the TiS_2 nanotubes. The TG analysis shows that the desorption of hydrogen from 75 to 185 °C gives a total loss of about 1.0 wt % H_2 (corresponding to $H_{1.2}TiS_2$). The DTA inspection suggests that there is only one potential phase transformation during the hydrogen desorption process. The XRD analysis of the sample after TG measurement shows that only one phase (hexagonal TiS_2) was observed. In fact, the amounts of hydrogen desorption in TG observation were detected at ambient pressure, illustrating that the weight loss was due to the portion of hydrogen remaining in the TiS_2 nanotubes after the hydrogen environment was removed. It means that about 60 wt % of the absorbed hydrogen at 4 MPa was already desorbed when lowering the hydrogen pressure to atmospheric conditions, but that 40 wt % of the absorbed hydrogen was still retained, suggesting that this remaining hydrogen is chemisorbed.

To gain insights into the relationship between the nanotube structures and the hydrogen-uptake properties, the sample after TG measurement was further investigated by TEM and HRTEM as shown in Figure 4. Interestingly, different types of defects were observed, including defective structures, as demonstrated by the defective deformation of the nanotubes (Figure 4, a and b), the point defects along the tube walls, and the plane defects in the nanotube tips (Figure 4, c and d, respectively). This behavior is attributed to the irregular expansion of the interlayers during the hydrogen absorption−desorption cycles. It is believed that the formation of the specific defects and defective structures results in

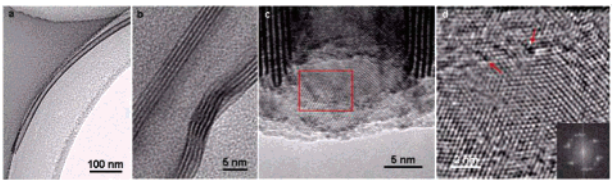

Figure 4. TEM (a) and HRTEM (b, c, d) characterization of the TiS_2 nanotubes after TG measurement. The rectangle in c marks the area magnified in d. The arrows in d display the defects, and the inset is the corresponding electron diffraction pattern.

suitable sites for catalytic reversible hydrogen storage and consequently affects the hydriding and dehydriding properties of TiS_2 nanotubes. The interesting question is how the hydrogen bonds to TiS_2 in the hydride nanotubes. To the best of our knowledge, there are two possible schemes that could be proposed: one is through a S−H bond, and the other, through a Ti−H bond. In the first case, we know that this S−H bond is weak and can be easily disrupted at relatively low temperature, which is consistent with the hydrogen release from the hydride nanotubes in the temperature range for TG as shown in Figure 3. If it is a Ti−H bond, it would be the first example of metal hydride with coexisting Ti−S and Ti−H bonds, indicating that hydrogen atoms are stored in the interstitial sites such as those of conventional metal hydrides.[1b] However, titanium hydride (TiH_2) is very stable, and the decomposition of TiH_2 occurs around 500 °C.[8] Furthermore, the open-ended TiS_2 nanotubes expose their edges at the open ends, which are only a small fraction of the total surface. Hence, it is more likely that the S−H bond takes place in the formation of TiS_2 nanotubes. These questions will have to be addressed in future studies.

In conclusion, multiwalled TiS_2 nanotubes with open-ended tips, which were synthesized through a chemical transport reaction, can absorb and desorb hydrogen reversibly with a capacity of 2.5 wt % hydrogen. Both the physisorption and the chemisorption play important roles in optimizing the hydrogen storage. Such properties should shed light on better understanding of the hydrogen absorption−desorption mechanism of metal-sulfide nanotubes.

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(7) The pressure−composition−temperature (P−C−T) curves for hydrogen adsorption and desorption were determined by using a computer-controlled "Gas Reaction Controller" apparatus, which was manufactured by the Advanced Materials Corporation (AMC, Pittsburgh, http://www.advanced-material.com). The TiS_2 nanotubes, typically 500 mg in weight, were placed into a stainless steel vacuum system. The volume in the hydrogen adsorption−desorption process had been carefully calibrated before the actual measurement. The hydrogen adsorption and desorption were carried out at temperatures of 25, 75, and 125 °C and under hydrogen pressures ranging from 0.01 to 40 atm. Ultrahigh purity hydrogen (99.999%) was used. The hydrogen adsorption amount was defined as the ratio of the mass gain and the mass of the starting TiS_2 nanotubes plus adsorbed hydrogen. For quality control purposes, using the AMC device, we obtained a hydrogen absorption value of $LaNi_5H_6$ for $LaNi_5$ alloy at 25 °C and under 40 atm hydrogen pressure. This ensures that the hydrogen uptake data for TiS_2 nanotubes are reliable.
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