Inorg. Chem. **2005**, *44*, 4124–4126

Inorganic Chemistry

Communication

Room-Temperature Hydrogen Uptake by TiO_2 Nanotubes

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Received February 1, 2005

TiO_2 nanotubes can reproducibly store up to ∼2 wt % H_2 at room temperature and 6 MPa. However, only about 75% of this stored hydrogen can be released when the hydrogen pressure is lowered to ambient conditions, suggesting that both physisorption and chemisorption are responsible for the hydrogen uptake. FTIR spectroscopy, temperature-programmed desorption (TPD), and pressure–composition (*P*–*C*) isotherms suggest that 75% of the H_2 is physisorbed and can be reversibly released upon pressure reduction. Approximately 13% is weakly chemisorbed and can be released at 70 °C as H_2, and ∼12% is bonded to oxide ions and released only at temperatures above 120 °C as H_2O.

One-dimensional nanostructured compounds are one of the most promising materials for hydrogen storage, owing to their unique chemical, physical, thermodynamic, and transport properties as compared to those of their bulk forms.[1] In addition to the study of hydrogen uptake by carbon nanotube (CNTs),[2,3] there is a growing interest in investigating nanostructured inorganic compounds as new advanced materials for hydrogen storage. Uptakes of 1−4 wt % H_2 have been recorded for boron nitride (BN), titanium sulfide (TiS_2), and molybdenum sulfide (MoS_2) nanotubes.[4−6] The addition of small amounts of transition metal oxides was found to greatly enhance the kinetics of hydrogen sorption on Mg-based metal hydrides.[7] Nevertheless, the mechanism of hydrogen storage with nanosized metal oxides is not well documented, except for that of ZnO nanowire.[8]

In this Communication, we report the hydrogen uptake of TiO_2 nanotubes (NTs) and investigate the mechanism using FTIR spectroscopy, temperature-programmed desorption (TPD), and pressure−composition (*P*−*C*) isotherms.

TiO_2 nanotubes were synthesized via a simple hydrothermal process[9] without the use of an autoclave. Typically, ∼2 g of commercial anatase TiO_2 powder (>99%, Aldrich) was added to 100 mL of 10 M NaOH, and the mixture was refluxed for ≥48 h at 120 °C. The resulting product was diluted with distilled water before filtration. The collected titania nanotubes were stirred in 0.1 M HCl at 70 °C overnight. This was repeated once more with fresh 0.1 M HCl and then thoroughly rinsed with distilled water. The extensive acid-washing procedure is essential to obtain titania nanotubes. XRD reveals that these TiO_2 NTs that underwent extensive acid-washing exhibited the anatase structure[9,10] (see Supporting Information). Characterizations and H_2 uptake measurements were carried out on these titania nanotubes that had undergone extensive acid-washing. On the basis of our TEM observation (see Figure 1), a formation mechanism of TiO_2 nanotubes is proposed. When bulk anatase TiO_2 (non-layer-structured material) is treated in 10 M NaOH at 120 °C, layer-structured titanates such as $Na_2Ti_3O_7$ can be formed as intermediate products. During the hydrothermal process, the Na^+ cations residing between the edge-shared [TiO_6] octahedral layers can be replaced gradually by H_2O molecules. The size of intercalated H_2O molecules is larger than that of Na^+ ions, so the interlayer distance becomes enlarged, and the static interaction between neighboring [TiO_6] octahedral sheets is weakened. Consequently, the layered titanate particles exfoliate to form nanosheets (see Figure 1b−d). To release strain energy, the nanosheets curl up from the edges to form TiO_2 nanotubes (see Figure 1e and 1f). This formation mechanism is similar to those reported for TiO_2 nanotubes obtained from layered titanates via soft chemistry.[11−13] It should be noted that there are still debates on the structure of the hydrothermally synthesized

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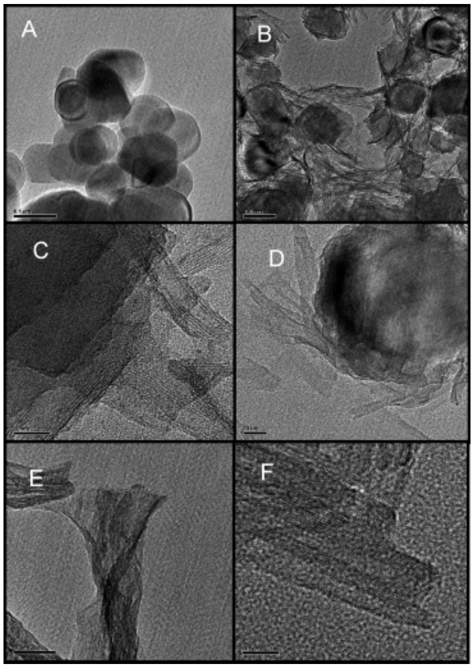

Figure 1. TEM study of the formation of TiO_2 nanotubes during the intermediate stages of 10 M NaOH hydrothermal treatment: (a) Starting anatase TiO_2, (b−d) partially formed nanosheets and nanotubes peeling off from the bulk TiO_2 particles, (e) curling of TiO_2 nanosheets, and (f) an open-ended tip of a TiO_2 nanotube.

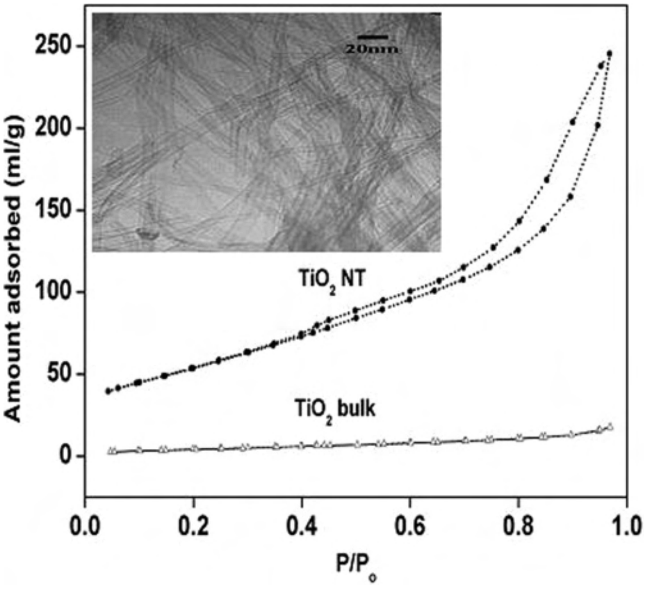

Figure 2. N_2 adsorption isotherms of TiO_2 nanotubes and bulk TiO_2 at 77 K. Inset: TEM image of completely formed TiO_2 nanotubes.

nanotubes, and protonic titanates are alternative assignments.[10,14,15]

As shown in Figure 2, the TiO_2 NTs are entangled together with hollow cores and open tips, very much like multiwalled carbon nanotubes (MWNTs). The outer diameter of the tubes is uniformly distributed around 10 nm, but the length varies from 200 nm to >1 μm. It is noted that our synthesis procedure yields high-quality TiO_2 nanotubes that contain very little lamellar structure, which can be observed for shorter NaOH treatment periods (e.g., 24 h) because of incomplete/partial formation of TiO_2 nanotubes (see Figure 1b). The TiO_2 NTs were characterized by nitrogen adsorption at 77 K (NOVA 3200, Quantachrome Corp., Figure 2). The N_2 adsorption isotherm of TiO_2 NT is typical of a type IV isotherm according to the IUPAC classification. An adsorption−desorption hysteresis loop is observed at $P/P_0 \approx 0.43$, indicating capillary condensation inside the mesoporous tubes. A smaller N_2 adsorption load is observed for bulk TiO_2 with no hysteresis loop (see Figure 2). The specific surface area (SSA) was determined by Brunauer−Emmet−Teller (BET) measurements in the P/P_0 range of 0.05−0.43, which is a typical BET multilayer adsorption. A 12-fold increase in SSA was noted when the bulk TiO_2 adopted a nanotubular structure, from 16 to 197 m^2/g. The mesopore size distributions of the samples were evaluated using Barret−Joyner−Halenda (BJH) methods. The mesopore volumes of bulk TiO_2 and TiO_2 NTs are 0.0301 and 0.379 mL/g, respectively, an increment of ~12 times. The average mesopore diameter for TiO_2 NTs is 7.70 nm, close to the TEM observation.

The hydrogen uptake by TiO_2 systems was measured with a commercial pressure−composition (P−C) isotherm (PCI) unit (Advanced Materials) as previously described.[16] Briefly, a TiO_2 sample of ~320 mg was first degassed at 250 °C and 1×10^{-3} Pa for at least 2 h. After the sample had cooled to room temperature, the hydrogen sorption process began. As shown in Figure 3a, the hydrogen concentration gradually increases as the pressure increases. At room temperature and a pressure of ~900 psi (~6 MPa), the atomic ratio H/M (M = TiO_2) is ~1.6, corresponding to ~2.0 wt % H_2 for TiO_2 NT. A much lower hydrogen concentration of ~0.8 wt % is noted for the bulk forms (see Figure 3a, red symbol profile). In preliminary tests of 10 consecutive cycles of H_2 adsorption and desorption at 25 °C, the hydrogen-storage capacity of the TiO_2 NTs decreased by ~7%, indicating a reasonably good recyclability in the H_2 adsorption and desorption process. When the pressure is reduced, the desorption curves for both bulk and nanotubular TiO_2 samples do not coincide with the adsorption curves. Only ~75% of the stored hydrogen can be released when the hydrogen pressure is lowered to atmospheric conditions, revealing the irreversible nature of the process. Obviously, the hydrogen molecules that can be released simply by reducing the pressure are physically adsorbed, whereas the ~25% of adsorbed hydrogen molecules that are retained on the sample at lower pressures are chemically adsorbed, and their desorption can occur only upon heating. This behavior is similar to the hydrogen sorption of ZnO nanowires and TiS_2 nanotubes,[5,8] for which it is estimated that 30−40% of the hydrogen is chemisorbed and can be released at elevated temperatures of 75−185 °C.

To understand the H_2 adsorption−desoprtion mechanism of TiO_2 NTs, FTIR spectroscopy and TPD were employed.

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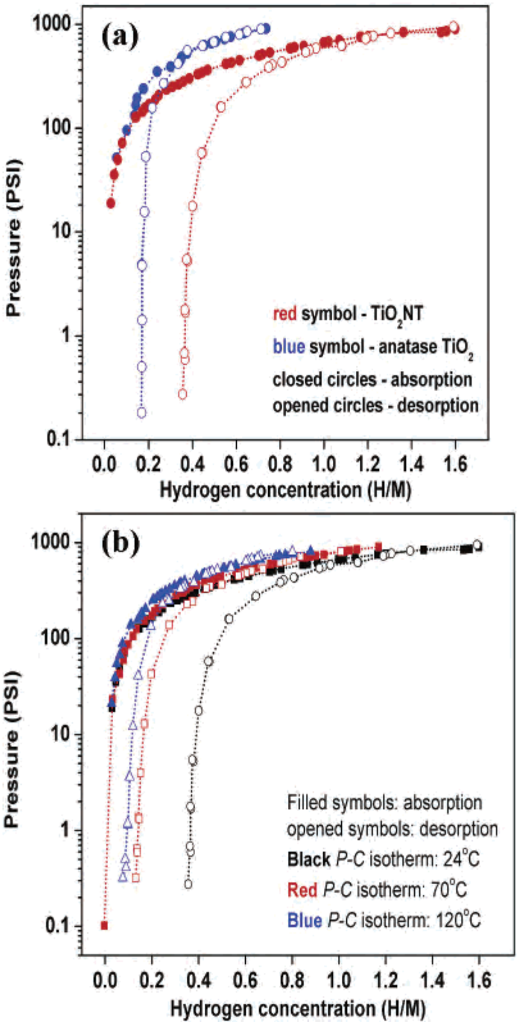

Figure 3. (a) $P-C$ isotherms of TiO_2 nanotubes and bulk TiO_2 at room temperature. (b) $P-C$ isotherms of TiO_2 nanotubes at 24, 70, and 120 °C.

FTIR spectra of TiO_2 NTs revealed a significant increase in the $-OH$ signal (3427 cm^{-1}) after the hydrogenation process (see Figure 4a). In addition, from temperature-programmed desorption (TPD), we observed a H_2 desorption peak at ~70 °C that extended to 160 °C (see Figure 4b). This strongly suggests that some hydrogen molecules were chemisorbed onto the TiO_2 NTs and therefore would not be released at room temperature so that the PCI desorption curve did not follow the adsorption curve. Some hydrogen molecules that are dissociatively adsorbed and bonded to the oxide ions can be released inevitably as H_2O at higher temperatures of 120−200 °C when the OH bonds are ruptured (see Supporting Information). Therefore, $P-C$ isotherms of the TiO_2 NTs were also obtained at two elevated temperatures of 70 and 120 °C (Figure 3b). It is noted that the maximum H_2 uptake is reduced, with 1.45 and 1.10 wt % hydrogen uptakes at 70 and 120 °C, respectively. The desorption curves approach closer to the absorption curves, with 0.25 and 0.13 wt % H_2 remaining for the 70 and 120 °C $P-C$ isotherms, respectively. Therefore, these TPD and PCI data give ~13% of room-temperature H_2 uptake (2 wt %) to weakly chemisorbed hydrogen and ~12 wt % to strongly chemisorbed hydrogen.

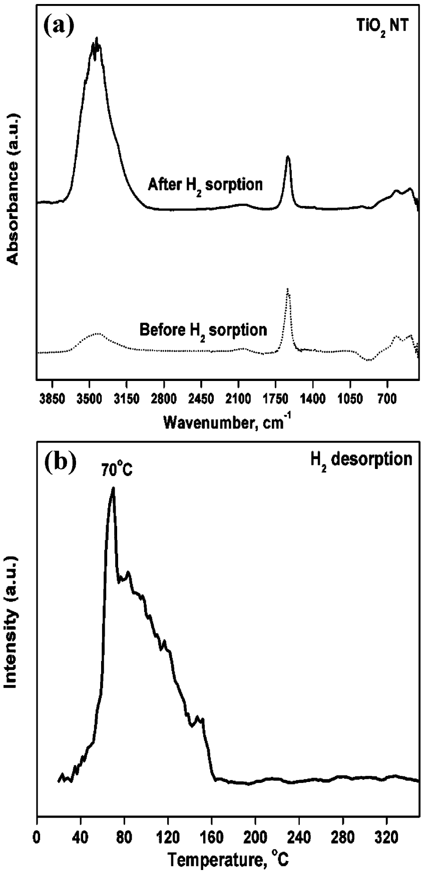

Figure 4. (a) FTIR spectra of TiO_2 nanotubes before and after H_2 sorption. (b) H_2 desorption process during TPD of hydrogenated TiO_2 nanotubes from room temperature to 350 °C, ramp rate = 10 °C/min, using argon as the carrier.

In summary, nanotubular form of TiO_2 has a H_2 sorption capacity of ~2 wt % at room temperature and 6 MPa. Approximately 75% of the H_2 is physisorbed and can be reversibly released upon pressure reduction. It is estimated that ~13% is weakly chemisorbed and can be released at 70 °C and ~12% is strongly chemisorbed and can be released only at temperatures above 120 °C.

Acknowledgment. S.H.L. is grateful for a Ph.D. scholarship from the National University of Singapore.

Supporting Information Available: Experimental section. Figures showing TEM images of initial bulk anatase TiO_2 powder and powder after 48 h of 10 M NaOH hydrothermal processing, XRD patterns of bulk anatase and TiO_2 nanotubes, XPS measurements, pore size distributions of TiO_2 nanotubes and bulk anatase, and H_2O desorption process during TPD of hydrogenated TiO_2 nanotubes. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0501723