

# Nanotubes with the TiO<sub>2</sub>-B structure

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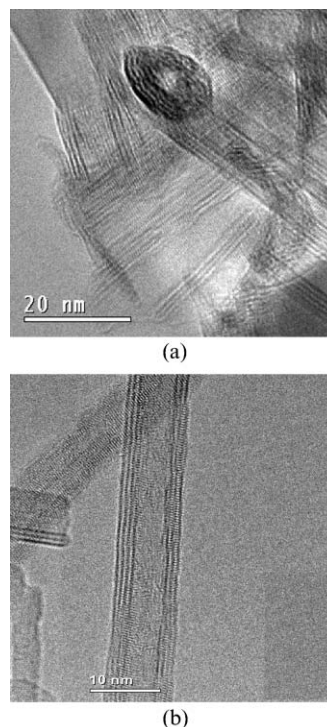
Here we report the first synthesis of TiO<sub>2</sub>-B nanotubes by a simple hydrothermal route; lithium may be intercalated up to a composition of Li<sub>0.98</sub>TiO<sub>2</sub> compared with Li<sub>0.91</sub>TiO<sub>2</sub> for the corresponding nanowires.

There is much current interest in TiO<sub>2</sub> nanotubes/nanowires because of their potential use in a wide variety of applications ranging from catalytic supports, photocatalysts, solar energy conversion, gas sensing and as intercalation electrodes in rechargeable lithium batteries or supercapacitors.<sup>1–6</sup> The dimensional confinement and the particular morphology of nanotubes/wires endows them with different and often enhanced properties.<sup>7</sup> Early work on TiO<sub>2</sub> nanotubes suggested that they could be prepared by a simple hydrothermal route.<sup>8</sup> However, it was shown later that the material arising directly from such a reaction is not TiO<sub>2</sub> but a sodium hydrogen titanate Na<sub>y</sub>H<sub>2–y</sub>Ti<sub>n</sub>O<sub>2n+1</sub>·xH<sub>2</sub>O.<sup>9,10</sup> Nanotubes with the structure of TiO<sub>2</sub>-anatase have now been prepared by suitable thermal treatment of acid washed product from a hydrothermal reaction.<sup>11</sup>

Recently we reported the first synthesis of TiO<sub>2</sub> nanowires by a hydrothermal route.<sup>7,12</sup> The crystal structure is that of TiO<sub>2</sub>-B, a polymorph of titanium dioxide composed of edge and corner sharing TiO<sub>6</sub> but with a slightly lower density than rutile, anatase or brookite.<sup>13–15</sup> TiO<sub>2</sub>-B nanowires are excellent intercalation hosts for Li, reaching compositions of Li<sub>0.91</sub>TiO<sub>2</sub>.<sup>12,16</sup> Here we report the first synthesis of nanotubes with the TiO<sub>2</sub>-B structure and some preliminary characterisation of these materials as electrodes in rechargeable lithium batteries.

TiO<sub>2</sub>-B nanotubes were synthesised by adding 6 g of anatase (Aldrich 99.8%) to 28 ml of a 15 M solution of NaOH in distilled water. The mixture was heated to 150 °C for 72 h in an autoclave of volume 40 ml. The product of the hydrothermal reaction was washed with 0.05 M HCl, dried in air then heated to 400 °C for 5 h. The synthesis conditions are somewhat similar to those used for the nanowires, the main differences being the temperature and volume of solution used, which were respectively 170 °C and 33 ml in the case of the nanowires. Higher temperatures favour larger tubes and then wire formation. Similar trends in hydrothermal synthesis have been noted very recently by Bavykin *et al.*<sup>17</sup> Acid washing produces layered hydrogen titanates which are known to transform to TiO<sub>2</sub>-B on heating.<sup>15</sup>

Characterisation of the nanotubes was carried out by a range of techniques including transmission electron microscopy, powder X-ray diffraction and galvanostatic cycling in an electrochemical cell. TEM data collected on the nanotubes are presented in Fig. 1. The tubes are viewed along their axis in Fig. 1(a) and a tube viewed perpendicular to this axis is highlighted in Fig. 1(b). The

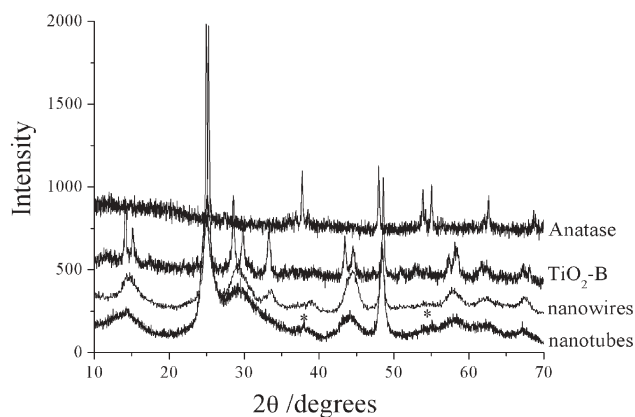


**Fig. 1** Transmission electron micrograph of TiO<sub>2</sub>-B nanotubes: (a) viewed along the axis; (b) a tube viewed perpendicular to its axis.

images are typical of the structures observed throughout the powder, indicating that the yield of nanotubes from the hydrothermal synthesis is high, estimated to be in excess of 90% from analysis of the TEM images. It is clear from Fig. 1 that the tubes are multiwalled with external diameters in the range 10–20 nm and with internal diameters in the range 5–8 nm. The external diameters of the nanotubes are less than those of the previously reported nanowires, which typically have diameters in the range 20–50 nm. The nanotubes can extend up to 1 μm in length.

Turning to the powder X-ray diffraction data, Fig. 2, diffraction patterns for TiO<sub>2</sub>-B nanotubes are presented and compared with those for bulk TiO<sub>2</sub>-B, TiO<sub>2</sub>-B nanowires and bulk TiO<sub>2</sub>-anatase. As expected, the peaks in the diffraction patterns for the nanotubes and nanowires are broadened due to dimensional confinement, especially so in the case of the nanotubes. Despite such broadening it is evident that the nanotubes, like the nanowires, adopt the structure of the TiO<sub>2</sub>-B. The adoption of the TiO<sub>2</sub>-B structure is also confirmed by Raman spectroscopy. It should be noted that the powder X-ray diffraction pattern for the TiO<sub>2</sub>-B nanotubes contains trace amounts of anatase. EDX analysis during

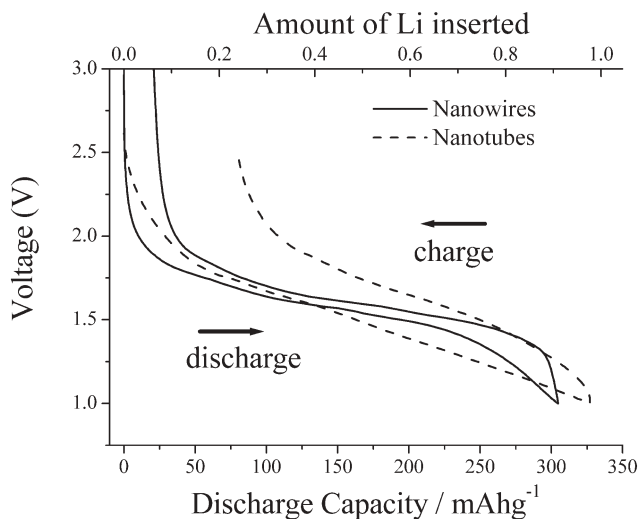
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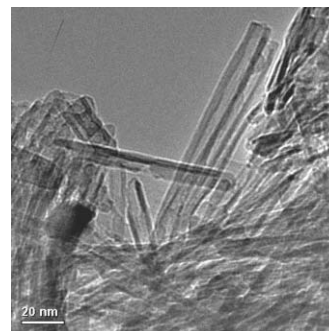
**Fig. 2** Powder X-ray diffraction patterns of TiO<sub>2</sub>-B nanotubes, TiO<sub>2</sub>-B nanowires, bulk TiO<sub>2</sub>-B and anatase. \* indicates anatase impurity.

examination of the materials in the TEM indicated an absence of any residual sodium, as did elemental analysis by ICP.

The behaviour of the TiO<sub>2</sub>-B nanotubes on lithium intercalation was investigated electrochemically. TiO<sub>2</sub>-B powder was mixed with super S carbon and a polymer binder, Kynar (a co-polymer based on polyvinylidene fluoride) in the weight ratios 75 : 18 : 7. This was then pressed into pellets.<sup>7</sup> The electrode was incorporated into an electrochemical cell along with a lithium metal electrode and an electrolyte consisting of a 1 molal solution of LiPF<sub>6</sub> in ethylene carbonate/dimethyl carbonate 1 : 1 (v/v (Merck)). The cells were cycled at a constant rate of 10 mA g<sup>-1</sup>. The variation of voltage with lithium content (state of charge) is shown in Fig. 3, where the data are compared with those for TiO<sub>2</sub>-B nanowires cycled under identical conditions. In the case of the nanowires the voltage does not vary significantly over a wide composition range around 1.5–1.6 V, furthermore, there is little separation between the charge and discharge profiles. In contrast, the voltage of the nanotubes appears to vary more continuously with lithium content, although the capacity to incorporate Li is marginally higher, corresponding to a composition of Li<sub>0.98</sub>TiO<sub>2</sub> at the end of discharge. It is also



**Fig. 3** Variation of potential, vs. Li/Li<sup>+</sup> (1 M) electrode, with Li content (charge passed) for TiO<sub>2</sub>-B nanotubes and TiO<sub>2</sub>-B nanowires cycled under identical conditions. Rate 10 mA g<sup>-1</sup> (current of 10 mA per g of TiO<sub>2</sub>-B).



**Fig. 4** Transmission electron micrograph of TiO<sub>2</sub>-B nanotubes at the end of discharge to 1 V.

apparent that there is a greater separation between the voltage on charge and discharge in the case of the nanotubes, which suggests inferior kinetics compared with the nanowires. Both the nanotubes and nanowires exhibit some degree of irreversibility in that more lithium may be inserted on discharge than extracted on the subsequent charge. The degree of the irreversibility is small for the nanowires but much more significant for the nanotubes. To understand these differences we have studied the nanotubes at the end of the first discharge with TEM, Fig. 4. Examination of Fig. 4 shows that the nanotube morphology has been largely retained, indicating that Li intercalation between the layers in the tube walls has not resulted in unscrolling of the tubes. More work will be required to investigate further the changes to the TiO<sub>2</sub>-B tubes that occur on Li intercalation. In the case of the TiO<sub>2</sub>-B nanowires we have shown previously that the nanowire morphology is retained at the end of discharge and remains intact even after at least 200 cycles.

In conclusion, we have reported the first synthesis of titanium dioxide nanotubes with the TiO<sub>2</sub>-B crystal structure. The synthesis involves a simple hydrothermal reaction and the nanotube yield is estimated to be > 90%. The outer tube diameters lie in the range from 10–20 nm and are smaller than those of the corresponding TiO<sub>2</sub>-nanowires (20–50 nm). The nanotubes are capable of lithium intercalation up to a composition of Li<sub>0.98</sub>TiO<sub>2</sub>-B, slightly in excess of the nanowires, Li<sub>0.91</sub>TiO<sub>2</sub>.

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