

Electronic Supplementary Information

Ultralong Monoclinic ZnV_2O_6 Nanowires: Their Shape-controlled Synthesis, New Growth Mechanism, and Highly Reversible Lithium Storage in Lithium-ion Batteries

Yan Sun,^{*a} Chunsheng Li,^{*a} Lina Wang,^a Yaozu Wang,^b Xuegang Ma,^c Peijuan Ma,^a Mingyang Song^a

^a College of Chemical Engineering, Hebei United University, Tangshan City, Hebei Province, 063009 (P. R. China)

Address correspondence to Yan Sun, juzi147@yahoo.com.cn; Chunsheng Li, lichsheng2008@yahoo.com.cn

^b Yisheng College, Hebei United University, Tangshan City, Hebei Province, 063009 (P. R. China)

^c Analysis and Testing Center, Hebei United University, Tangshan City, Hebei Province, 063009 (P. R. China)

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Table S-1. Summary of the experimental parameters and the corresponding structures of zinc vanadium oxide

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micro/nanomaterials

Samp le*	T (°C)	t (h)	Morphology	Specific surface area (m ² /g)	Phase
1	200	168	ultralong nanowires (diameter:70-120 nm, length: 80-100 μm)	17.125	<i>m</i> -ZnV ₂ O ₆
2	200	3	microflowers assembled with nanosheets (diameter: 3 μm)	4.959	Zn ₂ V ₂ O ₇ and ZnV ₂ O ₆
3	200	12	coexistence of microsheets (diameter:1-2 μm) and nanowires (diameter: 80 nm, length: 5-20 μm)	6.307	ZnV ₂ O ₆ and Zn ₂ V ₂ O ₇
4	200	48	meso/nanoweires (diameter: 100-400 nm, length: 10-35 μm)	11.26	<i>m</i> -ZnV ₂ O ₆
5	160	168	microflowers (diameter: 3 μm)	6.759	coexistent of ZnV ₂ O ₆ , ZnV ₃ O ₈ , VO ₂ and ZnO
6	180	168	coexistence of ultralong nanowires (diameter: 80-150 nm, length: 30 μm) and microsheets	9.659	coexistent of ZnV ₂ O ₆ , ZnV ₃ O ₈ , VO ₂ and ZnO
7	Thermal treatment of ZnO and V ₂ O ₅ powders at 600 °C for 12 h in air atmosphere. microbulk with layered structures (size: 2-10 μm)			1.784	<i>m</i> -ZnV ₂ O ₆

* The concentration of Zn(NO₃)₂ solution is 0.25 mol/L.

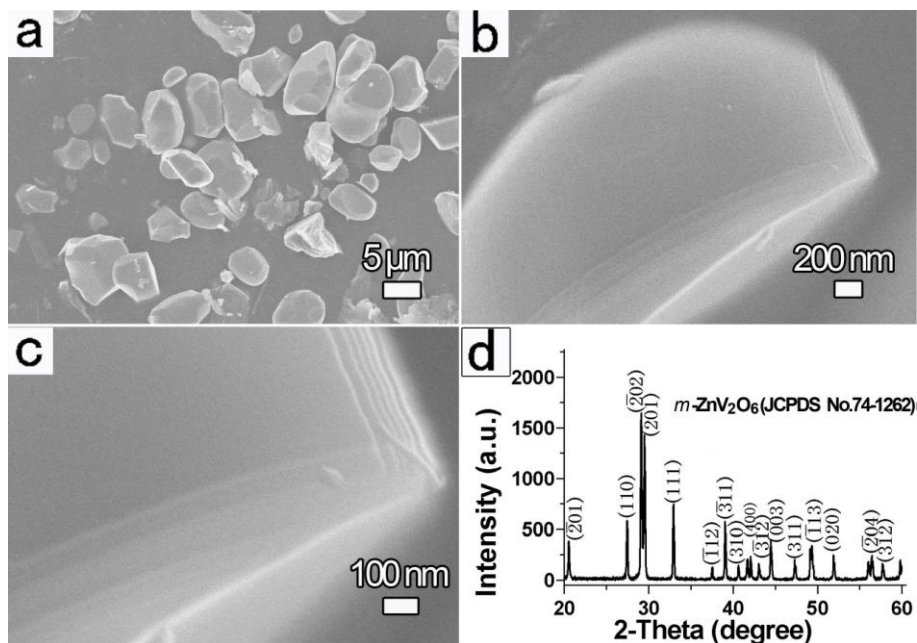


Fig. S-1. (a-c) SEM images of typical sample 8 synthesized through solid-state reaction at 600 °C for 12 h. (d)

XRD pattern of as-obtained m - ZnV_2O_6 product.

5 Monoclinic (m -) ZnV_2O_6 bulk particles were fabricated via simple solid-state reaction method using ZnO and V_2O_5 powders as raw materials. The ZnO and V_2O_5 reagents were of analytical grade and purchased from Tianjin Jinke Fine Chemical Institute, and Tianjin Damao Chemical Reagent Factory (China), respectively. Stoichiometric amounts of ZnO and V_2O_5 powders are mixed in an agate mortar for two hours, and subsequent
10 calcined at 600 °C for 12 h in a conventional air oven. From the further SEM analysis, the diameter of particles is around 2-10 μm (Figure S-1 a-b), and the thickness of individual powder with layered structure is only 15-20 nm as illustrated in Figure S-1 c. While, the XRD pattern is indexed to the monoclinic phase of ZnV_2O_6 and is corresponding to the standard values [space group: C2 (No. 5), ICDD-JCPDS Card No. 74-1262]. Afterwards, the as-prepared product was ground for 10 min into homogenous fine powders for the following electrochemical characterizations.

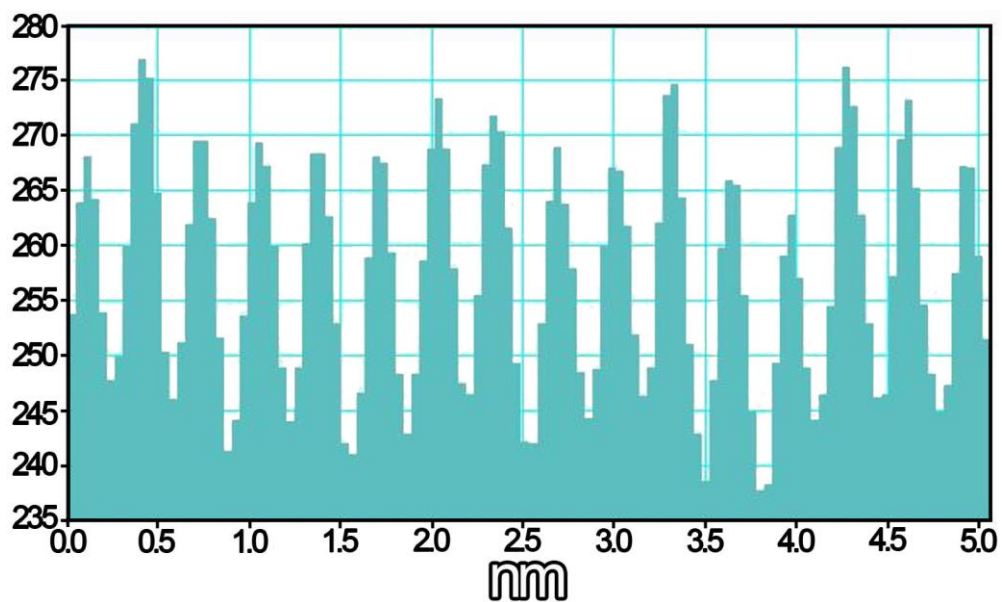
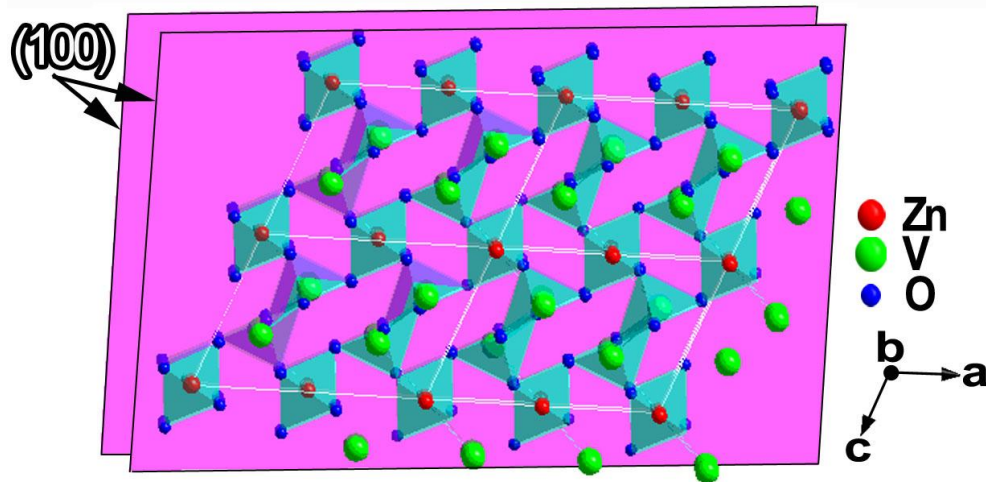


Fig. S-2. Line profile from the HRTEM image for the white square in Figure 1e of the full paper. From the profile, the interlayer distance of 0.326 nm for the clear fringes can be calculated.



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Fig. S-3. Crystallographic view of m - ZnV_2O_6 along the b -axis. The two planes with red color imply the (110) planes of the single-crystalline nanowires.

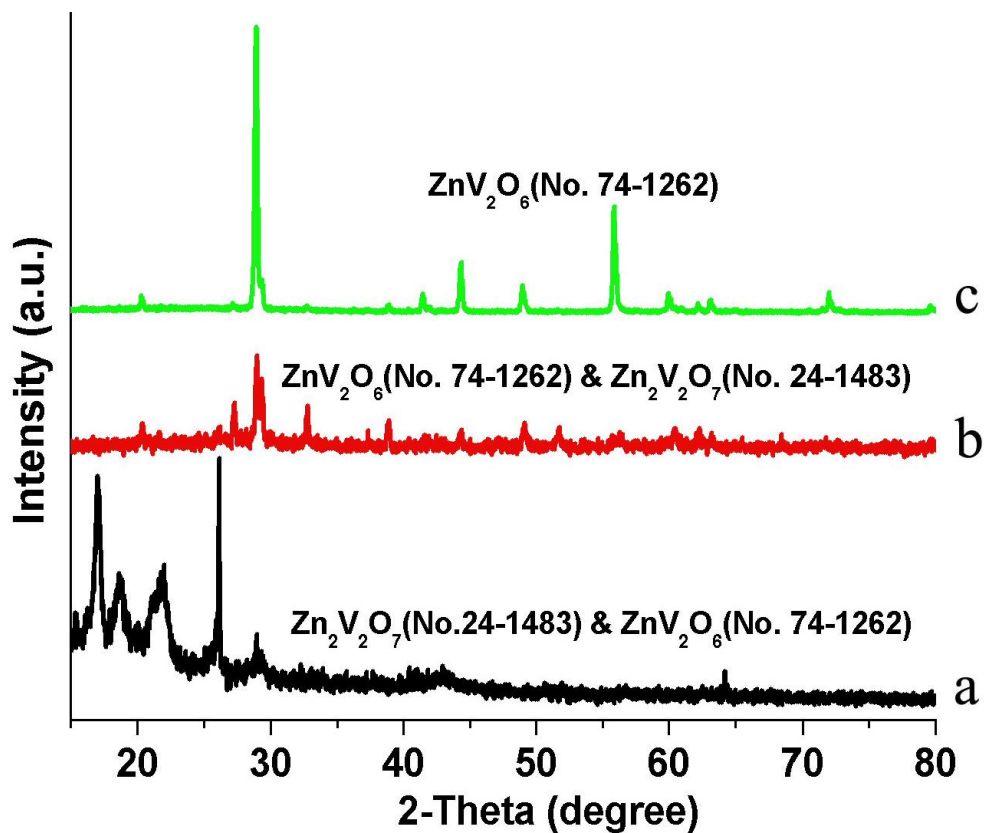


Fig. S-4. XRD of zinc vanadium oxide synthesized at various reaction time at the same reaction temperature of 200 °C and the $Zn(NO_3)_2$ concentration of 0.25 mol/L: (a) 3 h, $Zn_2V_2O_7$ (No. 24-1483) and ZnV_2O_6 (No. 74-1262), microflowers for sample 2; (b) 12 h, ZnV_2O_6 (No. 74-1262) and $Zn_2V_2O_7$ (No. 24-1483), the coexistence of microsheets and nanowires for sample 3; and (c) 48 h, ZnV_2O_6 (No. 74-1262), meso/nanowires for sample 4.

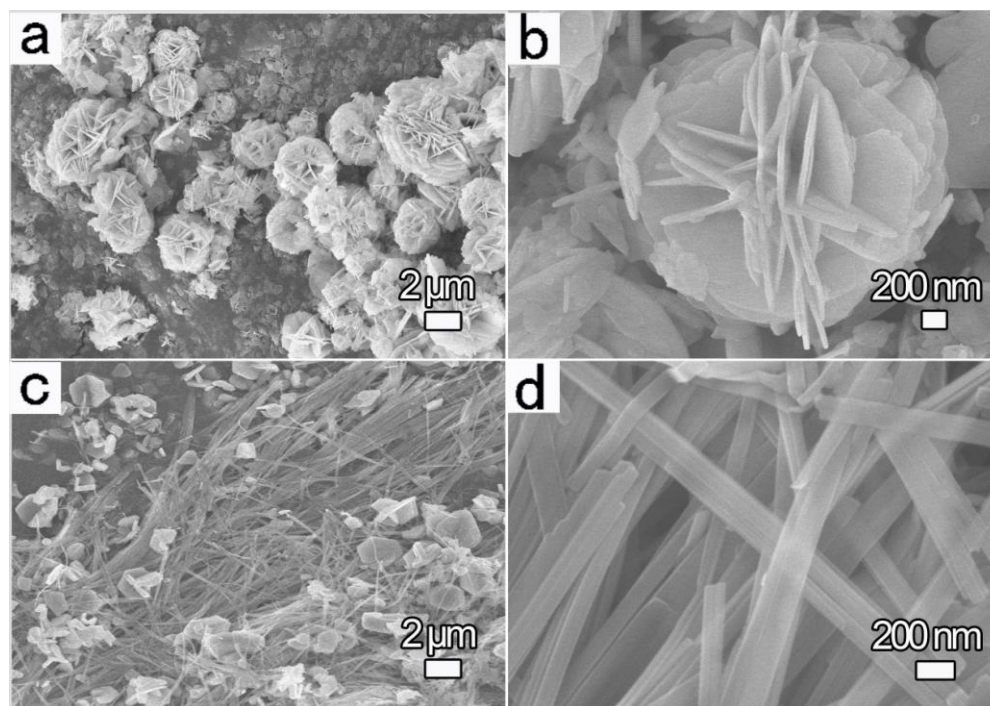


Fig. S-5. SEM images of products obtained at variety of hydrothermal temperatures with the same dwell time of 168 h and starting concentration of 0.25 mol/L $Zn(NO_3)_2$: (a-b) 160 °C, uniform microflowers for sample 5; and (c-d) 180 °C, the coexistence of ultralong nanowires and microsheets for sample 6.

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The kinetic of the synthesizing process at different temperatures can greatly influence the morphologies and phases of final products. Figure S-5 shows the relationship between synthesizing temperatures and corresponding morphologies from flower-like micro/nanomaterials to nanowires. At a low temperature of 160 °C, Figure S-5 a-b gives the overall shape of sample 5, indicating that the product composed of large quantities of microflowers with uniform average size of 3 μm. Each flower-like structure is made up of several nanosheets with very thinner thickness of 10-15 nm (Figure S-5 b), and these sheets are originated from a same nucleation. Interestingly, Figure S-5 c-d reveals the coexistence of ultralong nanowires and irregular microsheets (sample 6) at the higher temperature of 180 °C. Where, the 1D wire-like sample has a diameter of 80-150 nm with a length up to 30 μm, giving an aspect ratio of over 200. Overall, 3D flower-like superstructures zinc vanadium oxides are mainly dominated at a relatively lower temperature of 160 °C, while the prevailing morphology of nanowires is favorable for inducing the preferential growth at an elevated temperature of 180 °C.

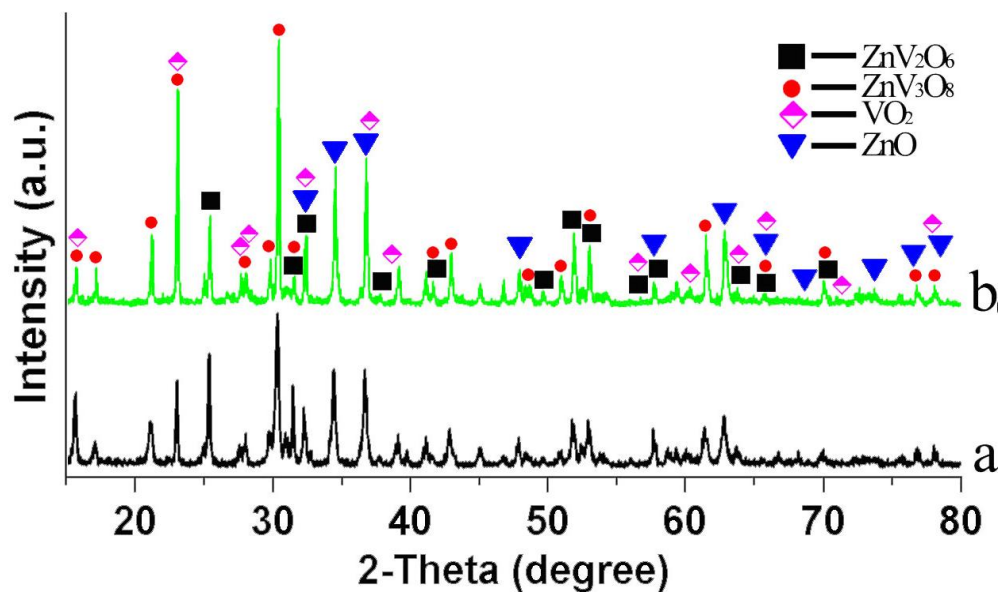


Fig. S-6. XRD patterns of the as-synthesized products with the coexistent phases of ZnV₂O₆, ZnV₃O₈, VO₂ and ZnO: (a) 160 °C, uniform microflowers for sample 5; (b) 180 °C, the coexistence of ultralong nanowires and microbulks for sample 6.

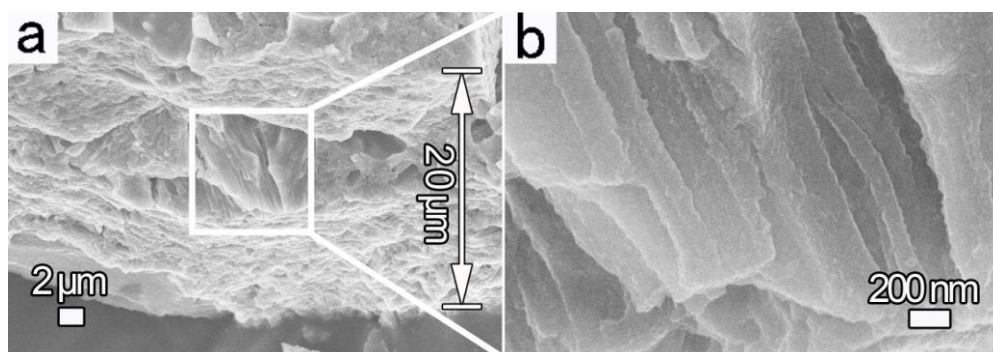


Fig. S-7. (a-b) SEM images of cross-section for the *m*-ZnV₂O₆ electrode after 80 charge/discharge cycles. The figure indicates that the thickness of the electrode is about 20 μm, and the topology of the nanowires with the average diameter of 100-200 nm is kept with no obvious change compared with Figure 1 b-d after series cycles.