Supplementary Information for

Carbon nanotube-penetrated mesoporous V$_2$O$_5$ microspheres as a high-performance cathode material for lithium-ion batteries

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Experimental section

1. Synthesis

Three-dimensional (3D) CNT/V$_2$O$_5$ nanocomposites were synthesized using an aerosol spray drying process followed by two-step thermal treatments. Pristine CNTs were prepared by chemical vapor deposition (CVD) in a fluidized bed reactor$^{81}$ and then purified using 20 wt-% nitric acid (HNO$_3$) to remove the catalyst impurities. Then, the purified CNTs were dried in an oven for use. All the other chemicals were analytical grade and were directly used without any further purification.

To prepare CNT/V$_2$O$_5$ nanocomposites, the first step is to disperse 60.0 mg of CNTs together with 0.5 g of surfactant F127 into 60 mL of H$_2$O using ultrasound for 30 min. Then, 0.72 g of ammonium metavanadate (NH$_4$VO$_3$), 1.2 g of oxalic acid (H$_2$C$_2$O$_4$·2H$_2$O), 0.3 g of sucrose and 0.5 g of surfactant F127 were dissolved into 40 mL of H$_2$O. The above two kinds of solution were mixed
together using magnetic stirring, forming the precursor dispersion. The dispersion was then sent through an atomizer using nitrogen as a carrier gas. The produced aerosol droplets passed through a glass tube heated at 450 °C; as-formed particles were collected using a filter. Then, the collected particles were annealed at 400 °C under hydrogen atmosphere for 2 hr and another 300 °C under air for 2 hr, forming the final CNT/V$_2$O$_5$ nanocomposites. For comparison, the collected spray-dried particles were directly annealed at 400 °C and 300 °C under air for 2 hr to prepare the control samples. To prepare V$_2$O$_5$ microspheres, aerosol spray drying process was carried out on a similar V-precursor solution without addition of CNTs. The collected particles were also treated using the same two-step thermal treatments of CNT/V$_2$O$_5$ nanocomposites.

2. Characterization

X-ray diffraction measurements were conducted on a Bruker D8 Advance diffractometer at 40.0 kV and 120 mA using Cu-Kα radiation (λ=1.54 Å). Raman spectra were recorded with He-Ne laser excitation at 633 nm using a Horiba Jobin Yvon LabRAM HR800 Raman spectrometer. Nitrogen sorption isotherms were measured at 77 K with a Micromeritics ASAP 2020 analyzer. The specific surface areas were calculated by the Brunauer–Emmett–Teller (BET) method using a desorption branch in a relative pressure ($P/P_0$) range from 0.04 to 0.25. Scanning electron microscopy (SEM) experiments were conducted on a JSM 7401F instrument operated at 3.0 kV. Transmission electron microscopy (TEM) experiments were carried out on a Tecnai G$^2$ F20 instrument operated at 120.0 kV. Energy dispersive spectroscopy (EDS) analysis was performed on the Tecnai G$^2$ F20 instrument using an equipped EDAX apparatus. Thermalgravimetric analysis (TGA) was conducted on a TGA Q50 instrument at 10° min$^{-1}$ under an oxygen flow.

3. Electrochemical measurement

To make the battery electrodes, 70 wt%- of as-synthesized CNT/V$_2$O$_5$ nanocomposite particleless
or V$_2$O$_5$ particles, 6 wt-% carbon black, 6 wt-% additional CNTs, and 18 wt-% poly(vinylidene fluoride) (PVDF) dispersed in N-methylpyrrolidinone (NMP) were mixed to form slurries. The homogenous slurries were coated on a titanium substrate and dried at 80 °C for 30 min under vacuum. As formed electrodes were then pressed at a pressure of 2 MPa and further dried under vacuum at 100 °C for another 12 h. The mass loading of active material was 1-2 mg cm$^{-2}$ on each current collector. The electrodes were then assembled into 2032-type coin cells. Glass fiber (GF/D) from Whatman was used as the separator. The electrolyte solution was a 1 mol L$^{-1}$ LiClO$_4$ in propylene carbonate (PC) solution and lithium foils were used as both the counter and reference electrodes. All the cells were assembled in an argon-filled glovebox. The cyclic voltammetry (CV) measurements were carried out on a CHI 660C electrochemical workstation. Electrochemical impedance spectroscopy (EIS) tests of cells before and after cycling were carried out on a Solartron 1860/1287 Electrochemical Interface. The constant-current charge and discharge measurements were conducted by a LAND CT2000 at different current densities in a voltage range between 1.8 and 4.0 V (vs. Li/Li$^+$).

**Fig. S1** (a) STEM and (b-d) elemental mapping images of CNT/V$_2$O$_5$ nanocomposite microspheres (C (red), O (orange) and V (green)).
Fig. S2 Thermogravimetric analysis of CNT/V$_2$O$_5$ nanocomposites.

Fig. S3 (a) Low-magnification SEM image and (b) the size distribution of CNT/V$_2$O$_5$ nanocomposite microspheres.
**Fig. S4** (a) SEM image and (b) Raman spectrum of CNT/V$_2$O$_5$ nanocomposites treated at 400 °C in air for 2 hr.

**Fig. S5** (a) SEM image and (b) XRD spectrum of CNT/V$_2$O$_5$ nanocomposites treated at 300 °C in air for 2 hr.

**Fig. S6** Charge/discharge curves of (a) CNT/V$_2$O$_5$ electrode in comparison with that of (b) V$_2$O$_5$ electrode at different rates (0.2-10 C, 1 C= 250 mA g$^{-1}$ for the total mass of electrode).
**Fig. S7** Rate capability of CNT/V$_2$O$_5$ electrode in comparison with that of pure CNT electrode.

**Fig. S8** The cycle performance of a CNT/V$_2$O$_5$ electrode at a rate of 0.5 C.

**References**