Nanomaterials

TiO_2-B Nanowires[**]

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Since the discovery of carbon nanotubes much interest has been shown in the preparation of nanotubes of greater chemical complexity, especially, in recent times, oxide nanotubes. Progress in this field has been reviewed recently by Rao and Nath and by Nesper and co-workers.[1] Of such materials, titanate nanotubes have received a great deal of attention, in part because TiO_2 can exhibit a wealth of important photovoltaic (solar energy conversion), photocatalytic, semiconductor, catalytic support, and gas-sensing properties, especially when prepared as a nanomaterial.[2]

Nanotubes may often only be synthesized in small quantities or by processes that are too complex for scale-up and hence practical application. In contrast, titanate nanotubes and nanowires may be synthesized by a simple hydrothermal reaction between NaOH and the anatase polymorph of titania (TiO_2-anatase).[3] Until recently it was believed that such nanotubes and nanowires were composed of TiO_2-anatase.[4] This hypothesis was called into question by Du et al., and later work suggested that the nanotubes are composed of the layered titanate $H_2Ti_3O_7$.[5] Sun and Li have recently confirmed that these nanotubes are indeed titanates, not TiO_2, and that as-synthesized materials can be described as $Na_xH_{2-x}Ti_3O_7$ with ($x = 0.75$).[6] In addition, Yang et al. produced the formulation $Na_2Ti_2O_4(OH)_2$.[7]

We have examined the titanate nanotubes and nanowires and also find that the composition and structure of both the tubes and wires are more complex than had been recognized previously. We find that the as-synthesized nanotubes and nanowires are sodium hydrogen titanates of general formula $Na_yH_{2-y}Ti_nO_{2n+1}\cdot x\,H_2O$. Acid washing of such materials results in ion exchange to produce the layered hydrogen titanates $H_2Ti_nO_{2n+1}\cdot x\,H_2O$, which exhibits features similar to $H_2Ti_3O_7$, $H_2Ti_4O_9\cdot H_2O$, and other members of the hydrogen titanate family. Structures and compositions of the tubes and wires will be discussed elsewhere.[8]

It is known that layered hydrogen titanates may be converted to the titanium dioxide polymorph TiO_2-B on heating.[9] In view of this we decided to investigate the thermal behavior of the nanotubes and nanowires and have succeeded in preparing TiO_2-B nanowires. Given that we now understand that previously prepared nanotubes/nanowires are $Na_yH_{2-y}Ti_nO_{2n+1}\cdot x\,H_2O$ or $H_2Ti_nO_{2n+1}\cdot x\,H_2O$ phases, this is the first synthesis of TiO_2 nanowires. The synthesis is again simple, and involves a hydrothermal reaction between NaOH and TiO_2, followed by acid washing and heating at 400 °C. Furthermore, TiO_2-B has the advantage over the other titanium dioxide polymorphs of being a relatively open structure. As such it is an excellent host for Li intercalation, leading to nanowires that can display simultaneously *n*-type electronic conductivity and lithium-ion transport, with the level of each being controllable by controlling the degree of intercalation. Hence by a simple route, it is now possible to prepare relatively large quantities of single-phase TiO_2 nanowires in high yield, and render them electronically and ionically conducting.

Titanate nanotubes/nanowires were synthesized as described in the Experimental Section.[3] Carrying out this reaction at around 150 °C with a 10 M NaOH solution yields nanotubes, whereas higher temperatures and/or higher NaOH concentrations yields nanowires. Washing the tubes or wires with dilute HCl promotes complete exchange of Na^+ by H^+ to form hydrogen titanates. On heating the tubes, they convert to anatase but with the loss of the tubular morphology. In contrast the wires behave quite differently; after washing with dilute acid and heating they convert to TiO_2-B but retain their cylindrical morphology. This begins at 200 °C, as observed by variable-temperature X-ray diffraction (Figure 1). Annealing a sample of the acid-washed wires at 400 °C for 4 h in air produces a material which gives the powder diffraction pattern shown in Figure 2. Although the diffraction peaks associated with the nanowires are somewhat broadened they match the pattern for TiO_2-B. Further confirmation that the nanowires are composed of TiO_2-B was obtained from Raman spectroscopy. Figure 3 shows a spectrum of the wires, annealed as described above, compared with a spectrum for bulk TiO_2-B. Although the spectrum obtained is somewhat broadened there is an excellent match with that obtained from bulk TiO_2-B.

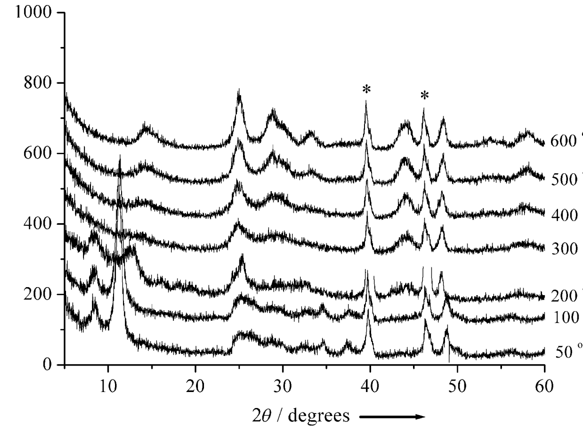

Figure 1. Variable-temperature powder X-ray diffraction patterns collected in air for titanate nanowires, after washing in dilute HCl. The asterisks indicate peaks from the sample holder. *I* = intensity.

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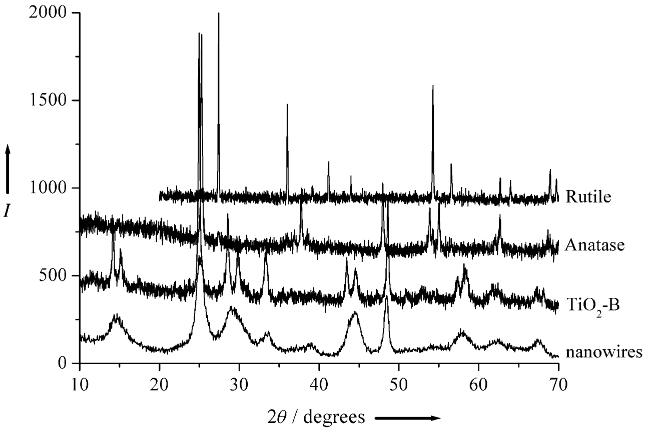

Figure 2. Powder X-ray diffraction pattern for TiO_2-B nanowires prepared by heating at 400 °C for 4 h in air. Powder patterns for bulk TiO_2-B, TiO_2-rutile and TiO_2-anatase are shown for comparison. I = intensity.

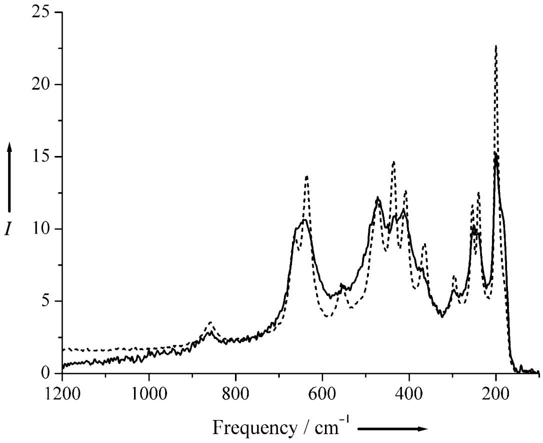

Figure 3. Raman spectra for TiO_2-B nanowires (——) and, for comparison, bulk TiO_2-B (-----). I = intensity.

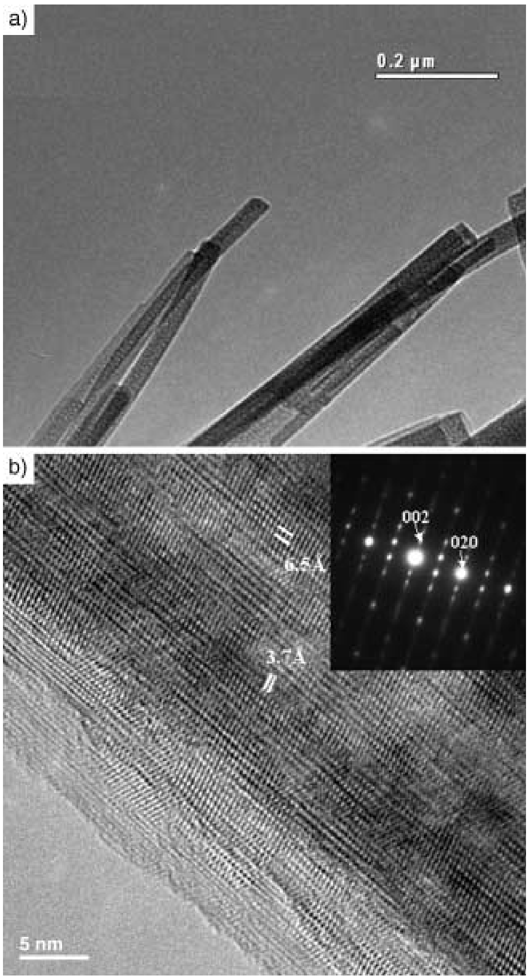

Figure 4. a) Low-resolution TEM image of the TiO_2-B nanowires; b) high-resolution lattice image viewed down the [100] projection (inset: electron diffraction pattern of a TiO_2-B nanowire).

Evidence that the nanowires have retained their morphology is shown in Figure 4. The low-resolution TEM image (Figure 4a) indicates the presence of a high proportion of nanowires with a typical diameter of 20–40 nm and a length of 2–10 µm. At higher magnification the HRTEM lattice images reveal more detail concerning the TiO_2-B structure of the nanowires (Figure 4b). By measuring the lattice fringes and from the electron diffraction patterns taken along different zone axes, the lattice parameters were found to be in agreement with those for the bulk TiO_2-B phase (a = 12.1787, b = 3.7412, c = 6.5249 Å; β = 107.054°).[9b] EDX confirmed the absence of sodium from the TiO_2-B nanowires.

The TiO_2-B nanowires are white and insulating, however, given the ability of bulk TiO_2-B to act as an intercalation host for Li, we investigated the possibility of inserting Li^+ and e^- into the nanowires, in order to render them ionically and electronically conducting, the latter an n-type semiconductor due to the reduction of Ti^{4+} centers. To demonstrate lithium intercalation, a working electrode was fabricated by grinding together TiO_2-B nanowires and Super-S carbon with a PTFE binder and then pressing a disk (also see Experimental Section). The variation of the voltage versus a (1 M) Li^+/Li electrode, as a function of the charge passed is shown in Figure 5. The voltage curve on intercalation (discharging) and deintercalation (charging) is smoother than the corresponding curve collected under identical conditions for bulk TiO_2-B. However the voltages of the charge/discharge plateaux are very similar, which indicates similar energetics for the intercalation reactions. The capacity of the TiO_2-B nanowires to intercalate Li is high, corresponding to 275 mA h g^{-1} and a composition of $Li_{0.82}TiO_2$. X-ray diffraction patterns and TEM data collected at the end of the charging process confirmed the retention of the TiO_2-B structure and the nanowire morphology. This experiment clearly demonstrates the ability of the TiO_2-B nanowires to support both Li^+ and e^- conductivity. It also demonstrates that this material may be of interest as a negative (low-voltage) electrode in lithium-ion batteries. Further confirmation that lithium may be intercalated into the nanowires was obtained by carrying out a chemical intercalation reaction using n-butyl lithium. The white solid turns blue/black, and the X-ray diffraction pattern again indicates retention of the TiO_2-B structure.

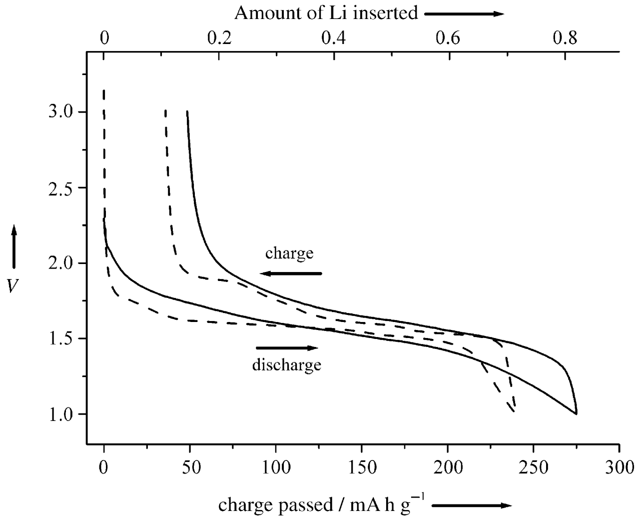

Figure 5. Variation of potential (versus a 1 M Li^+/Li electrode) with Li content (charge passed) for TiO_2-B nanowires (——) and bulk TiO_2-B (-----) cycled under identical conditions. Rate: 10 mA g^{-1} (10 mA of charge passed per gram of TiO_2-B); voltage limits: +1 and +3 V. V = potential.

In conclusion, it has been shown that titanate nanotubes lose their tubular morphology on heating and form TiO_2-anatase whereas the corresponding nanowires retain their morphology and convert to TiO_2-B. Li^+ ions and e^- may be inserted into the TiO_2-B nanowires, rendering them ionically and electronically conducting, and then subsequently removed.

Experimental Section

Titanate nanotubes were synthesized by adding TiO_2-anatase to a 10 M aqueous solution of NaOH. After stirring for 1 h the resulting suspension was transferred to a teflon-lined autoclave and heated to 150 °C for 72 h. The product was acid-washed, which involved stirring the sample in 0.05 M HCl solution for 2 h. The material was then filtered, washed with distilled water, and dried at 80 °C for 15 h. To synthesize titanate nanowires, a similar procedure was followed but using 15 M NaOH solution and a reaction temperature of 170 °C. TiO_2-B nanowires were prepared by heating the acid-washed titanate nanowires at 400 °C for 4 h in air. Room-temperature powder X-ray diffraction was performed on a Stoe STADI/P diffractometer operating in transmission mode with $Cu_{K\alpha 1}$ radiation. Variable-temperature measurements were carried out on a Philips X'Pert system ($Cu_{K\alpha}$ radiation) in Bragg-Brentano geometry fitted with a Bühler high-temperature stage. Raman spectra were obtained from disks, formed by pressing powders, on a Perkin-Elmer System 2000. Transmission electron microscopy was performed on a Jeol JEM-2011 instrument fitted with an EDX facility. Electrochemical properties were measured on electrodes prepared using mixtures comprising 75 % active material, 18 % Super-S carbon and 7 wt % PTFE, pressed into pellets. The cells consisted of this electrode, a lithium metal counterelectrode and the electrolyte, a 1 M solution of $LiPF_6$ in ethylene carbonate/dimethyl carbonate (1:1 v/v; Merck). The cells were constructed and handled in an Ar-filled MBraun glovebox. Electrochemical measurements were carried out using a Biologic MacPile II system.

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