

Supplementary Materials: Controlled Hydrothermal Growth and Li⁺ Storage Performance of 1D VO_x Nanobelts with Variable Vanadium Valence

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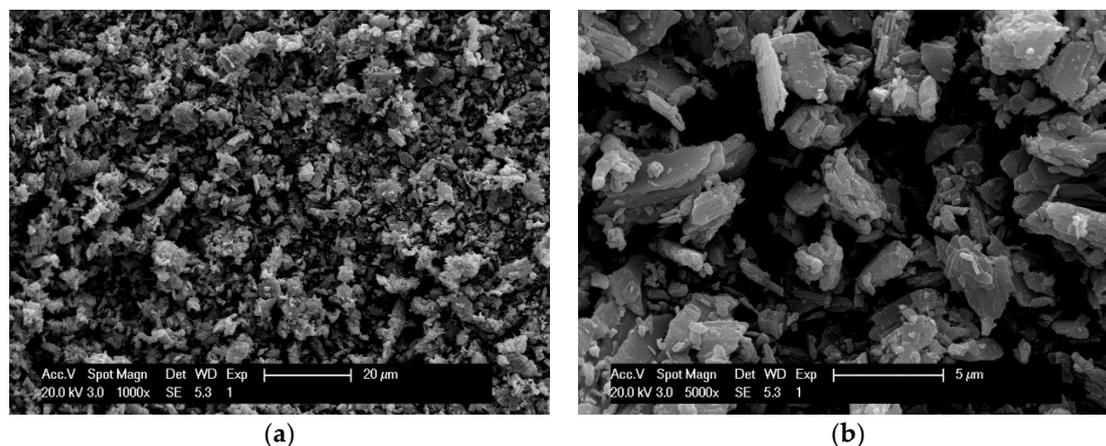


Figure 1. SEM images of commercial V₂O₅ powder at 1000 (a) and 5000 (b) times magnification, respectively.

The Figure S1 above is the SEM images of commercial V₂O₅ powder at different magnifications. We can see that the size distribution of V₂O₅ particles is not uniform and their diameter is in the range from hundreds of nanometers to a dozen of micrometers. The shape of these V₂O₅ particles is also irregular. V₂O₅ itself has low solubility in water, but it will form the metastable vanadium oxide precursors, which disperse well, in the special high temperature and pressure hydrothermal environment. Then, the oriented crystallization growth of VO_x happens, leading to the formation of one-dimensional nano-belted structure.

Reducing action of ethanol (EtOH) under hydrothermal condition: The hydrothermal reaction itself could provide a reductive atmosphere [1]. EtOH can behave as a kind of weak reducing agent in the hydrothermal environment. Some reports on the use of ethanol as a reducing agent have been reported [2,3]. EtOH will be oxidized and converted to aldehydes and at the same time vanadium element would be reduced to the lower valence state [Possible reaction equation can be roughly written as $(5-2x)\text{CH}_3\text{CH}_2\text{OH} + \text{V}_2\text{O}_5 \rightarrow 2\text{VO}_x + (5-2x)\text{CH}_3\text{CHO} + (5-2x)\text{H}_2\text{O}$ ($2 < x < 2.5$)].

The inductive reducing action of MWCNTs: MWCNTs are not well dispersed in water and it only shows the temporary state of suspension in solution. However, under the special high-temperature and pressure liquid environment of hydrothermal reaction, MWCNTs can be dispersed evenly to ensure their sufficient contact with vanadium oxide precursors. Because the MWCNTs here used were previously treated with mixed concentrated acids in order to get better dispersion in liquid condition. Generally, the mixed concentrated acids are H₂SO₄ (>70 wt%) and HNO₃ (~65 wt%) according to 3:1 (volume ratio). The acid treatment process will create some surface hydroxyl, carbonyl and carboxyl functional groups [4,5]. These functional groups on MWCNTs contribute to the further reduction of vanadium oxide precursors under the hydrothermal condition and the presence of EtOH.

The possible growth mechanism of vanadium oxide nanobelt: Under the special high temperature and high pressure hydrothermal condition, the commercial V₂O₅ powder will disperse to form the metastable VO_x precursor. Owing to the role of energy modulation under hydrothermal condition, the growth kinetics of vanadium oxide precursor is faster in a specific direction during the process of self-assembly crystallization and conversely the growth in other orientations are inhibited, resulting in a one-dimensional VO_x nano-belted morphology. As some literatures reported

[6,7], we know that hydrothermal reaction is a common method that can be adopted to prepare a series of one-dimensional metal oxide nanomaterials.

In the post-sintering of VO_x NBs in air, the V valence state will increase by in-situ oxidation, but the 1D morphology of VO_x NBs could be maintained and form V₂O₅ NBs with high V valence state.

References:

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