Electronic Supplementary Information (ESI)

Facile synthesis of layered LiV_3O_8 hollow nanospheres as superior cathode materials for high-rate Li-ion batteries

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Experimental section

Synthesis of uniform V_2O_3 hollow nanosphere precursors

V_2O_3 hollow nanospheres were synthesized through a template-free solvothermal route. In a typical synthesis, 0.4 g vanadium (IV) acetylacetone were dissolved in 20–40 mL N,N-dimethyllformamide (DMF) and stirred for about 1 h. A clear transparent solution was formed, which was transferred into a 30–50 mL Teflon-lined stainless steel autoclave. The autoclave was sealed and maintained at 220 ºC for 36 h. After the solution was cooled down to room temperature, the obtained black products were collected by centrifuging the mixture, which were then washed with absolute ethanol and distilled water several times and dried at 80 °C for 6 h.

Synthesis of LiV_3O_8 porous and hollow nanosphere products

The above-obtained crystalline V_2O_3 precursor and $LiOH{\cdot}H_2O$ (V:Li = 3:1.05, molar ratio) was mixed in methanol under magnetic stirring and kept for 12 h. The mixture solution was heated to 50 °C to evaporate the methanol. The powder mixture produced was firstly heat treatment at 150 °C for 10h in vacuum, and finally annealed at 450 °C for 10 h in air. Finally, a brown LiV_3O_8 powder sample was thus obtained.

Synthesis of LiV_3O_8 solid nanosphere materials

The fabrication of LiV_3O_8 solid nanosphere cathode products is similar to LiV_3O_8 hollow nanosphere except for applying V_2O_3 solid nanospheres (obtained via a shorter solvothermal crystallization time) as the vanadium precursor.

Synthesis of LiV_3O_8 bulk materials

LiV_3O_8 bulk materials were prepared by a conventional solid-state reaction by heating

a mixture of V_2O_5 and $LiOH{\cdot}H_2O$ (V:Li = 3:1.05, molar ratio) to a temperature of 650 °C. The resulting melt was quenched to room temperature leading to a brown solid consisting of crystalline of LiV_3O_8 particles.

Materials characterization

The collected products were characterized by an X-ray diffractometry (XRD) on a Rigaku-DMax 2400 diffractometer equipped with the graphite monochromatized Cu Kα radiation flux at a scanning rate of $0.02°s^{-1}$. Scanning electron microscopy (SEM) analysis was carried using a JSM-6700F scanning electron microscope. The structure of these hollow nanospheres was investigated by means of transmission electron microscopy (TEM, Philips, TecnaiG2 20). The N_2 adsorption/desorption isotherm was obtained at 77 K using Beishide Instrument-ST, 3H-2000PS2.

Electrochemical test

The electrochemical performances of the as-prepared LiV_3O_8 products were measured by using CR2025 coin cells at 2.0–4.0V with NEWARE-BTS-5V20mA battery test system. For the preparation of the working electrode, a mixture of LiV_3O_8 hollow nanospheres active material, carbon black, and polyvinylidene fluoride (PVDF) in the weight ratio of 80:15:5 was ground in a mortar with *N*-methy1-2-pyrrolidone (NMP) as solvent to make slurry. A lithium foil was used as the counter electrode and a solution of 1M $LiPF_6$ in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 in volume) was used as electrolyte. The typical electrode was dried at 120 °C for 12 h

under vacuum before assembled into coin cell in an argon-filled glove box. The charge/discharge curves and cycling capacity were evaluated by NEWARE-BTS-5V20mA battery tester, in the cut-off voltages of 2.0 and 4.0 V.

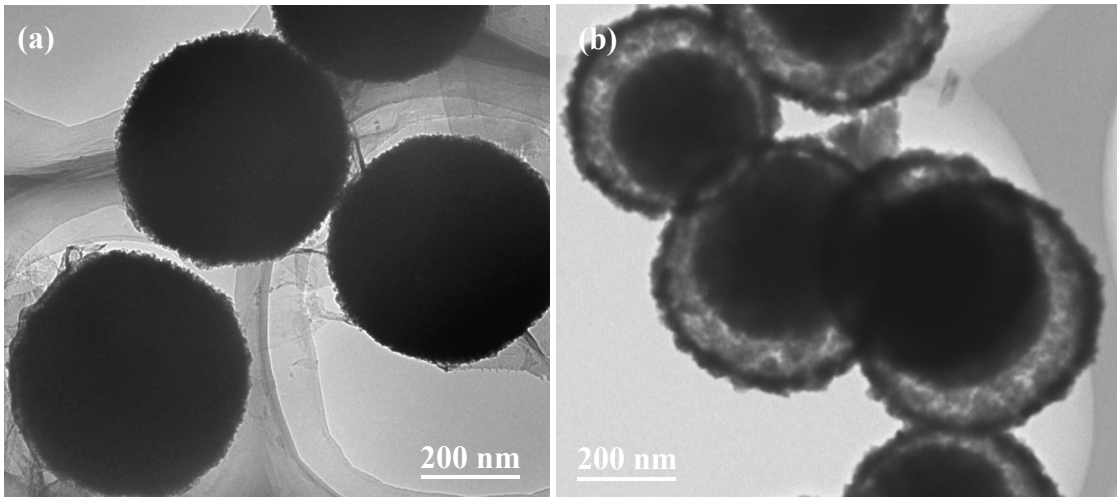

Fig. S1 TEM images of solid (a) and core-shell (b)V_2O_3 nanosphere precursors.

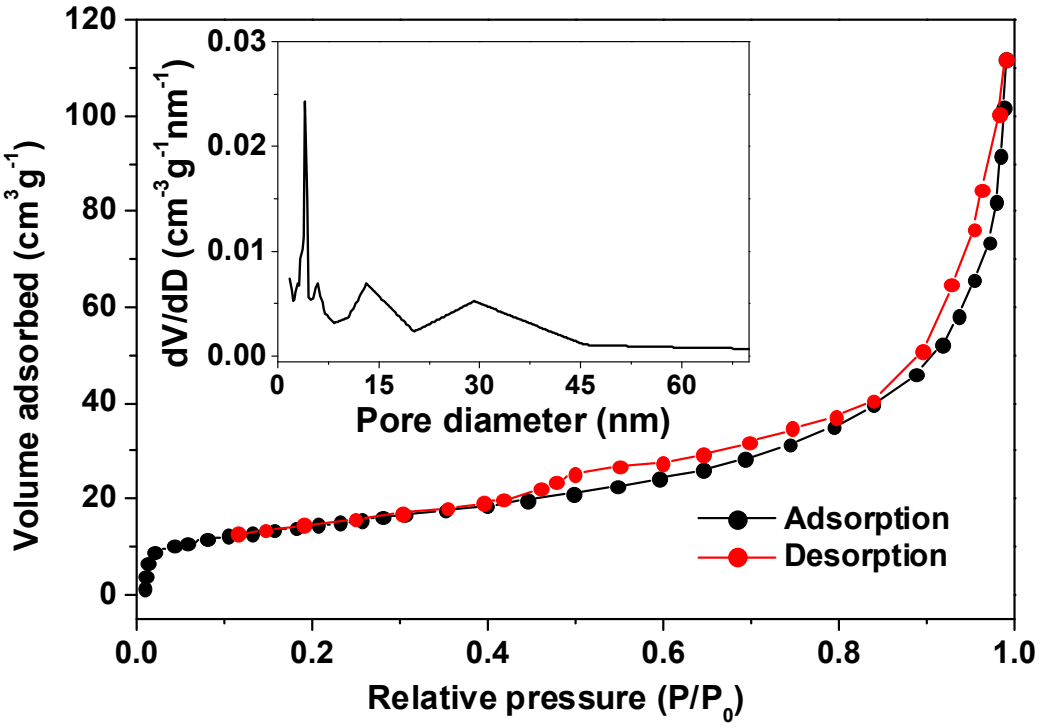

Fig. S2 N_2 adsorption/desorption isotherm and the corresponding pore size distribution of LiV_3O_8 porous and hollow nanospheres calculated using BJH method.

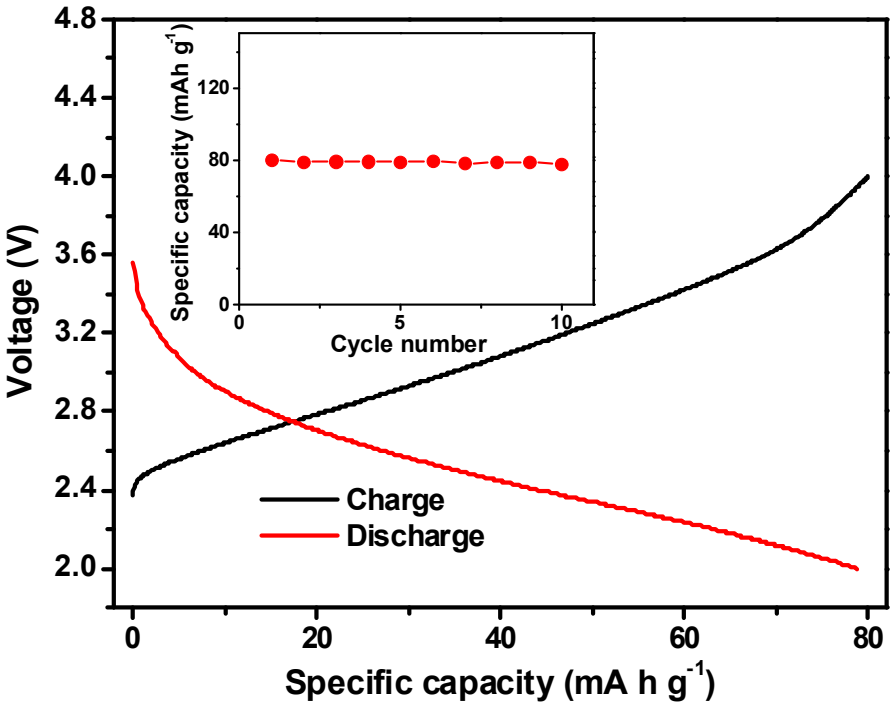

Fig. S3 Electrochemical performances of LiV_3O_8 porous and hollow nanosphere cathode materials in the high current density of 20C rate. The inset shows the cycling performance of these unique microstructured LiV_3O_8 materials.

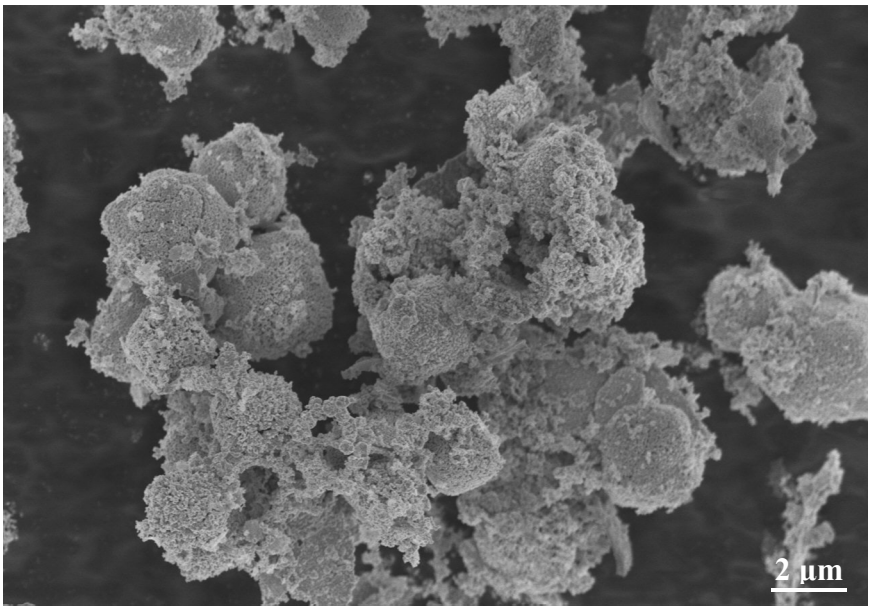

Fig. S4 SEM images of LiV_3O_8 bulk materials prepared by a conventional solid-state reaction.

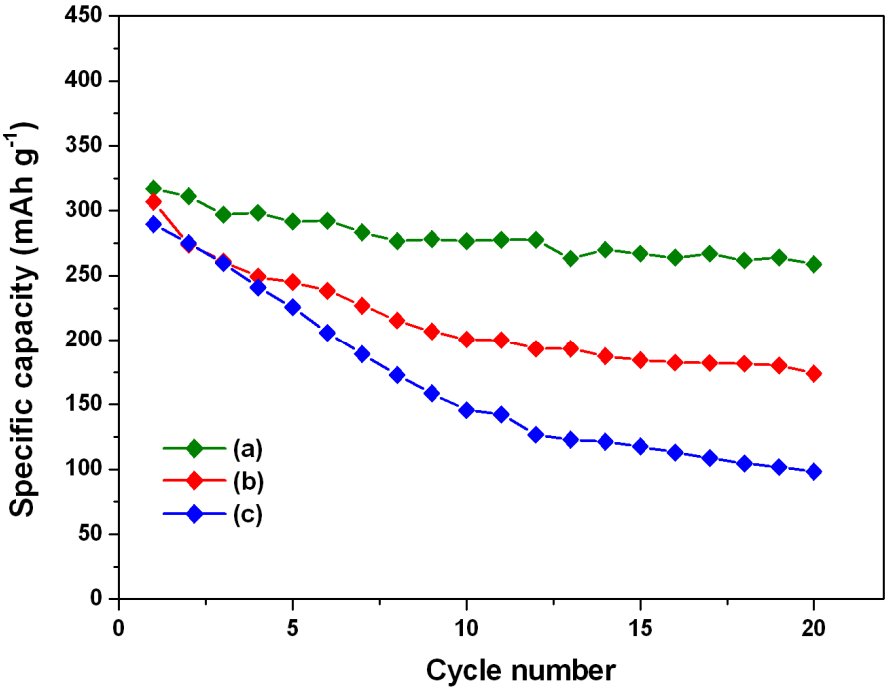

Fig. S5 Cycling performance of LiV_3O_8 hollow nanospheres (a), LiV_3O_8 solid nanospheres (b) and LiV_3O_8 bulk materials (c) at a current density of 0.1C.