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A General and Simple Method to Synthesize Well-crystallized Nanostructured Vanadium Oxides for High Performance Li-ion Batteries

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Experimental Section

Materials

The starting materials, including V_2O_5 and oxalic acid ($H_2C_2O_4$- • $2H_2O$), were obtained from Sinopharm Chemical Reagent Co., Ltd., China. All chemical reagents were of analytical grade and used without further purification.

Synthesis

The synthesis process of HTMM was further optimized based on results of previous studies. Three kinds of 1D-vanadium oxides with high crystallinity, namely, V_3O_7•H_2O, VO_2 (B), and VO_2 (A), were synthesized through HTMM under hydrothermal conditions. V_2O_5 was used as the vanadium source, and oxalic acid ($H_2C_2O_4$• $2H_2O$) was used as the reducing agent. The preparation process was simple, and the autoclave-filling ratio (approximately 25%) was smaller than in other methods. First, appropriate amounts of V_2O_5 and de-ionized water were placed in one of the two chambers of a Teflon-lined multi-chamber autoclave, whereas corresponding amounts of oxalic acid solution were poured into the other chamber. These solutions were then heated to 240 °C for different times.

After cooling the autoclave to room temperature, the formed precipitates were washed several times with de-ionized water and ethanol. The precipitates were then dried at 80 °C for 10 h.

Characterization

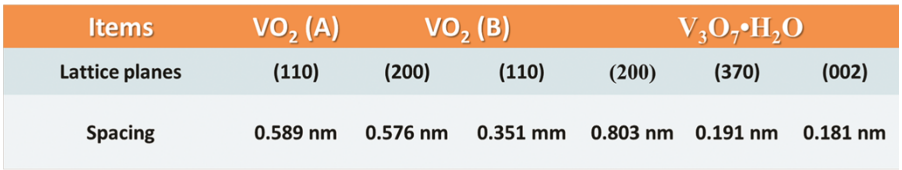
The phase structure of the resultant powders was determined by powder X-ray diffraction (Bruker D8 Advance, Germany) using Cu Kα radiation (λ = 0.15,418 nm).

The morphologies of the prepared particles were observed by field emission scanning electron microscopy (HITACHI S-4800, Japan) and transmission electron microscopy (TEM; Tecnai G2 F30 S-Twin TEM, FEI, USA). The optical properties of the samples were tested by Fourier transform infrared spectroscopy (FTIR; NEXUS670, USA) using an adapted heating controlled cell. The FTIR patterns of the solid samples were measured using the KBr pellet technique. Approximately 1 wt% of the samples and 99 wt% of KBr were mixed homogeneously, and the mixture was pressed to a pellet.

Electrochemical testing

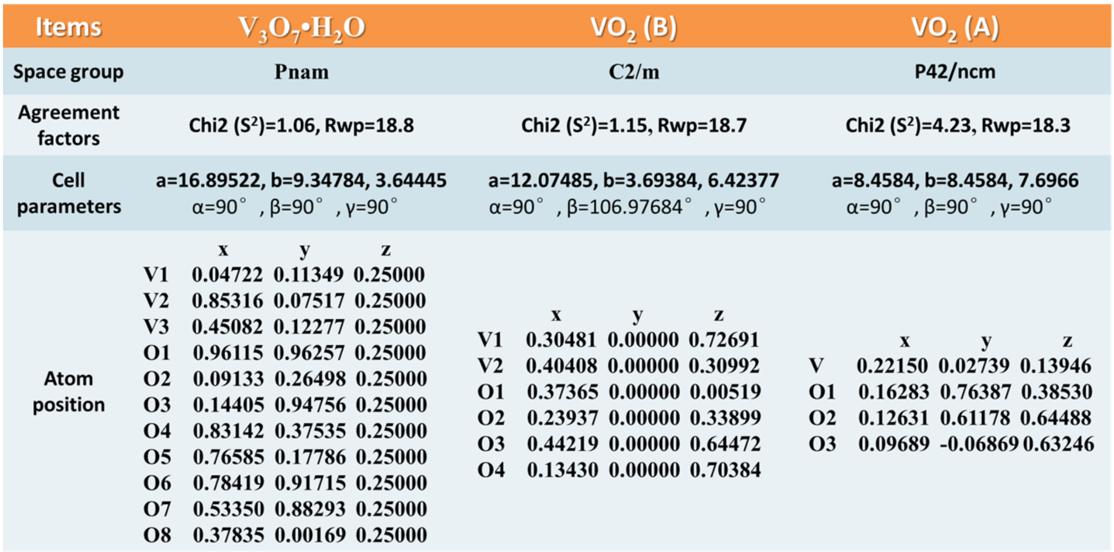
The active materials [VO_2 (A), VO_2 (B), and $V_3O_7 \bullet H_2O$], acetylene black, and polytetrafluoroethylene were mixed well into weight ratios of 7:2:1, 7:2:1, and 6:3:1, respectively, to obtain a slurry. The obtained slurry was casted on aluminum foil to obtain a laminate. The laminate was dried for 5 min under an incandescent lamp before drying in a vacuum oven at 75 °C for 12 h. The dried laminate was punched into round discs with diameters of 12 mm. Coin cells (2032) were assembled in an argon-filled glove box with O_2 concentrations of less than 1 ppm. A lithium metal foil was used as a counter electrode, and Celgard2400 was used as a separator. The electrolyte solution was 1.0 M $LiPF_6$ in EC/DEC (1:1 vol/vol). Galvanostatic charge/discharge measurement was performed by a multichannel battery testing system (LAND CT2001A). All electrochemical measurements were conducted at room temperature.

Table S1 Interlay spacing of some representative lattice planes



Items	VO_2 (A)	VO_2 (B)		V_3O_7•H_2O		
Lattice planes	(110)	(200)	(110)	(200)	(370)	(002)
Spacing	0.589 nm	0.576 nm	0.351 mm	0.803 nm	0.191 nm	0.181 nm

Table S2 Detailed refined data of V_3O_7•H_2O nanobelts, VO_2 (B) nanosheets and VO_2 (A) nanorods.



Items	V_3O_7•H_2O	VO_2 (B)	VO_2 (A)
Space group	Pnam	C2/m	P42/ncm
Agreement factors	Chi2 (S^2)=1.06, Rwp=18.8	Chi2 (S^2)=1.15, Rwp=18.7	Chi2 (S^2)=4.23, Rwp=18.3
Cell parameters	a=16.89522, b=9.34784, 3.64445 α=90°, β=90°, γ=90°	a=12.07485, b=3.69384, 6.42377 α=90°, β=106.97684°, γ=90°	a=8.4584, b=8.4584, 7.6966 α=90°, β=90°, γ=90°
Atom position	x y z V1 0.04722 0.11349 0.25000 V2 0.85316 0.07517 0.25000 V3 0.45082 0.12277 0.25000 O1 0.96115 0.96257 0.25000 O2 0.09133 0.26498 0.25000 O3 0.14405 0.94756 0.25000 O4 0.83142 0.37535 0.25000 O5 0.76585 0.17786 0.25000 O6 0.78419 0.91715 0.25000 O7 0.53350 0.88293 0.25000 O8 0.37835 0.00169 0.25000	x y z V1 0.30481 0.00000 0.72691 V2 0.40408 0.00000 0.30992 O1 0.37365 0.00000 0.00519 O2 0.23937 0.00000 0.33899 O3 0.44219 0.00000 0.64472 O4 0.13430 0.00000 0.70384	x y z V 0.22150 0.02739 0.13946 O1 0.16283 0.76387 0.38530 O2 0.12631 0.61178 0.64488 O3 0.09689 -0.06869 0.63246

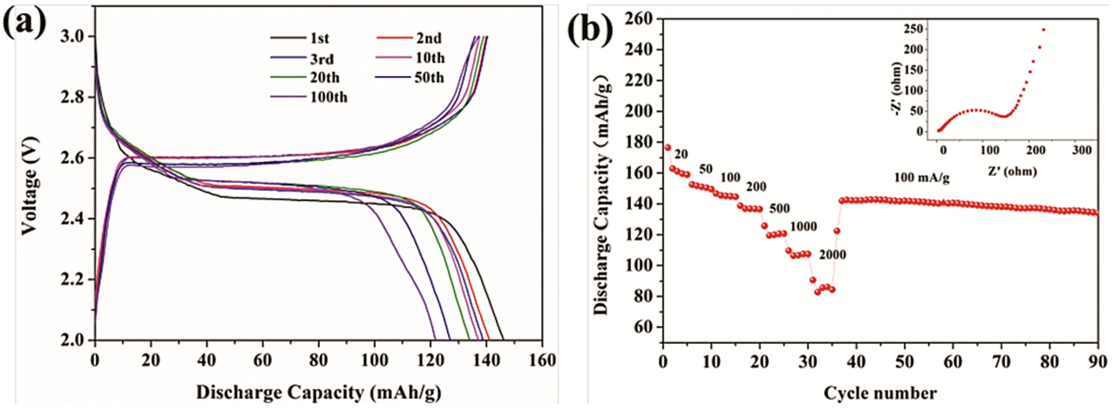


Fig. S1 Electrochemical measurements of VO_2 (B) nanosheets. (a) Charge-discharge curves at 100 mA/g; (b) rate properties (inset is the EIS measurement).

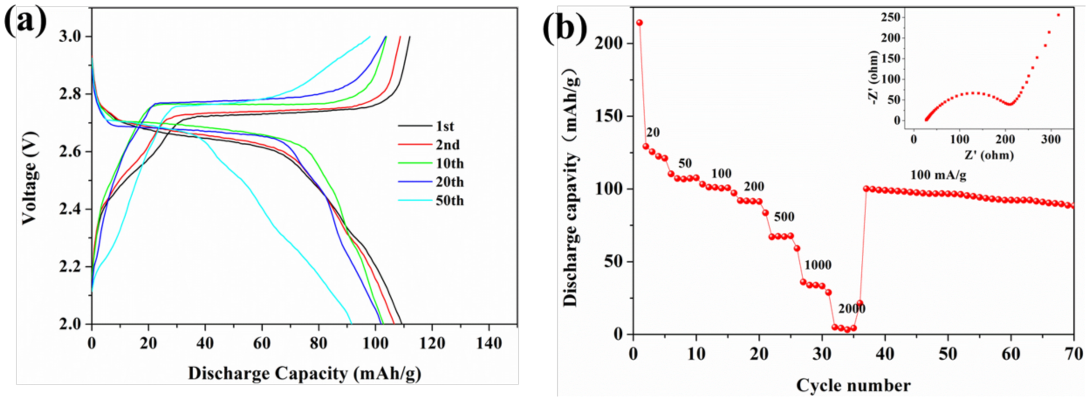


Fig. S2 Electrochemical measurements of VO_2 (A) nanorods.. (a) Charge-discharge curves at 100 mA/g; (b) rate properties (inset is the EIS measurement).

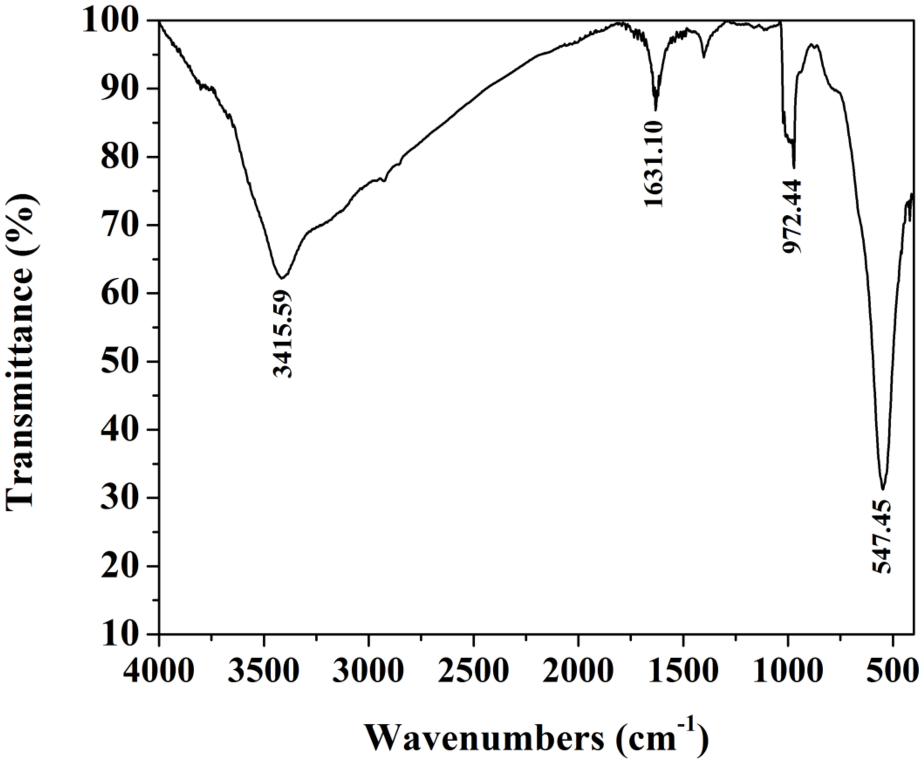


Fig. S3 FTIR patterns of V_3O_7•H_2O nanobelts.