

TiO₂ Branched Nanostructure Anode Material Prepared by Seeding Method for High-performance Lithium Ion Batteries

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Abstract : We demonstrate rutile TiO₂ branched nanostructure (TiO₂-BN) electrodes synthesized by seeding method for enhanced lithium intercalation properties. The morphology and crystalline nature of the TiO₂-BN were clearly observed by field-emission transmission electron microscopy and fast Fourier transform pattern. The TiO₂-BN electrodes showed excellent capacity and high rate performance. The improved lithium-ion intercalation properties of the TiO₂-BN may be attributed to relatively large specific surface area and short transport distance of the branched nanostructure.

Keywords : Branched nanostructure, Lithium ion batteries, Rutile, TiO₂

1. Introduction

Lithium-ion batteries (LIBs) are essential portable power sources because of their high-energy density, high-power density, and long cycle life.^{1,2)} Typically, graphite-based materials have been a typical anode material to apply commercial LIBs. Because of several disadvantages of graphite anode materials such as initial capacity loss and structural deformation, it is urgently required to develop novel materials and structures with high-performance lithium intercalation.^{3,4)} As an alternative of graphite, titanium dioxide (TiO₂) utilized in a variety of applications such as photocatalytic activity,^{5,6)} catalyst supports,⁷⁾ and gas sensors⁸⁾ is regarded as a promising lithium insertion/extraction material with low production cost and high capacity.⁹⁾

TiO₂ nanostructured materials such as nanorods, nanowires, and nanotubes have been studied in order to achieve excellent LIBs with high energy density, large capacity, rate performance and long cycle life.^{10,11)} Considerable efforts have been made to explore diverse synthetic methods ranging from

vapor-phase techniques to solution-growth processes for the synthesis of nanostructure TiO₂.¹²⁾ In particular, it is well known that various types of TiO₂ nanostructures can be synthesized through strong acid treatment under hydrothermal or non-hydrothermal conditions.¹³⁾

Herein, we synthesized rutile TiO₂ branched nanostructures (TiO₂-BNs) for LIBs via hydrothermal process without any surfactant and template. The structural characterization of the TiO₂-BNs was performed using high-resolution transmission electron microscopy (HR-TEM), fast Fourier transform (FFT), X-ray diffraction (XRD) analysis, and nitrogen sorption measurement. To analyze the performance for LIBs using the TiO₂-BNs as an anode, charge-discharge and rate cycling curves of the electrodes were measured using a lithium coin cell at room temperature.

2. Experimental

For the preparation of seeds of TiO₂-BNs, 8 mL of titanium(IV) isopropoxide (TTIP (97%), Aldrich) was dropped in 40 mL of 10 M hydrochloric acid (HCl (35%), Aldrich) with constant stirring at 25°C

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for 1 h and then kept at 120°C for 24 h. After the hydrothermal process, the resulting precipitates were cooled to room temperature, washed several times with ethanol and distilled water, and then precipitated using centrifuge at 10,000 rpm. The white TiO₂ seeds were obtained after drying at 50°C oven. The TiO₂-BN was synthesized by means of a seeding method with TiO₂ seeds. The seed-solution (12 wt%) was injected in 30 mL of 0.5 M HCl with constant stirring at 25°C and then kept constant for 15 min. After that, the 2 mL of TTIP as precursor was dropped in mixture solution and kept constant for 1 h and kept at 90°C for 4 h. The resulting precipitates were cooled to 25°C, washed several times with ethanol and distilled water, and precipitated using centrifuge at 8,000 rpm, and then dried at 50°C drying oven.

The morphology and size distribution of the samples were characterized by FE-TEM (a Tecnai G2 F30 system) operating at 300 kV. TEM samples were prepared by placing drops of powder suspension dispersed in ethanol on a carbon-coated copper grid. XRD analysis was carried out using Rigaku X-ray diffractometer with Cu K_α ($\lambda = 0.15418$ nm) source with a Ni filter. The source was operated at 40 kV and 100 mA. The 2θ angular scan from 20° to 60° was explored at a scan rate of 5° min⁻¹. The resolution in the scans was kept at 0.02°. Nitrogen adsorption and desorption isotherms were measured at 77 K using a Micromeritics ASAP 2020. Before the adsorption measurements, all samples were outgassed at 473 K for 360 min in the port of the adsorption analyzer. The starting relative pressure was 0.995 P/P° and ending relative pressure was 0.01 P/P°.

The electrodes were prepared by mixing 70 wt% TiO₂-BN as an active material, 20 wt% acetylene black as a conducting agent, and 10 wt% polyvinylidene fluoride (PVDF) as a binder. In order to obtain the slurry, several drops of N-methylpyrrolidone were added into the mixture of TiO₂-BN with acetylene black and PVDF. The prepared slurry was homogenized by stirring and then coated uniformly on ~11 μ m thick copper foil substrates. The electrode dried in an oven at 80°C for 12 h and then cooled down to room temperature. The cells were assembled in a high purity argon filled

glove box using the TiO₂-BN as the working electrode and lithium foil as the counter and reference electrodes and a separator that was saturated with the electrolyte solution that consisted of 1.1 M LiPF₆ dissolved in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) with a volume ratio of EC/DMC = 1:1.

The lithium intercalation properties of the assembled cells were recorded with charge/discharge curves between 3.0 and 1.0 V. The charge/discharge tests were galvanostatically cycled between 3.0 and 1.0 V for 100 cycles at a current rate of 1 C. After charge/discharge tests for 5 cycles at a current rate of 0.5 C, rate cycle performance tests were also carried out at various current rates from 0.5 to 20 C in order to confirm the rate capability. All of the lithium intercalation measurements were completed at room temperature.

3. Results and Discussion

As shown in Fig. 1(a) and (b), the TiO₂-BNs obtained by a seeding method seem to be a three-dimensional structure with branches grown along one-dimensional backbones. The diameter and length of the TiO₂-BNs are ~20 and ~110 nm,

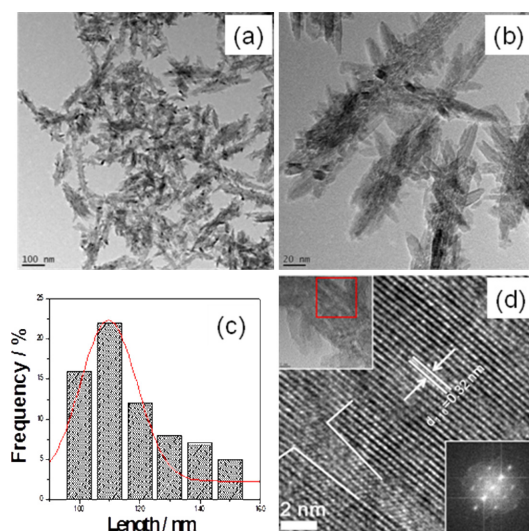


Fig. 1. (a), (b) TEM images of TiO₂-BNs; (c) Size-distribution histogram of TiO₂-BNs; (d) HR-TEM image of TiO₂-BNs (The insets indicate a TEM image of TiO₂-BNs and the corresponding FFT pattern.).

respectively (Fig. 1(c)). As shown in Fig. 1(d) of high-resolution TEM image, the $\text{TiO}_2\text{-BN}$ was exposed to (110) plane corresponding to d -spacing of 0.32 nm. The FFT pattern of the inset in the Fig. 1(d) indicates the (101) and (110) plane of rutile phases. Fig. 2 shows the XRD pattern of the $\text{TiO}_2\text{-BNs}$ representing rutile phase with tetragonal crystal structure ($a = b = 0.452$ nm, $c = 0.294$ nm, space group $P4_2/mnm$). According to the reference (JCPDS No. 88-1175) of the TiO_2 rutile phase, the

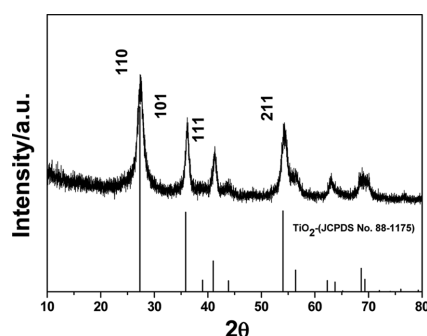


Fig. 2. Wide-angle XRD pattern of $\text{TiO}_2\text{-BNs}$.

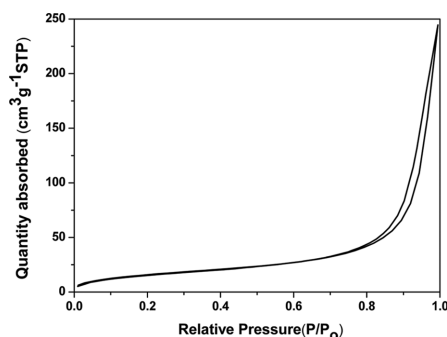


Fig. 3. Nitrogen adsorption/desorption isotherm curve of $\text{TiO}_2\text{-BNs}$.

$\text{TiO}_2\text{-BNs}$ show the similar intensity ratio of the principal XRD peaks to that of the reference. As shown in Fig. 3. The BET specific surface area of the $\text{TiO}_2\text{-BNs}$ is $\sim 60.3 \text{ m}^2 \text{ g}^{-1}$ and is much larger than that of the typical rutile TiO_2 nanoparticles.⁹⁾

Fig. 4(a) shows 1st and 2nd discharge-charge curves of the $\text{TiO}_2\text{-BNs}$ at a current density of 1 C. At the cycling rate of 1 C, the first charge capacity of the $\text{TiO}_2\text{-BNs}$ is $300 \text{ mAh} \cdot \text{g}^{-1}$ and much larger than that of the typical rutile TiO_2 electrode.⁹⁾ Furthermore, the $\text{TiO}_2\text{-BNs}$ as a rutile TiO_2 electrode exhibit an irreversibility between 1st and 2nd cycle and two plateaus due to phase transition from rutile to spinel and then rock salt.^{14,15)} The cycling performance and coulombic efficiency of the $\text{TiO}_2\text{-BNs}$ at a current rate of 1 C for 100 cycles are indicated in Fig. 4(b). The $\text{TiO}_2\text{-BNs}$ exhibit the reversible capacity of $\sim 190 \text{ mAh} \cdot \text{g}^{-1}$ and high coulombic efficiency of $\sim 92.5\%$ up to 100 cycles. To investigate rate cycling performance of the $\text{TiO}_2\text{-BN}$ electrode, the discharge-charge rates were increased stepwise from 0.5 to 20 C as indicated in Fig. 4(c), the specific charge capacities of $\text{TiO}_2\text{-BNs}$ are $215 \text{ mAh} \cdot \text{g}^{-1}$ at 0.5 C; $119 \text{ mAh} \cdot \text{g}^{-1}$ at 5 C; $43 \text{ mAh} \cdot \text{g}^{-1}$ at 20 C. This represents that even at high current rates from 5 to 20 C, $\text{TiO}_2\text{-BNs}$ can display an excellent rate cycling performance. The remarkably large capacity of $216 \text{ mAh} \cdot \text{g}^{-1}$ can be obtained when the current rate is returned to 0.5 C after 60 cycles at different current rates. The improved lithium-ion intercalation properties of $\text{TiO}_2\text{-BNs}$ may be attributed to large specific surface area, short transport distance of nanostructure, and freedom for volume change accompanied by lithium-ion intercalation.¹⁶⁾

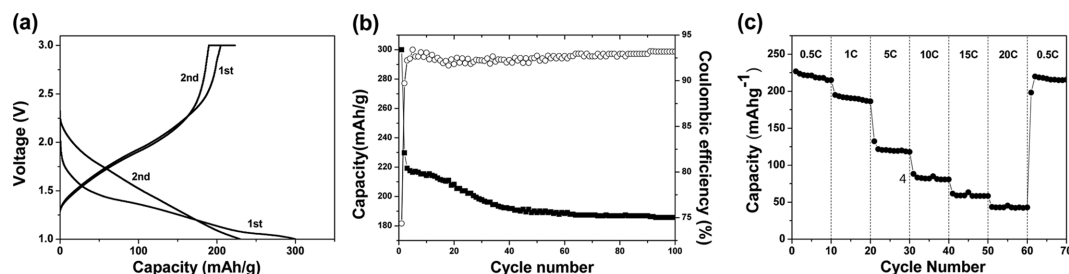


Fig. 4. (a) 1st and 2nd discharge-charge curves of the $\text{TiO}_2\text{-BNs}$ at a current density of 1 C; (b) The cycling performance and coulombic efficiency of the $\text{TiO}_2\text{-BNs}$ at a current rate of 1 C for 100 cycles; (c) Rate capability of the $\text{TiO}_2\text{-BNs}$ from 0.5 C to 20 C.

4. Conclusions

In summary, using seeding method in hydrothermal process without any surfactant and template, we have prepared three-dimensional TiO₂-BN anode materials. The TiO₂-BNs showed large capacity, high coulombic efficiency, and excellent high rate cycling performance in lithium intercalation properties, and the facilitating lithium ion motion in the nanostructure electrode.

Acknowledgments

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