Macaroni-Like Blue-Gray Nb$_2$O$_5$ Nanotubes for High-Reversible Lithium-Ion Storage

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Due to the high reliability and high theoretical capacity, lithium-ion batteries (LIBs) have been widely studied in the world. Nevertheless, the existing LIB systems currently exhibit comparatively low capacities restricted by the anode materials. Herein, blue-gray Nb$_2$O$_5$ (B-Nb$_2$O$_5$) nanotubes are prepared which are rich in oxygen vacancy by a facile chemical vapor deposition (CVD) method and a further hydrogen annealing reduction as the anode material for LIBs, presenting a high discharge capacity of 375 mA h g$^{-1}$ at 100 mA g$^{-1}$ and a good rate performance up to 5 A g$^{-1}$ with 126 mA h g$^{-1}$. The detailed ex situ X-ray diffraction (XRD) and X-ray photoelectron spectra (XPS) characterizations verified the high-reversible process, which Li$^+$ should insert/extract from the (001) planes of Nb$_2$O$_5$ crystal. Combined with a reversible PF$_6^-$ intercalation into/deintercalation from graphite cathode, a B-Nb$_2$O$_5$/graphite dual-ion cell can run about 50 cycles with the discharge capacity retention approaching 23 mA h g$^{-1}$ at 100 mA g$^{-1}$. The importance of the modulation of morphology and vacancy in improving overall electrochemical performance is highlighted.

1. Introduction

For increasing demands of high-performance energy storage system in electric vehicles and personal electronics, lithium-ion batteries (LIBs) have triggered intensively research interest because of high energy density and long-term cycle performance.[1–6] Graphite, as a current commercial anode material, shows poor theoretical capacity (about 372 mA h g$^{-1}$) that restricts the capacity of the whole device.[7] Thus, it is highly desirable to search for low-cost anode materials with high specific capacity and long-term cyclability. In this regard, transition-metal oxides, such as MnO$_2$,[8,9] MnO$_2$,[10] Mn$_3$O$_4$,[11] Co$_3$O$_4$,[12,13] CuO,[14,15] Fe$_3$O$_4$,[16,17] and Fe$_2$O$_3$,[18,19] sulfides like Co$_1$–S,[20] and carbides[21,22] have been extensively exploited because of their high rechargeable capacities. Among them, Nb$_2$O$_5$ is a potential material in energy storage like lithium-/sodium-ion batteries or supercapacitors,[23–30] except for its applications in photocatalytic,[31] electron transport layer in solar cell,[32,33] and electronic-like electron field emitters.[34] Nb$_2$O$_5$ shows so many admirable attributes including adjustable morphologies, controllable crystal type, and easy to synthesis that makes it be a kind of promising anode materials. Compared with industrialized carbon anode, Nb$_2$O$_5$ possesses better rate performance and power density.[7] Moreover, high-performing silicon–carbon anode still suffer from the severe volume expansion,[35] whereas the Nb$_2$O$_5$ presents a higher structural stability and minimal volume expansion (less than 5%).[36] Furthermore, it has been applied in aluminium-ion battery system with an impressive specific capacity of $\sim$563 mA h g$^{-1}$[37] and showed an anomalously fast energy storage behavior in LIBs.[23,24] Qu et al. reported flower-like T-Nb$_2$O$_5$[38] and T-Nb$_2$O$_5$-based composite[39,40] for improved performance LIB anode, delivered specific capacity range from 178.2 to 332 mA h g$^{-1}$ after 100 cycles at 0.2 A g$^{-1}$ current density. All these suggested the crystal structure of Nb$_2$O$_5$ may be a suitable host material for the high-rate insertion/extraction of metal ions. However, most of developed Nb$_2$O$_5$ release its merit in fast charging and discharging by composting with conductive substrate such as graphene[41] and silver,[46] or creating defect after the introduction of extraneous element such as nitrogen[36] via fussy preparation method.

In this work, blue-gray Nb$_2$O$_5$ (B-Nb$_2$O$_5$) nanotubes were prepared by a facile chemical vapor deposition (CVD) method from a single NbCl$_5$ precursor followed by a further 4h hydrogen annealing reduction at 600 °C. It was different from the typical preparation methods that contained multiple raw materials and time-consuming reactions with hazardous hydrofluoric acid.
The obtained Nb2O5 showed a well-defined morphology and blue-gray color originating from the oxygen vacancy defect. Working as an anode of LIBs, the Nb2O5-based battery delivered a high discharge capacity of about 300 mA h g$^{-1}$ at the current density of 0.5 A g$^{-1}$ with coulombic efficiency approaching 100% after 500 cycles based on the reversible insertion/extraction of Li$^{+}$ into/from the (001) planes of Nb2O5 crystal. In addition, a prototype Nb2O5/graphite dual-ion battery can be also operated normally, indicating a good versatility.

2. Result and Discussions

We prepared blue-gray oxygen vacancy Nb2O5 (B-Nb2O5) nanotubes by one-step CVD and further hydrogen annealing reduction, as schematically shown in Figure 1a. Typically, anhydrous NbCl5 powder was calcined and evaporated in a tube furnace at the temperature of 600 °C for 4 h. As thus, white Nb2O5 nanotubes (W-Nb2O5 nanotubes) were obtained in the intine of the quartz tube of furnace. Then W-Nb2O5 nanotubes were reduced by the hydrogen to obtain B-Nb2O5 nanotubes (Figure S1, Supporting Information). As control, commercial Nb2O5 powder were also reduced at the same conditions (denote C-Nb2O5). Electron microscopy was used to characterize the morphology. As shown in Figure 1b–d, scanning electron microscopy (SEM) images revealed that B-Nb2O5 nanotubes were uniform nanotubes with diameter ≈150 nm and length range from 5 to 10 μm. The transmission electron microscopy (TEM) images suggested that the thickness of nanotubes was about 25 nm (Figure 1e,f). The energy dispersive X-ray spectrometer (EDS) coupled with scanning transmission electron microscopy (STEM) was used to collect elemental distribution. Figure 1g shows that Nb and O elements were coexistent and uniformly distributed of in B-Nb2O5 nanotubes. After anatomizing the EDS results shown in Figure S2, Supporting Information, we discovered that the oxygen content was lower compared with the theoretical value of Nb2O5. The calculated oxygen defects concentration of B-Nb2O5 nanotubes was up to 9.83%. This value was the highest among W-Nb2O5 nanotubes, C-Nb2O5, and commercial Nb2O5 powder measured at the same parameter (Figure S3 and S4, Supporting Information).

Further structural and chemical probe characterizations are shown in Figure 2. Tilted to [010] crystal projection for crystal plane observation (detailed method in Figure S5, Supporting Information), high-resolution TEM (HRTEM) image (Figure 2a and Figure S5, Supporting Information) of B-Nb2O5 nanotubes proved that the preferred growth orientation was along the [001] direction. Fast Fourier Transform (FFT, Figure 2b) pattern suggested orthorhombic symmetry of the lattice face and [001] growth orientation. Inverse Fast Fourier Transformation (IFFT, Figure 2c) image gave a clear crystal structure. According to the aforementioned characterizations, the crystal structure of

![Figure 1. a) Schematic illustration of the preparation process of B-Nb2O5 nanotubes, b–d) SEM images of B-Nb2O5 nanotubes, e,f) low-magnification TEM images, g) high-angle annular dark field-STEM and corresponding EDS element mapping.](image-url)
B-Nb$_2$O$_5$ nanotubes was orthorhombic phase (space group is Pbam55), as shown in Figure 2d. Powder X-ray diffraction (XRD) patterns and Reitveld refinement were used to further study the phase compositions and crystalline structure of the B-Nb$_2$O$_5$ nanotubes (Figure 2e). The clear peaks in the pattern confirmed B-Nb$_2$O$_5$ nanotubes were pure orthorhombic phase with relatively high crystallinity. All peaks can be assigned to the orthorhombic Nb$_2$O$_5$ (JCPDS no. 30-0873). No characteristic peaks arising from possible impurities such as metal Nb, TT-Nb$_2$O$_5$, M-Nb$_2$O$_5$ (tetragonal), and NbO$_2$ were detected, indicating the high purity of the sample, and phase stability during the reduction process. The XRD patterns of control samples are shown in Figure S6 and Table S2, Supporting Information. According to the Reitveld refinements for B-Nb$_2$O$_5$ nanotubes and control samples, calculated O defect concentration of B-Nb$_2$O$_5$ nanotubes was up to 12%, which is significantly higher than other three samples. Meanwhile, the Raman signal was a good indicator to analysis defect structure of crystalline. Compared with commercial Nb$_2$O$_5$, weakened A$_{1g}$ band around 980 cm$^{-1}$ might arise from oxygen vacancy defects on the surface (Figure 2f), which corresponded to the Nb–O stretching. X-ray photoelectron spectra (XPS) were collected to qualitatively and quantitatively investigate the surface elements, valence, and surface oxygen defect concentration of B-Nb$_2$O$_5$ nanotubes. Figure 2g shows the high-resolution spectrum for Nb 3d and two characteristic peaks at 206.9 and 209.7 eV were ascribed to the Nb 3d$_{5/2}$ and Nb 3d$_{3/2}$ bands. The full width at half maximum (FWHM) of B-Nb$_2$O$_5$ nanotubes is significantly larger than W-Nb$_2$O$_5$ nanotubes and the FWHM of C-Nb$_2$O$_5$ is significantly larger than commercial Nb$_2$O$_5$. These indicated that the content of Nb on the surface of B-Nb$_2$O$_5$ and C-Nb$_2$O$_5$ is increased after hydrogen reduction process, further proving the generation of surface O defects. In the scan region of the O 1s (Figure 2h), the peak at 529.8 eV was assigned to the O–Nb bonds. We discovered that the oxygen content was lower compared with the commercial Nb$_2$O$_5$. The calculated surface oxygen defect concentration of B-Nb$_2$O$_5$ nanotubes was up to 13.1%. This value was the highest among W-Nb$_2$O$_5$ nanotubes, C-Nb$_2$O$_5$, and commercial Nb$_2$O$_5$ powder measured at the same condition (Table S1, Supporting Information). The crystal structure and morphology
change little from thermal reduction process, but the color turn blue-gray and the O vacancy defects were markedly increased. In addition, after calcined to 800 °C in air, the B-Nb_2O_5 return to white color and weight increased (Figure S7, Supporting Information). This is also in agreement with reported literature.\(^{44}\)

The electrochemical performance of B-Nb_2O_5 nanotubes were evaluated by used as anode electrode for LIBs. Before the assembly of coin cell, we found anode consisting of B-Nb_2O_5 nanotubes was more compact in contrast to commercial Nb_2O_5 (Figure S8, Supporting Information). Such electrode structure was beneficial to electron conducting and sturdiness during repeated cycling process. Figure 3a shows the cyclic voltammogram (CV) curves of B-Nb_2O_5 nanotubes by combining with the metal Li as a counter electrode, which examined the electrochemical property at scan rate of 0.2 mV s\(^{-1}\). From the first cathodic scan, a strong cathodic peak at 0.59 V was observed, which should be attributed to the formation of solid electrolyte interface (SEI). The cathodic peak around 0.75 V is assigned to organic salts (such as lithium ethylene carbonate) precipitates on the anode during the first few cycles, preventing further decomposition of the electrolyte.\(^{45}\) After the first cycle, the dominant cathodic peak observed at 1.61 V and anodic peak at 1.94 V were corresponded to the process that Li\(^+\) intercalated into/deintercalated from B-Nb_2O_5 nanotubes lattice. However, the commercial samples experienced some additional electrochemical processes except for the redox pair of 1.61/1.94 V (Figure S9, Supporting Information), which may be caused by the side reactions between B-Nb_2O_5 nanotubes anode and electrolyte. Correspondingly, typical galvanostatic discharge/charge curves for B-Nb_2O_5 nanotubes were observed at 1.50–1.95 V (Figure 3b). The discharge slope of 1.50–1.95 V was ascribed to Li\(^+\) intercalation into Nb_2O_5 lattice and the charging slope of 1.40–2.00 V was attributed to Li\(^+\) deintercalation from the intercalated Nb_2O_5 lattice, in line with the results of CV tests. To testify the superiority of oxygen defect and nanotube morphology of B-Nb_2O_5 in reducing the resistance of batteries, the electrochemical impedance spectroscopy (EIS) analysis of the B-Nb_2O_5 nanotubes and control samples are shown in Figure 3c. The semicircles and sloping lines were attributed to the charge transfer resistance (\(R_{ct}\)) and Li\(^+\) diffusion resistance, respectively.\(^{46}\) B-Nb_2O_5 nanotube electrodes

![Figure 3.](image-url)
exhibited the lowest $R_c$ value ($\approx 50 \Omega$) compared with those of W-Nb$_2$O$_5$ nanotubes ($\approx 81 \Omega$), C-Nb$_2$O$_5$ ($\approx 89 \Omega$), and commercial Nb$_2$O$_5$ ($\approx 178 \Omega$), suggesting that the nanotube structure and oxygen vacancy were conducive to improve Li$^+$ diffusion in Nb$_2$O$_5$ and electrode kinetics. As shown in the tests of rate performance, the discharge specific capacities of B-Nb$_2$O$_5$ nanotubes were 349, 300, 262, 225, 183, and 126 mA h g$^{-1}$ under different current densities of 0.1, 0.2, 0.5, 1.0, 2.0, 5.0 A g$^{-1}$, respectively (Figure 3d), suggesting a good rate performance. The discharge capacity of B-Nb$_2$O$_5$ nanotubes was higher than that of W-Nb$_2$O$_5$ nanotubes, and better than the discharge capacities of C-Nb$_2$O$_5$ and commercial Nb$_2$O$_5$. This results certified that both morphology and vacancy contributed a better rate performance, in accordance with the comparison of galvanostatic charge–discharge profiles from these four samples at the small current density of 0.1 A g$^{-1}$ (Figure 3e). At the current density of 0.5 A g$^{-1}$, the capacity of commercial Nb$_2$O$_5$, C-Nb$_2$O$_5$, W-Nb$_2$O$_5$ nanotubes, and B-Nb$_2$O$_5$ nanotubes were about 115.3, 130.2, 292.1, and 337.2 mA h g$^{-1}$ after 200 cycles, respectively (Figure 3f). B-Nb$_2$O$_5$ nanotubes electrode still afforded about 300 mA h g$^{-1}$ after 500 cycles, suggesting that the structure of B-Nb$_2$O$_5$ nanotubes was beneficial to Li$^+$ storage.

To study the cyclic performances at high current density, these four samples were assembled with Li metal to operate at 1 A g$^{-1}$ current density. After 1500 cycles, residual capacity of the B-Nb$_2$O$_5$ nanotubes was still over 200 mA h g$^{-1}$, whereas W-Nb$_2$O$_5$ nanotubes, C-Nb$_2$O$_5$, and commercial Nb$_2$O$_5$ were only about 165, 150, and 90 mA h g$^{-1}$, respectively (Figure 4a). Even after 2000 cycles, B-Nb$_2$O$_5$ nanotubes electrode can run more than 2000 cycles with the capacity retention of 72.36% (165.2 mA h g$^{-1}$). Li$^+$ storage performance of B-Nb$_2$O$_5$ nanotubes toward LIBs application was comparable with the previously reported results (Table S3, Supporting Information). For Li$^+$ storage mechanism in Nb$_2$O$_5$, ex situ XRD was conducted for the lattice changes during the galvanostatic charge–discharge process. As shown in Figure 4b, the

![Figure 4.](https://www.advancedsciencenews.com)

Figure 4. a) Long-cycle performance comparison at 1 A g$^{-1}$, b) schematic illustration of the as-assembled 2032-type LIBs half-cell, c) galvanostatic charge–discharge profiles of an ex situ B-Nb$_2$O$_5$ nanotubes LIBs cell, d) corresponding ex situ XRD patterns, and e) ex situ XPS spectrum of B-Nb$_2$O$_5$ nanotubes at Nb 3d region, f) Li 1s region, and g) O 1s region.
as-assembled 2032-type LIBs half-cell consist of a Li foil, separator, B-Nb$_2$O$_5$ nanotubes anode with copper current collector, and moderate electrolyte. The charge–discharge curves and points 1–8 were selected for ex situ XRD tests (Figure 4c,d). When the battery was fully discharged to 0.01 V (point 1), the evolution of the patterns revealed a shift of the (001) peak reflections to 21.54° ($d = 4.12$ Å). While charged to 1.5 V (point 2), no change happened in XRD patterns. At the point of charge to 2.2 V (point 3) and discharge to 1.4 V (point 6), the (001) peak of B-Nb$_2$O$_5$ nanotubes split into a doublet peak (21.28°, $d = 4.17$ Å and 21.80°, $d = 4.07$ Å), which might arise from the extraction from/insertion into the (001) lattice of Nb$_2$O$_5$ crystal.$^{[47]}$ After fully charged to 3.0 V (point 4), the (001) peak turned back to 21.67° ($d = 4.09$ Å). At the point of discharge to 1.5 V (point 5), no change happened in XRD patterns compared with point 4. The XRD patterns of points 7 and 8 (recharged to 3.0 V) are similar to the points 1 and 4, indicating good electrochemical reversibility of B-Nb$_2$O$_5$ nanotubes LIBs. Moreover, ex situ XPS spectrum was used to record the valance state of B-Nb$_2$O$_5$ nanotubes. At lower discharge potential state, Nb 3d peak diminished and regained at higher charge potential (Figure 4e), which might be ascribed to the Li species deposited during discharging process and dissolved during charging process. Li 1s peak (Figure 4f) shifted to higher binding energy during charging process and reversed to opposite direction during discharging process, which can be attributed to Li$^+$ reversible electrochemical redox reactions. The O 1s peak became complicated after first discharge to 0.01 V, suggested the formation of SEI layer that mainly contained Li$_2$CO$_3$ and lithium alkyl carbonate from the O 1s peak (Figure 4g).

Based on the excellent performances of B-Nb$_2$O$_5$ nanotubes in LIBs half-cell tests, we assembled dual-ion batteries$^{[48,49]}$ with B-Nb$_2$O$_5$ nanotubes as an anode material and graphite as a cathode (Figure 5a). During the charge processes, Li$^+$ from

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**Figure 5.** a) Schematic illustration of full cell with B-Nb$_2$O$_5$ nanotubes as anode material and graphite as cathode, b) Charging–discharging curves of graphite cathode in situ Raman cell, inset is a digital image of in situ Raman cell, c) in situ Raman of graphite cathode during charge process, d) in situ Raman of graphite cathode during discharge process, e) discharge potential curves, f) cyclic performance of the full cell, and inset is a blue LED ran by the full cell.
the solution can be rapidly inserted into B-Nb₂O₅ nanotubes anode, while PF₆⁻ quickly intercalated into the interlayers of graphite. As the cathode, graphite possessed high discharging platform (4.00–4.85 V). In situ Raman was implemented to probe the electrochemical mechanism of graphite (Figure 5b). Charging to 5.5 V, E₉ peak and A₁₈ peak of PF₆⁻ diminished, and G band of graphite (1584 cm⁻¹) vanished and split into a doublet, 1612 cm⁻¹ for E₉g(i) and 1629 cm⁻¹ for E₉g(b) upon PF₆⁻ intercalation (Figure 5c). During discharging to 0 V, E₉ peak of PF₆⁻ reappeared due to the PF₆⁻ deintercalation from graphite interlayers (Figure 5d). Detailed Raman data are shown in Figure S10, Supporting Information. In consequence, B-Nb₂O₅/graphite battery experiences Li⁺ insertion/extraction from Nb₂O₅ lattice. Combined with a reversible PF₆⁻ intercalation into/deintercalation from graphite cathode, at the current density of 0.1 A g⁻¹, B-Nb₂O₅/graphite dual-ion cell can provide a high capacity of ~23 mA h g⁻¹ after 50 cycles. This work demonstrated that the morphology and vacancy design of transitional metal oxides as advanced anode materials was a promising strategy for developing novel full-cell Li⁺ batteries.

3. Conclusion

In summary, we controlled prepared blue-gray oxygen vacancy defect Nb₂O₅ nanotubes via a CVD method. As anode materials, the as-prepared B-Nb₂O₅ nanotubes offered high specific capacity and remarkable cycling stability in LIBs (200 mA h g⁻¹ over 1500 cycles at 1 A g⁻¹), much superior to those of commercial Nb₂O₅, C-Nb₂O₅ and W-Nb₂O₅ nanotubes. Detailed ex situ XRD and XPS analyses at different reaction processes revealed that the lithiation mechanism involved a reversible Li⁺ insertion into/extraction from Nb₂O₅ lattice. Combined with a reversible PF₆⁻ intercalation into/deintercalation from graphite cathode, at the current density of 0.1 A g⁻¹, B-Nb₂O₅/graphite dual-ion cell can provide a high capacity of ~23 mA h g⁻¹ after 50 cycles. This work demonstrated that the morphology and vacancy design of transitional metal oxides as advanced anode materials was a promising strategy for developing novel full-cell Li⁺ batteries.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords

high capacities, high rates, lithium-ion batteries, Nb₂O₅ nanotubes, oxygen vacancies

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