TiO$_2$(B)@carbon composite nanowires as anode for lithium ion batteries with enhanced reversible capacity and cyclic performance

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http://ro.uow.edu.au/engpapers/1347

**Publication Details**

TiO$_2$(B)@carbon composite nanowires as anode for lithium ion batteries with enhanced reversible capacity and cyclic performance†

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Received 10th November 2010, Accepted 1st April 2011
DOI: 10.1039/c0jm03873c

Novel TiO$_2$(B)@carbon composite nanowires were simply prepared by a two-step hydrothermal process with subsequent heat treatment in argon. The nanostructures exhibit the unique feature of having TiO$_2$(B) encapsulated inside and an amorphous carbon layer coating the outside. The unique core/shell structure and chemical composition is likely to lead to perfect performance in many applications. In this paper, the results of Li-ion battery testing are presented to demonstrate the superior cyclic performance and rate capability of the TiO$_2$(B)@carbon nanowires. The composite nanowires exhibit a high reversible capacity of 560 mAh g$^{-1}$ after 100 cycles at the current density of 30 mA g$^{-1}$, and excellent cycling stability and rate capability (200 mAh g$^{-1}$ when cycled at the current density of 750 mA g$^{-1}$), indicating that the composite is a promising anode candidate for Li-ion batteries.

Introduction

Carbon has attracted special attention due to its fascinating applications in the field of lithium ion batteries. Although it is one of the most commonly used carbonaceous materials in commercial lithium ion batteries, graphite suffers from its low solid-state diffusion coefficient of lithium, which results in high diffusion resistance during the charge–discharge process and poor Li$^+$ storage capacity, both of which are a challenge to further application in high-performance lithium ion batteries (LIBs). Similarly, most one-dimensional carbonaceous materials, such as carbon nanotubes and carbon nanofibers, are subject to extensive capacity fading, owing to large irreversible capacities stemming from the decomposition of the electrolyte on the electrode during charge/discharge processes. Some others are unsuitable for practical application owing to their complicated chemical and physical synthesis processes.

Various attempts to improve the Li$^+$ storage capacity and cyclability of carbonaceous materials, such as decreasing the particle size, using porous forms of carbon, coating with hard carbon, and employment of one-dimensional (1D) hybrid carbonaceous materials, have been reported. However, they are still not satisfactory, due to the poor cycling stability, cost of manufacturing, and/or insufficient capacity improvement. Thus, there are still many challenges in simply synthesizing carbonaceous materials that will show high capacity and good cycling stability when employed in the lithium ion battery.

TiO$_2$(B) is a metastable monoclinic modification of titanium dioxide. The kinetics of lithium storage in TiO$_2$(B) are governed by a pseudo-capacitive faradaic process, which is not limited by solid-state diffusion of Li$^+$. TiO$_2$(B) has an open structure with freely accessible channels for Li$^+$-transport perpendicular to the (010) face, which allows easy Li$^+$ transport and fast charging of the TiO$_2$(B). Therefore, one of the possible strategies to improve the electrochemical properties of carbonaceous materials is to enhance the Li$^+$ transport and mechanical performance via introduction of the unique architecture of TiO$_2$(B)@carbon core/shell nanowires. This combination is of electrochemical interest because it is a novel one-dimensional carbonaceous composite consisting of a TiO$_2$(B) nanofiber core, which provides open channels for Li$^+$ transport, and a hard carbon shell possessing high Li$^+$ capacity. In this paper, we report novel TiO$_2$(B)@carbon core/shell nanowires prepared by a hydrothermal reaction between NaOH and TiO$_2$ powder, followed by another hydrothermal process in glucose solution and subsequent heat treatment in argon. These TiO$_2$(B)@carbon core/shell nanowires exhibit excellent discharge performance and good cyclability, revealing their potential for application in lithium ion batteries.

Experimental

Synthesis of TiO$_2$(B)@carbon composite nanowires

Synthesis of TiO$_2$(B)@carbon composite nanowires was performed by a facile two-step hydrothermal process with...
post-treatment. Typically, the precursors, titanate nanowires, were synthesized by adding 4.5 g TiO$_2$-anatase (99.8%, Aldrich) to a 15 M aqueous solution of NaOH. After stirring for 1 h, the resulting suspension was transferred to a Teflon-lined autoclave and heated at 150 °C for 72 h. The product was acid washed, which involved stirring the sample in 0.1 M HCl solution for 1 h, twice, in the parent H$_2$Ti$_3$O$_7$ nanowires.$^{18-21}$ The material was then filtered, repeatedly washed with distilled water, and dried at 80 °C for 20 h, until pH ≈ 7. Subsequently, 0.75 g of as-prepared H$_2$Ti$_3$O$_7$ nanowires was easily dispersed by ultrasonication in 15 ml of 0.8 M aqueous glucose solution. The suspension was transferred to a 30 ml Teflon-lined autoclave, which was then heated in an oven at 180 °C for at least 4 h. The product was harvested by centrifugation and washed with deionized water and ethanol, respectively, at least five times. After drying at 50 °C, the resulting brown powder was carbonized at 450 °C for 4 h under an inert atmosphere. Finally, some black powder was obtained.

Materials characterization

Thermogravimetric analysis (TGA) of the as-prepared TiO$_2$(B) supported carbon nanowires was carried out with a TGA/DSC1 type instrument (METTLER TOLEDO, Switzerland) at a heating rate of 10 °C min$^{-1}$ from 25 to 1000 °C in air. The morphology of the nanowires was evaluated using a JEOL 7500FA field emission scanning electron microscope (FE-SEM, JEOL, Tokyo, Japan) and a JEOL 2011F transmission electron microscope (TEM, JEOL, Tokyo, Japan). Energy dispersive X-ray spectroscopy (EDX, JEOL 7500FA) was used to confirm the carbon and TiO$_2$ contents. X-Ray photoelectron spectroscopy (XPS) experiments were carried out on a VG Scientific ESCALAB 2201XL instrument using aluminium K$\alpha$ X-ray radiation during XPS analysis.

Electrochemical characterization

Electrochemical properties were measured on electrodes prepared by compressing a mixture of as-prepared TiO$_2$(B) supported carbon hybrid nanowires, carbon black (Super P, MMM, Belgium), and poly(vinyl difluoride) (PVDF) binder in a weight ratio of 70 : 15 : 15 and pasting the mixture onto copper foil. Pure lithium metal foil was used for the counter and reference electrodes. The electrolyte was LiPF$_6$ (1 M) in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1 : 1 v/v; MERCK KgA, Germany). Coin cells were assembled in a high-purity argon-filled glove box (Mbraun, Unilab, Germany). The galvanostatic method was used to measure the electrochemical capacity of the electrodes at room temperature with a LAND-CT2001A instrument and a charge–discharge current density of 30 mA g$^{-1}$. Rate capability tests of the electrodes were then carried out systematically. The cut-off potentials for charge and discharge were set at 3.0 and 0.01 V versus Li$^+$/Li, respectively. To explore the contribution of the TiO$_2$ in the composite to the capacity of electrodes, the cycling performance of electrodes was also investigated with cut-off potentials of 3.0 and 1.0 V versus Li$^+$/Li, respectively. Cyclic voltammetry was performed on a ChI660B electrochemical workstation.

Results and discussion

As shown in Fig. 1, although no sharp characteristic peaks appear, possibly owing to the poor crystallinity of the titanate after the hydrothermal process and the interference of the high carbon content in the TiO$_2$@carbon nanowires, according to the TGA result (see Supporting Information Fig. S1†), the X-ray diffraction (XRD) patterns of the as-synthesized parent titanate nanowires and TiO$_2$(B)@carbon hybrid nanowires still reveal that the titanate nanowires are initially H$_2$Ti$_3$O$_7$ with a monoclinic structure (JCPDS 47-0561) and undergo a subsequent partial phase transition into TiO$_2$(B) (JCPDS 74-1940), which comprises the cores of the final TiO$_2$@carbon hybrid nanowires, after the glucose-hydrothermal and the argon heat treatment processes. TiO$_2$(B) is the main detected phase of TiO$_2$@carbon hybrid nanowires and belongs to space group C2/m (12) with lattice parameters $a$ = 12.1787 Å, $b$ = 3.7412 Å, $c$ = 6.5249 Å, and $\beta$ = 107.054°, while H$_2$Ti$_3$O$_7$ is the main phase of the parent titanate nanowires belonging to the same space group C2/m (12) with lattice parameters $a$ = 16.023 Å, $b$ = 3.749 Å, $c$ = 9.191 Å, and $\beta$ = 101.45°. Obviously, the glucose-hydrothermal and following argon heat treatment processes facilitate the conversion from H$_2$Ti$_3$O$_7$ phase into TiO$_2$(B) with continuous freely accessible parallel channels.$^{18-21}$ which may enhance the Li$^+$ transport in the hybrid nanowire due to the large amount of lithium ions that can be accommodated without any remarkable distortion of structure during charge/discharge cycling.

The field-emission scanning electron microscope (FE-SEM) images clearly show a general view of randomly aligned H$_2$Ti$_3$O$_7$ nanowires with diameters of 30–120 nm and lengths extending to a few micrometres (Fig. 2(a,b)). Elemental evaporated gold nanoparticles were used to reduce the electrostatic charging during SEM imaging and can be clearly seen in Fig. 2(b). Furthermore, as shown in Fig. 2(b) and its inset, some H$_2$Ti$_3$O$_7$ nanowires have become attached together to form one thicker rod or three-dimensional (3D) microstructure. These microrods and 3D microstructures that are formed by this process are ultimately responsible for the many mesoporosities or gaps in the electrode materials, which are more favorable to the diffusion of electrolyte. After the glucose-hydrothermal process and

![Fig. 1 X-Ray diffraction patterns of as-prepared H$_2$Ti$_3$O$_7$ nanowires and TiO$_2$(B)@carbon nanowires: (a) H$_2$Ti$_3$O$_7$ nanowires with monoclinic structure (JCPDS 47-0561), (b) TiO$_2$(B)@carbon nanowires with monoclinic TiO$_2$(B) core (JCPDS 74-1940), as indexed in the patterns.](image-url)
Fig. 3 (a) TEM image and SAED pattern (inset) of single $\text{H}_2\text{Ti}_3\text{O}_7$ nanowire, (b) low-magnification TEM image and SAED pattern (inset) of $\text{H}_2\text{Ti}_3\text{O}_7$ nanowires, (c) TEM image and SAED pattern (inset) of single TiO$_2$(B)@carbon composite nanowire, (d) HRTEM image of a section of a TiO$_2$(B)@carbon composite nanowire.

and their high-resolution spectra are shown in Fig. 4(a–c), respectively. Fig. 4(a) displays the high resolution spectrum of the Cl$_1$s region of the as-prepared TiO$_2$(B)/C composite fitted to four peaks, including un-oxidized graphic carbon. The two large peaks at 285.0 eV and 285.42 eV are attributed to hydrocarbon, while the peak at 286.31 eV can be assigned to disordered carbon or oxidant carbon, such as in alcohols. As shown in Fig. 4(b), a portion of the response could come from TiO$_2$, as evidenced by the O1s binding energy (BE) peak at ~530.73 eV, while the peak at 532.31 eV may be due to the OH radical, adsorbed oxygen, or carbonyl. As for the high BE peak at 533.92 eV, it possibly originates from alcohol or adsorbed H$_2$O, which is in good accordance with the fitted Cl$_1$s peaks. The Ti2p spectrum (Fig. 4(c)) for TiO$_2$(B)/C comprises two symmetrical peaks with BEs at 459.13 eV and 464.92 eV, which are attributable to Ti2p3/2 and Ti2p1/2, respectively. The separation between these two peaks is 5.79 eV, slightly larger than the energy splitting reported for TiO$_2$. The cause is possibly the encapsulation of TiO$_2$(B) in carbon. From a combination of the XRD, FE-SEM, TEM, and XPS results, it is concluded that the synthesized TiO$_2$(B)/C hybrid nanowires consist of TiO$_2$(B) and carbon. After the glucose-hydrothermal process and following heat treatment, the parent $\text{H}_2\text{Ti}_3\text{O}_7$ nanowire is converted into TiO$_2$(B)/C nanowire, consisting of a TiO$_2$(B) crystal core inside a shell of porous hard carbon. In addition, some mesoporosities or gaps are formed by thicker rods (Fig. 2(a–b)) and 3D microstructures in the sample, all of which favor the enhancement of the electrochemical performance of the electrode.

The electrochemical performance of the TiO$_2$(B) supported carbon hybrid nanowire electrode was systematically investigated (Fig. 5). Cyclic voltammograms (CVs) of TiO$_2$(B) supported carbon hybrid nanowires from the first to the fifth cycle at a scan rate of 0.1 mV s$^{-1}$ in the voltage range of 0.01–3.0 V were obtained and are presented in Fig. 5(a). The first cycle curve is different from the other ones, possibly owing to the formation of a solid/electrolyte interphase (SEI) on the surface of the active

Fig. 2 FE-SEM images of as-synthesized $\text{H}_2\text{Ti}_3\text{O}_7$ nanowires and TiO$_2$(B)@carbon composite nanowires: (a) $\text{H}_2\text{Ti}_3\text{O}_7$ nanowires, (b) $\text{H}_2\text{Ti}_3\text{O}_7$ nanowires at high magnification and at higher magnification (inset), (c) TiO$_2$(B)@carbon composite nanowires, (d) single TiO$_2$(B)@carbon composite nanowire with porous surface structure. (Gold nanoparticles with grain size of ~5–10 nm were evaporated on the surface of the $\text{H}_2\text{Ti}_3\text{O}_7$ nanowire samples to reduce electrostatic charging during SEM imaging.)

subsequent heat treatment in argon, as shown in Fig. 2(c,d), these TiO$_2$(B)@carbon nanowires become slightly thicker than the $\text{H}_2\text{Ti}_3\text{O}_7$ nanowires, mainly owing to the encapsulation of TiO$_2$ nanowires in a single thick layer of porous hard carbon (see Fig. 2(d)), which is favorable for both lithium ion storage and Li$^+$ diffusion, possibly stemming from the high specific surface area and the many micropores in this porous carbon.

Transmission electron microscopy (TEM) of the as-synthesized $\text{H}_2\text{Ti}_3\text{O}_7$ nanowires and TiO$_2$(B) supported carbon hybrid nanowires provides further structural and morphological information (Fig. 3). Each $\text{H}_2\text{Ti}_3\text{O}_7$ nanowire is a monocrystal with monoclinic structure (Fig. 3(a) and its inset), which is similar to the results of Peng’s group. However, due to the random orientation of the $\text{H}_2\text{Ti}_3\text{O}_7$ nanowires, as shown in Fig. 3(b) and the selected area electron diffraction (SAED) pattern in its inset, the $\text{H}_2\text{Ti}_3\text{O}_7$ nanowires are collectively characterized by a polycrystalline ring-shaped SAED pattern. As shown in Fig. 3(c), TiO$_2$(B)@carbon nanowires, inheriting the monoclinic structure characteristics of $\text{H}_2\text{Ti}_3\text{O}_7$ nanowires, also extend along the [010]$_B$ direction. Additionally, there is a very thick layer of carbon on the surface of the TiO$_2$(B) nanowires (Fig. 3(c,d)), and this carbon layer forms an effective core/shell 1D structure in conjunction with the TiO$_2$(B) nanowire itself. Consequently, the TiO$_2$(B) core in the hybrid nanowire provides a continuous channel favorable to Li$^+$ transport along the length axis of the nanowire, as well as providing a mechanical support function for the high content of porous carbon, up to 36.67% by weight (Fig. S2†). This TiO$_2$(B) support, to some extent, helps to alleviate the stress produced during lithium intercalation/deintercalation.

As shown in Fig. 4, X-ray photoelectron spectroscopy (XPS) analysis of the TiO$_2$(B)/C hybrid nanowires was conducted from 0 to 1100 eV. Obvious Cl$_1$s, O1s, and Ti2p peaks were detected, as determined from deintercalation.

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material. In the first cycle, the cathodic/anodic peak pair at 0.012 V and 0.14 V is associated with lithium ion insertion into/extraction out of the carbon material, while another cathodic/anodic peak pair at around 0.6 V suggests the decomposition of solvent, with the decomposition products acting as an SEI on the surface of the carbonaceous shells. There remain three cathodic/anodic peak pairs at 1.46 V and 1.57 V, 1.55 V and 1.72 V, and 1.74 V and 2.0 V in the first cycle curve, which are possibly attributable to lithium ion insertion into/extraction out of TiO2 in the composite. Notably, the three cathodic/anodic peak pairs in the first cycle finally merge into one cathodic/anodic peak pair at 1.46 V and 1.72 V in the subsequent cycles, probably because of the fundamental variation in the charge transport mechanisms from diffusion-confined charge transport to surface-confined charge transport in this TiO2(B)/C composite electrode, with the carbon shell being activated by the lithium ion insertion during the first cycle. Additionally, beginning from the 3rd CV cycle, the electrode delivers good reversible behavior.

The cycling performance of the TiO2(B)/C composite electrode from the 1st to the 100th cycle was obtained at a constant current of approximately 30 mA g⁻¹, with a cut-off voltage window of 0.01 V to 3.0 V (versus Li/Li⁺). Fig. 5(b) displays the voltage profiles of electrochemical cells containing these TiO2(B)@carbon composites at the current density of 30 mA g⁻¹. The voltage profiles indicate that the composite electrode has the typical characteristics of a carbon nanomaterial electrode. The first discharge and charge steps deliver a specific capacity of 1278 and 673 mAh g⁻¹, respectively. The large initial capacity loss of the TiO2(B)@carbon composite electrode can be partly attributed to the formation of a thick SEI layer on the electrode surface during the first discharge step and the high specific surface area of the porous carbon in the TiO2(B)@carbon composite, which

**Fig. 4** XPS high-resolution spectra of the (a) C1s, (b) O1s, and (c) Ti2p regions of as-prepared TiO2(B)@carbon composite nanowires.  

**Fig. 5** Electrochemical performance of TiO2(B)@carbon composite nanowires electrode cycled between 0.01 and 3.0 V vs. Li+/Li: (a) cyclic voltammograms of TiO2(B)@carbon composite nanowires electrode from the first cycle to the fifth cycle at a scan rate of 0.1 mV s⁻¹ in the voltage range of 0.0–3.0 V. (b) Voltage profiles for selected cycles of TiO2(B)@carbon composite nanowires composite electrode at the current density of 30 mA g⁻¹. (c) Capacity vs. cycle number curves from the first cycle to the 100th cycle for the TiO2(B)@carbon composite nanowires at the current density of 30 mA g⁻¹. (d) Discharge capacity of TiO2(B)@carbon composite nanowires electrode as a function of the discharge rate (30, 150, 300, 750 mA g⁻¹); the inset is the discharge capacity–rate capability curve of the TiO2(B)@carbon composite nanowires electrode.
sacrifices a much higher quantity of irreversible Li\(^+\) to form the SEI layer as compared with common carbonaceous materials. In addition, the high content of amorphous or disordered carbon in the composite is likely to be partly responsible for the high initial irreversible capacity because of the relatively low carbonization temperature for our sample. Fig. 5(c) shows the curves of discharge capacity versus cycle number for the TiO\(_2\)(B)@carbon composite electrode at the current density of 30 mA g\(^{-1}\). The TiO\(_2\)(B)@carbon composite electrode exhibits good cyclic performance and a high reversible specific capacity of over 705 mAh g\(^{-1}\) in the first 10 cycles, and it maintains a reversible capacity after 100 cycles of approximately 560 mAh g\(^{-1}\). Fig. 5(d) shows the rate capability of the TiO\(_2\)(B)@carbon composite electrode, which delivers a capacity of about 711 mAh g\(^{-1}\) at the current density of 30 mA g\(^{-1}\) after 6 cycles. This value decreases to 482 mAh g\(^{-1}\) at the current density of 150 mA g\(^{-1}\), 364 mAh g\(^{-1}\) at the current density of 300 mA g\(^{-1}\), and 200 mAh g\(^{-1}\) at the current density of 750 mA g\(^{-1}\).

The excellent electrochemical performance of the TiO\(_2\)(B)/C composite electrode is probably due to its special morphology. As demonstrated in Scheme S1 (Supporting Information†), the TiO\(_2\)(B)@carbon composite nanowire, consisting of a TiO\(_2\)(B) crystal core inside a shell of porous hard carbon, possesses one continuous channel along its axis, which is favorable for lithium ion diffusion during charge/discharge processes. For comparison, the cycling performances of the TiO\(_2\)(B)/C composite electrode between 1.0 and 3.0 V vs. Li\(^+\)/Li and the glucose-hydrothermal process-derived pure carbon electrode between 0.01 and 3.0 V vs. Li\(^+\)/Li were also investigated under the same conditions and are shown in Fig. S3 and S4† respectively. The capacity portion mainly attributable to the fact that TiO\(_2\)(B) in the composite electrode is very low and fades quickly (see Fig. S3†), as compared with Fig. 5(c). The initial discharge capacity of the pure carbon electrode is as high as 1148.4 mAh g\(^{-1}\), even though the cycling performance of the pure carbon electrode is poor (see Fig. S4†), which is probably attributable to larger particles or agglomerates in the morphology of the pure carbon derived from the direct glucose-hydrothermal method than for the one-dimensional porous carbon on the TiO\(_2\)(B)@carbon composite nanowires. Accordingly, it is the one-dimensional porous hard carbon shell in this special morphology, not the pure carbon that, to some extent, accelerates diffusion for both electrons and lithium ions, ensuring a high electrode-electrolyte contact area and eventually making the greater part of the contribution to the capacity. Moreover, the TiO\(_2\)(B) core, to some extent, also acts as an effective mechanical support to alleviate the stress produced during lithium intercalation/deintercalation and preserve the one dimensional core/shell structure even after 100 charge/discharge cycles, as shown in Fig. 6(a,b) and its inset. In addition, the mesoporosities or gaps formed by thicker rods and 3D microstructures (see Fig. 2(c,d)) in the sample are helpful in improving the electrochemical performance of the electrode, possibly because of their contribution to the electrolyte or lithium ion diffusion during charge/discharge processes.

Conclusions

In summary, a novel TiO\(_2\)(B)/C composite, namely, TiO\(_2\)(B)@carbon composite nanowires consisting of a TiO\(_2\)(B) core encapsulated in a porous carbon shell, has been successfully synthesized by an alkali hydrothermal method, followed by another hydrothermal process in glucose solution and subsequent heat treatment in argon. As a potential anode material for lithium ion batteries, this composite displays a high reversible capacity of 560 mAh g\(^{-1}\) after 100 cycles at the current density of 30 mA g\(^{-1}\). It also exhibits a reversible discharge capacity of 200 mAh g\(^{-1}\) when cycled at the current density of 750 mA g\(^{-1}\). This novel TiO\(_2\)(B)/C composite core/shell structure has one continuous channel along its axis, facilitating lithium ion diffusion and effective mechanical support of the TiO\(_2\)(B) core, alleviating the stress produced during charge/discharge processes. This composite is very promising as a potential anode material for LIBs, even though the composition and structure of these materials require further improvement.

Acknowledgements

Part of the work was funded by an Australian Research Council (ARC) Linkage Grant (DP1094261), the Postdoctoral Foundation Program of Fuzhou University (BSH-0601), the Natural Science Foundation Program of Fujian Province (2010J01332, A0510011), and the Talent Foundation Program of Fuzhou University. The authors also would like to thank Dr Tania Silver at the University of Wollongong for critical reading of the manuscript and Mr Attard Darren for his great contribution.

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