Na$_2$Ti$_7$O$_{15}$ Nanowires with an Oriented Tunnel Structure and High Mechanical Stability: A Potential Anode of Sodium-Ion Batteries and Gas Sensing Materials

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Featured Application: Sodium-ion batteries and gas sensing materials.

Abstract: Na$_2$Ti$_7$O$_{15}$ (NTO) can be selected as candidate anode for high-performance sodium-ion batteries (SIBs). However, there are few reports of research on the mechanical properties of low-dimensional NTO, which is important for the stability of SIBs. In this work, by using the one-step hydrothermal method, NTO nanowires (NWs) with good orientation were prepared successfully. The transmission electron microscopy (TEM) and selected area electron diffraction (SAED) showed that the NTO NWs had a good aspect ratio and dispersion, with lengths over 20 µm. Further microstructure analysis showed that the nanowires grew along the (020) direction, and there were some “stripe” structures along the growing direction, which provides a good tunnel structure for Na ion channels. Further, the in situ mechanical analysis showed that the NTO NWs had excellent elastic deformation characteristics and mechanical structural stability. In addition, the NTO NWs also showed a good gas sensitivity to NO and NH$_3$. Our results showed that the prepared NTO nanowires with a stripe tunnel oriented-structure and excellent mechanical properties may have a potential application in SIBs or other wearable sensor devices.

Keywords: Na$_2$Ti$_7$O$_{15}$; nanowires; tunnel structure; mechanical properties; sodium-ion batteries

1. Introduction

Sodium titanate, as a typical alkali titanate, has attracted much attention in recent years [1,2]. The corresponding one-dimensional nanostructures, such as nanowires [3], nanorods [3,4], nanotubes [5–7], and nanofibers [8,9], consisting of titanium oxide layer and interlayer Na ions, possess novel photocatalytic properties and can be used as gas potentiometric sensors [10], electrochemical storage [11], and for the adsorptive removal of heavy metals [8]. It is also of interest for bioactive material research [12,13]. For the preparation of nanoscale sodium titanate, there are many methods, such as hydrothermal treatment on a template [5], a hydrothermal reaction in alkaline solution [11], and the sol-gel method using alkoxide precursors [10]. Based on our previous study, during the hydrothermal synthesis process of bismuth sodium titanate [14], it was found that under super precursor concentrations, one-dimensional sodium titanate structures will be generated, which are
usually considered as intermediate products [15]. Some nanofibers of NaTi$_2$O$_4$ or Na$_2$Ti$_4$O$_9$ have been found in our previous work [14]. Recently, Na$_2$TiO$_{15}$ (NTO) nanotubes with a tunnel structure have been used for the anode materials of sodium ion batteries (SIBs), showing a high reversible capacity and excellent stability [7]. By first-principles calculations, the doping modulation of NTO can also enhance the electronic conductivity as an anode material for SIBs [16]. However, to the best of our knowledge, there are few studies on the mechanical properties of nanostructured NTO, which is critical to the stability of SIBs [17]. During repeated charge–discharge cycles, the anode materials always undergo huge volume changes [18]. Therefore, for the stability of SIBs, the excellent mechanical properties (such as big elastic deformation and high Young’s modulus) of the anode materials should be studied.

As a metastable structure in the Na$_2$Ti$_{2n}$O$_{2n+1}$ series, the microstructure and mechanical properties of Na$_2$Ti$_7$O$_{15}$ have been rarely reported [2,7,16,19]. In this paper, using the one-step hydrothermal method, Na$_2$Ti$_7$O$_{15}$ nanowires (NTO NWs) with good orientation and a large aspect ratio were prepared successfully. This was accompanied by Na$_{0.5}$Bi$_{0.5}$TiO$_3$ hydrothermal synthesis at a relatively low reaction pressure, which can be extracted by phase separation technology. The microstructure analysis showed that the NTO NWs were growing along the (020) direction, and there were some “stripe” super lattices along the growing direction, which may be beneficial for the transport of Na ions in SIBs. Moreover, based on the analysis of the in situ microscopic mechanical characteristics, the as-prepared NTO NWs had excellent mechanical properties, fitting for the stability of SIBs. Our studies may suggest a new candidate anode material for high-performance SIBs.

2. Materials and Methods

2.1. Hydrothermal Synthesis

In this work, the Na$_2$Ti$_7$O$_{15}$ nanowires were a by-product of the ferroelectric Na$_{0.5}$Bi$_{0.5}$TiO$_3$ particles synthesized using a hydrothermal method at relatively low reaction pressure. Titanium dioxide (TiO$_2$) was used as a titanium source, employing NaOH as both the sodium source and the mineralizer. The detailed growth procedure was as follows: Firstly, dissolving NaOH into distilled water with a concentration of 16 mol/L, adding the mixture of 0.25 mol/L Bi(NO$_3$)$_3$·5H$_2$O and 0.5 mol/L TiO$_2$, and stirring for 1 h. Then, the mixture of NaOH solution was transferred into a Teflon-lined stainless-steel autoclave, and the filling volume was 50% of the total volume, which is less than the 80% filling level for an optimal Na$_{0.5}$Bi$_{0.5}$TiO$_3$ product [14]. Subsequently, the reactor was sealed with steel cans and heated at 200 °C for 70 h, followed by slow furnace cooling to room temperature. Finally, opening the stainless-steel autoclave, two solid products were observed: a quantity of white foam in the upper part of the reactor, and the pancake powder (Na$_{0.5}$Bi$_{0.5}$TiO$_3$ particles) at the bottom. The upper white foam product was separated and extracted gently. Eventually, the extracted white product was filtered and washed with deionized water several times until the pH value of the supernatant approached 7, then dried in a vacuum oven at 60 °C for 48 h.

2.2. Structural and Mechanical Characterization

The morphology and composition morphology of the as-synthesized products were characterized by field-emission scanning electron microscope (SEM, Hitachi S-4800, Tokyo, Japan) with an energy dispersive spectrometer (EDS). The microscopic morphology and selected area electron diffraction (SAED) pattern of the products were characterized using transmission electron microscopy (TEM, FEI-Titan 60-300 G2; and JEOL-2010). A commercial scanning tunneling microscope-transmission electron microscope probing system (STM-TEM, Nanofactory Instruments) and a self-designed scanning electron microscope-scanning probe microscope (SEM/SPM) joint system were applied to study in situ the microscopic mechanical properties of the as-prepared nanowires.
3. Results and Discussion

3.1. Morphology and Structural Analysis

The obtained white powder samples were dispersed by ultrasound treatment and observed by scanning electron microscopy (SEM) for a panoramic view. It was found that they were one-dimensional nanostructures. As shown in Figure 1a, the length was more than 20 μm and the width varied from tens to hundreds of nanometers. It is clear that the as-prepared nanowires were well-shaped and uniform, with a good aspect ratio and dispersion. Figure 1b shows the EDS spectrum taken from the nanowires, which shows that the nanowires contained Na, Ti and O. This suggested that the nanowires are a kind of alkali sodium titanate. The nanowires samples were further analyzed by TEM, as shown in Figure 1d–g. Figure 1d,e show one nanowire and its corresponding selected area electron diffraction (SAED) pattern, and Figure 1f,g show another nanowire and its corresponding SAED pattern. Based on the SAED analysis, the nanowires were identified as a NTO phase, and all the nanowires grew along the (020) direction. For the Na2Ti7O15 phase (space group No. 8, Cm), the schematic atomic structure observed along b axis is shown in Figure 1c, in which alternating groups of three and four TiO6 octahedra share corners and edges to form a tunnel structure along the b axis, and Na⁺-ions are located within the tunnels [7].

![Figure 1](image.png)

**Figure 1.** Morphology, component and structure of the as-prepared Na2Ti7O15 nanowires. (a) SEM image; (b) EDS spectrum; (c) Schematic representation of the structure of Na2Ti7O15; (d,e) TEM image of one selected nanowire and its corresponding SAED pattern with the incident electron beam direction along (100) zone axis; (f,g) TEM image of another selected nanowire and its corresponding SAED pattern observed along the (100) zone axis.

Furthermore, a nano-region was selected on the nanowire sample (see the inset in Figure 2a) and further observed using aberration-corrected TEM. As shown in Figure 2a, the high resolution TEM (HRTEM) image shows that there were some “stripe” structures along the growth direction in the nanowires. Figure 2b shows the fast Fourier transform (FFT) pattern corresponding to the selected region (red frame) in Figure 2a, which shows the HRTEM that was observed along the (100) zone axis and the "stripe" structures along the b axis of Na2Ti7O15. In addition, some fine stripes between the diffraction spots in the SAED patterns (Figure 1e,g) and the FFT pattern (Figure 2b) reveal that there were some stacking faults parallel to the (001) plane. Further enlarging some areas in Figure 2a,
Figure 2c shows a clearer HRTEM image of the “stripe” structures. It is obvious that the “stripe” structures consist of the bright and dark atomic planes parallel to the (001) plane. However, it was difficult to identify the channel structure along b axis from the projected unit cell of Na2Ti7O15 along the (100) direction, because of its complicated atomic structure and the undetermined HRTEM imaging condition. We produced the simulation HRTEM images based on the Na2Ti7O15 structures along the (100) observation direction, and obtained a series of simulation images with the defocus varying from −600 to 600 Å and thickness varying from 0–600 Å. By comparing the experimental HRTEM image with the theoretical simulation results, the simulation HRTEM image obtained at the condition of −100 Å (defocus) and 150 Å (sample thickness) was selected to be shown in Figure 2d. This means that the channel structure of the NTO NWs along the b axis presented a dark contrast at this sample thickness and imaging condition.

From the structural configuration of the Na2Ti7O15 in Figure 1c, the channel structure formed by sharing the corners and edges of octahedral TiO6 was only along the b axis, and the Na ions were only located inside the channel. Most interestingly, the striped NTO NWs had an oriented structure along the (020) direction (b axis), as shown in Figure 2, which was the same as the channel direction of the Na ions in the NTO NWs. The channel direction of the Na ions was just along the NTO NW growth direction, which benefits the transport of Na ions. In contrast to the structure of the nanotubes [5], the stripe structure of the NTO NWs may be advantageous for Na ion diffusion, similar to the layer anode materials in SIBs [20]. The well-shaped and uniform NTO NWs presented a good channel structure along the nanowire axial direction and the characteristics of Na ions located in the channels. These special channel structures in the NTO NWs will greatly help the transport of Na ions for high-performance SIBs.

3.2. Mechanical Properties

As mentioned above, the good morphological characteristics and tunnel structure of the NTO NWs can be used as anode materials in SIBs. However, for the stability of the SIBs, the anode materials...
should have good mechanical stability for the volume change effect in the charge–discharge process. Here, we present the experimental results of studying the in situ mechanical properties.

First, a commercial STM-TEM probing device was used to test in situ the elasticity of nanowires under transmission electron microscopy. As shown in Figure 3a, the NTO NWs were able to stand independently and had good strength, and one of the appropriate small NTO NWs was selected and extracted. The diameter of the nanowire was about 100 nm, the length was more than 10 μm, and the aspect ratio was more than 100. The STM probe was used to push the nanowire into contact with another fixed end and perform the reciprocating compression elasticity test. As shown in Figure 3b–i, the nanowire was gradually pressurized by the micro-movement of the needle tip. When the nanowire was bent into a certain curvature, the pressure on the needle tip was slowly released, and then the nanowire could be restored to the original state, thus completing one loading cycle. During the experiment, one cycle could last less than 5 s, and the nanowire could quickly restore to its original state. After ten cycles, the nanowire was still intact. This shows that the NTO NWs had good elastic deformation characteristics and mechanical structure stability. Using the maximum deformation position obtained from the in situ TEM images, the curvature radius \( r \) was about 3.81 μm, obtained by fitting Figure 3i. The nanowire diameter \( d \) of the selected NTO NW was about 0.1 μm. The elastic strain \( \varepsilon \) can be simply described by the bending deformation model:

\[
\varepsilon = \frac{d}{d + R} \times 100\%
\]

The calculated elastic strain was about 2.56%. However, with in situ tests, because one end of the nanowire is not fixed, it is not easy for the fixed end to slip on the contact surface and restore the linear shape when the external force is too large. As a result, the elastic strain limit of the NTO NWs was not reached. Due to the good recovery of the multi-cycle deformation test, it can be deduced that the actual elastic strain may be far greater than 2.56%, which will be beneficial for anode materials in high-stability SIBs [21].

**Figure 3.** In situ TEM elastic strain analysis of the NTO NW. (a) Selection and extraction in the NTO NWs for deformation test; (b–i) Different states during the deformation of the NTO NW.
For the anode materials of high-performance SIBs, a flexible structure with a low modulus of elasticity along the stress direction is necessary [22]. The elastic constant of the NTO NW was then further studied using a SEM/SPM combined system. In Figure 4a and the inset schematic diagram, the SEM images of the mechanical test and experimental model are presented. The result of the relationship curve between the load and displacement of the NTO NW, as shown in Figure 4b, is a proportional relation. Therefore, the Young’s modulus E can be computed using the following equation [23]:

\[
E = \frac{F L^3}{k \Delta d l}
\]  

(2)

Here, \(k\) is a parameter related to the boundary conditions, where \(k = 192\) when ends-clamped and \(k = 48\) when ends-free. In this test, both ends of the nanowire are free. \(F\) is the force, \(\Delta d\) is the midpoint displacement of the nanowire, \(L\) is the hanging length of the nanowire, \(l\) is the moment of inertia (for cylindrical nanowires, \(I = \frac{\pi r^4}{4}\), \(r\) is the radius of the NWs), and \(F/\Delta d\) is the slope of the loading curve. According to the measured data in Figure 4 and Equation (2), the Young’s modulus \(E\) of the NTO NWs was about 26.5 GPa. This indicates a good flexible structure perpendicular to the NW axial direction, which can suffer large stress during charging–discharging by the expansion or contraction of Na ion transport in tunnel channels.

![Figure 4](image)

**Figure 4.** In situ mechanical properties of the NTO NW measured by a SEM/SPM system. (a) SEM images of mechanical test; and schematic diagram of experimental model (the inset); (b) Relationship curve between the load and displacement of the NTO NW.

3.3. **GasSensitive Properties**

Furthermore, the gas-sensitive properties of the NTO NWs were studied using a self-assembly gas-sensitive testing system (Figure 5). The as-prepared NTO powders were mixed in alcohol to form a slurry and then coated onto the Al₂O₃ microtube to form a thick sensing film. The NTO NWs-coated microtube was then fixed with six poles, of which the four Pt electrodes were used for resistance test and the other two poles were used for connecting a heating resistance wire inserted through the microtube. Then, the resistance testing was available for the as-prepared NWs coated on ceramic cylinders with an internal heater. The changeable resistance with the gas concentration indicates the gas sensitivity of the NTO NWs. In Figure 6, it is clear that the NTO NWs have good gas sensitivity for both NO or NH₃ at 350 °C, in which the response time was about 25 s and the recovery time was about 170 s, with high stability. In view of their flexible structure and good mechanical properties, the NTO NWs can be used as the gas sensor in novel wearable nano-devices, which may be used in special high-temperature environments, such as aerospace or high-temperature reaction furnaces.
4. Conclusions

Using phase separation technology, accompanied with low reaction pressure in the liquid phase growth, \( \text{Na}_2\text{Ti}_7\text{O}_{15} \) NWs were successfully prepared. The NTO NWs had good morphology, good dispersion and a large aspect ratio. The HRTEM analysis revealed that the NW structure had Na ions for high-performance SIBs. Further in situ TEM mechanical properties showed that the NTO NWs had a large elastic strain of over 2.56% and a relatively flexible Young’s modulus of 26.5 GPa, which may be propitious to the advancement of the high reversible capacity and excellent stability of SIBs. Moreover, the as-prepared NTO NWs also showed good gas sensitivity. Our work not only suggests a potential anode material for high-performance SIBs, but also presents a good gas sensing material that can be used in flexible wearable devices.

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