Electronic Supplementary Information

Additive-free synthesis of 3D porous V_2O_5 hierarchical microspheres with enhanced lithium storage properties

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Experimental details

Materials synthesis. The synthesis of V_2O_5 microspheres (V_2O_5-ms) was simply achieved by a solvothermal reaction followed by calcination in air. In a typical synthesis, vanadium (V) oxytriisopropoxide ($VO(OiPr)_3$, 0.5 mL) was injected into 15 mL of acetic acid (HAc) and the solution was stirred for several minutes. The mixture was transferred to a Teflon-lined stainless steel autoclave (4746 high pressure vessel, Parr Instrument Company, USA), which was then heated to 200 °C and kept at that temperature for 1.5 h. After the autoclave was cooled down, the product was separated and washed several times by centrifugation with ethanol, followed by drying at 60 °C. The V_2O_5 microsphere sample, V_2O_5-ms, was obtained after the gray powder was heated at 350 °C for 0.5 h, with a heating rate of 0.5 °C min^{-1}. For comparison purposes, V_2O_5 nanoparticles (V_2O_5-np) were also prepared by a similar method (with the time for the solvothermal reaction prolonged to 24 h), which was followed by a similar calcination process at 350 °C for 0.5 h.

Materials characterization. The crystal phase was examined by X-ray powder diffraction (XRD; GBC MMA diffractometer, Cu Kα radiation, $\lambda = 1.5406$ Å). The morphologies of the samples were investigated by field-emission scanning electron microscopy (FESEM; JEOL JSM-7500FA). Transmission electron microscopy (TEM) images were collected on a JEOL 2011 200 kV instrument. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface area, using sorption data at a relative pressure ranging from 0.005 to 0.1. Due to the limited amount of materials, tap densities were roughly tested by mechanically tapping a measuring cylinder containing a certain amount of samples. The two samples were tested under exactly same conditions, therefore the results are comparable. The tap density in g per cm^3 was calculated by the formula: Mass/Volume. The results show that the tap density of V_2O_5-ms (0.6 g cm^{-3}) is higher than that of V_2O_5-np (0.46 g cm^{-3}).

Electrochemical measurements. The working electrodes were prepared by mixing 75 wt% active material (e.g., V_2O_5-ms or V_2O_5-np), 15 wt% conductive agent (carbon black, Super-P-Li), and 10 wt% binder (polyvinylidene difluoride (PVDF), Sigma-Aldrich) in N-methyl-2-pyrrolidinone (NMP) to form a homogeneous slurry, which was uniformly pasted onto aluminum foil. The prepared working electrodes were dried in a vacuum oven at 100 °C over 12 h and were then ready for assembly in test cells. Electrochemical cells (CR2032 coin type) using the active materials as working electrode, Li foil as the counter and reference electrode, a microporous polypropylene film as the separator, and 1 M $LiPF_6$ in a 1:1 (v/v) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) as the electrolyte were assembled in an Ar-filled glove box (H_2O, $O_2 < 0.1$ ppm, Mbraun, Unilab, USA). The cells were galvanostatically charged and discharged over a voltage range of 2.5 – 4 V versus Li/Li$^+$ at different constant current densities, based on the weight of the samples on a Land CT2001A cycler. Electrochemical impedance spectroscopy (EIS) was performed using an Ametek PARSTAT®2273 electrochemistry workstation. The AC amplitude was 5 mV, and the frequency range applied was 1 MHz to 0.01 Hz. The thickness of the electrodes is about 24-32 μm, and the area is about 1 cm^2.

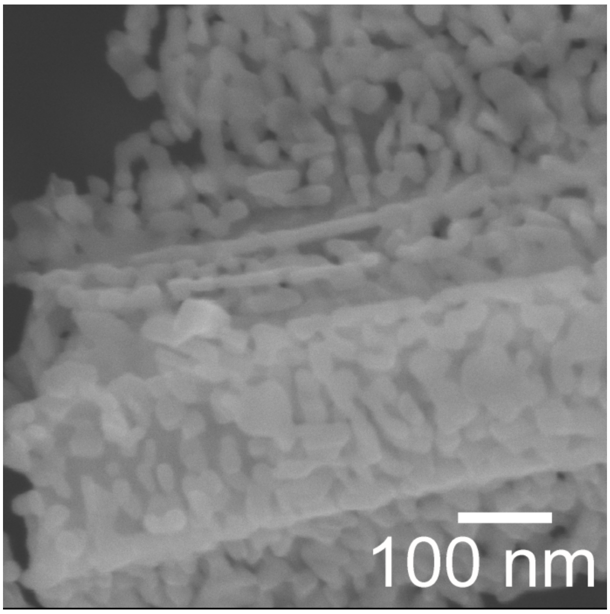

Figure S1. FESEM image of the V_2O_5-np material.

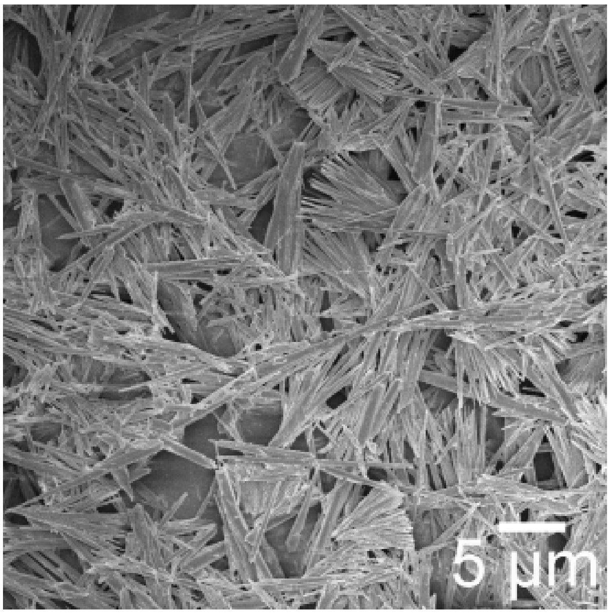

Figure S2. FESEM image of the precursor synthesized at 200 ºC for about 5 minutes. (The autoclave was heated from room temperature to 200 ºC and then kept at that temperature for 5 minutes.)

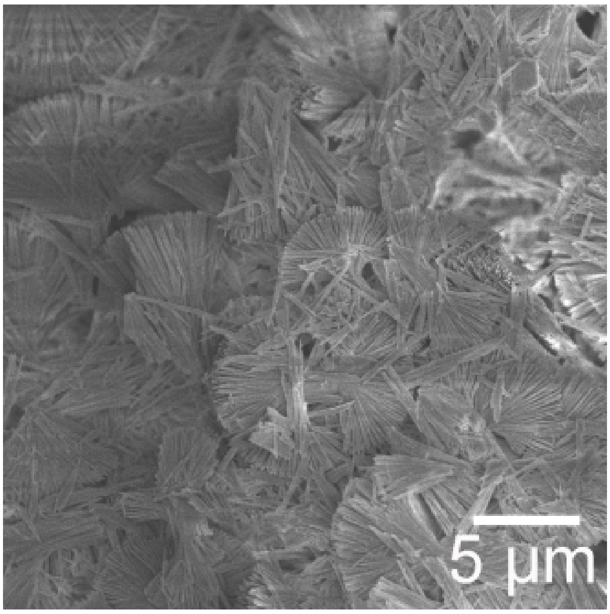

Figure S3. FESEM image of the precursor synthesized at 200 ºC for about 15 minutes. (The autoclave was heated from room temperature to 200 ºC and then kept at that temperature for 15 minutes.)

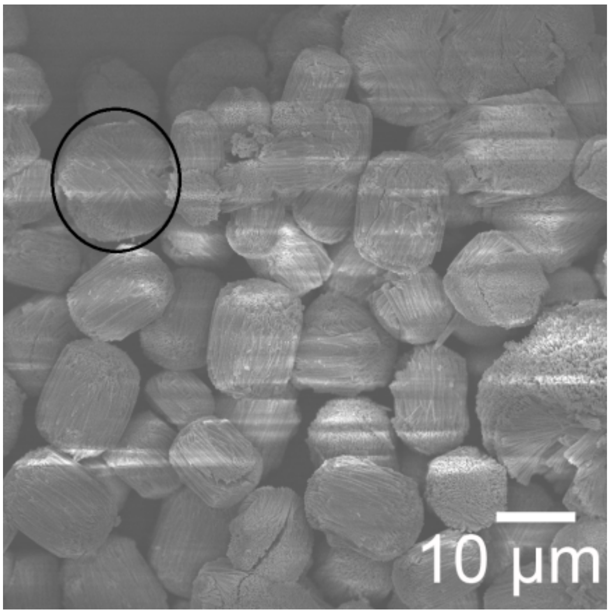

Figure S4. FESEM image of the precursor synthesized at 200 ºC for about 30 minutes. (The autoclave was heated from room temperature to 200 ºC and then kept at that temperature for 30 minutes.) The circled particle shows the arrangement of the constituent nanofibers.

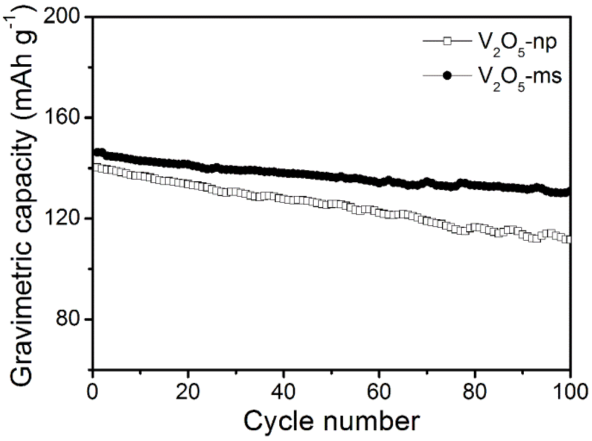

Figure S5. Cycling performance of V_2O_5-np and V_2O_5-ms at the current rate of 0.5 C.

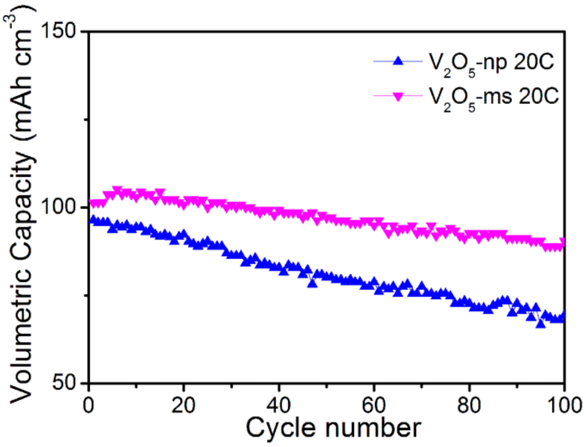

Figure S6. Volumetric capacities of V_2O_5-np and V_2O_5-ms at the current rate of 20 C.

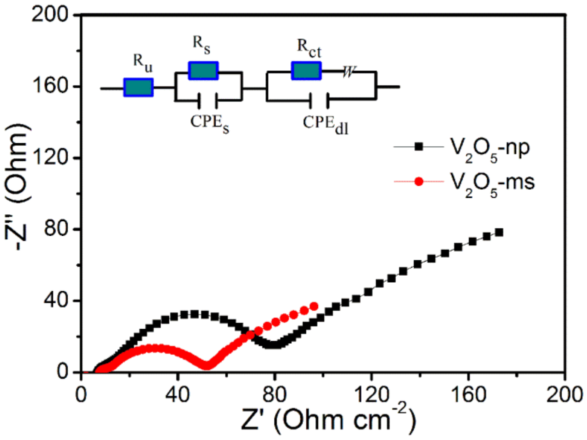

Figure S7. Electrochemical impedance spectra of V_2O_5 electrodes after 5 charge/discharge cycles and the equivalent circuit (inset) used to fit the impedance data.

Figure S7 shows the Nyquist plots of the V_2O_5-ms and V_2O_5-np electrodes after 5 charge/discharge cycles. In the equivalent circuit (inset), CPE_s and CPE_{dl} refer to the constant phase element of the surface layer and that of double layer, respectively. R_u represents uncompensated resistance between the lithium reference and the working electrode; and W is the Warburg impedance, reflecting the solid-state diffusion of Li^+ ions into the bulk of the active materials. R_s and R_{ct} represent the resistance of the SEI layer and the charge-transfer resistance, respectively. The Nyquist plots shown in the figure are similar, displaying two depressed semicircles and an inclined line in the low frequency region, which represents the Warburg impedance. The two semicircles presented in the high-frequency region and high-middle frequency region could be assigned to the resistance R_s of the SEI layer and the charge transfer resistance (R_{ct}), respectively.[1, 2]

Table S1. The electrochemical performances (cycling performance at relevant current rate or density, and rate capability) of the V_2O_5-ms and the reported V_2O_5 materials.

Materials	Voltage range	Capacity (mA h g^{-1}) / Cycle number	Current rate or density	Rate capacity (mA h g^{-1}) at relevant Current rate or density
As-prepared V_2O_5-ms in this work	2.5 – 4 V	101 / 100	20 C	105 at 30 C
3D porous V_2O_5[3]	2.5 – 4 V	110 / 200 ~ 115 / 100	10 C 10 C	86.7 at 56 C
V_2O_5 / graphene[4]	1.5 – 4 V	~ 110 / 100	1.6 A g^{-1} (4 C)	
V_2O_5 microspheres[5]	2.5 – 4 V	~ 135 / 100	0.2 C	92.2 at 15 C
V_2O_5 / CNTs composites[6]	2 – 4 V	104 / 200 ~ 123 / 100	5 C 5 C	169 at 10 C
Porous V_2O_5 nanotubes[7]	2.5 – 4 V	105 / 250 ~ 114 / 100	2 A g^{-1} (~ 13.5 C) 2 A g^{-1} (~ 13.5 C)	62.5 at 15 A g^{-1} (~101 C)

References

1. M. D. Levi, K. Gamolsky, D. Aurbach, U. Heider and R. Oesten, *Electrochim. Acta*, 2000, **45**, 1781.
2. D. Applestone and A. Manthiram, *RSC Adv.*, 2012, **2**, 5411.
3. S. Q. Wang, S. R. Li, Y. Sun, X. Y. Feng and C. H. Chen, *Energy Environ. Sci.*, 2011, **4**, 2854.
4. H. M. Liu and W. S. Yang, *Energy Environ. Sci.*, 2011, **4**, 4000.
5. S. Q. Wang, Z. D. Lu, D. Wang, C. G. Li, C. H. Chen and Y. D. Yin, *J. Mater. Chem.*, 2011, **21**, 6365.
6. X. L. Jia, Z. Chen, A. Suwarnasarn, L. Rice, X. L. Wang, H. Sohn, Q. Zhang, B. M. Wu, F. Wei and Y. F. Lu, *Energy Environ. Sci.*, 2012, **5**, 6845.
7. H. G. Wang, D. L. Ma, Y. Huang and X. B. Zhang, *Chem. Eur. J.*, 2012, **18**, 8987.