Electronic Supplementary Information (ESI)

Template-free solvothermal synthesis of yolk-shell V_2O_5 microspheres as cathode materials for Li-ion batteries†

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Experimental section

Synthesis of monodisperse V_2O_5 yolk-shell microspheres

V_2O_5 yolk-shell microspheres were synthesized through a template-free solvothermal route and subsequent heat-treatment process in ambient air. In a typical synthesis process of V_2O_3 yolk-shell microspheres, 0.55 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 24 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. V_2O_5 yolk-shell microspheres were synthesized by heat treating these black V_2O_3 precursors at 400 ºC for 2 h in air.

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 JEOL-5600LV scanning electron microscope. The structure of these yolk-shell microspheres was investigated by means of transmission electron microscopy (TEM, Philips, TecnaiG2 20).

Electrochemical test

The electrochemical performances of the as-prepared yolk-shell V_2O_5 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 yolk-shell V_2O_5 microspheres 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.

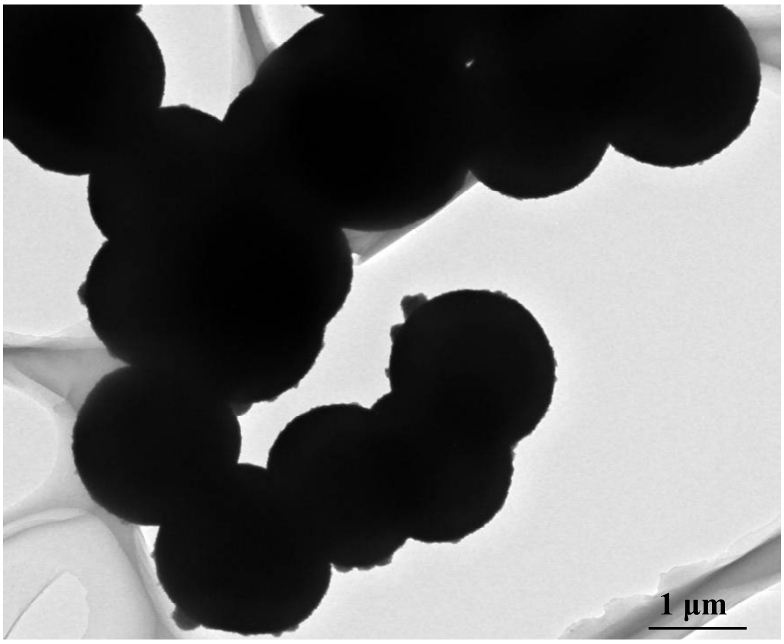

Fig. S1 TEM images of V_2O_3 solid microsphere intermediates.

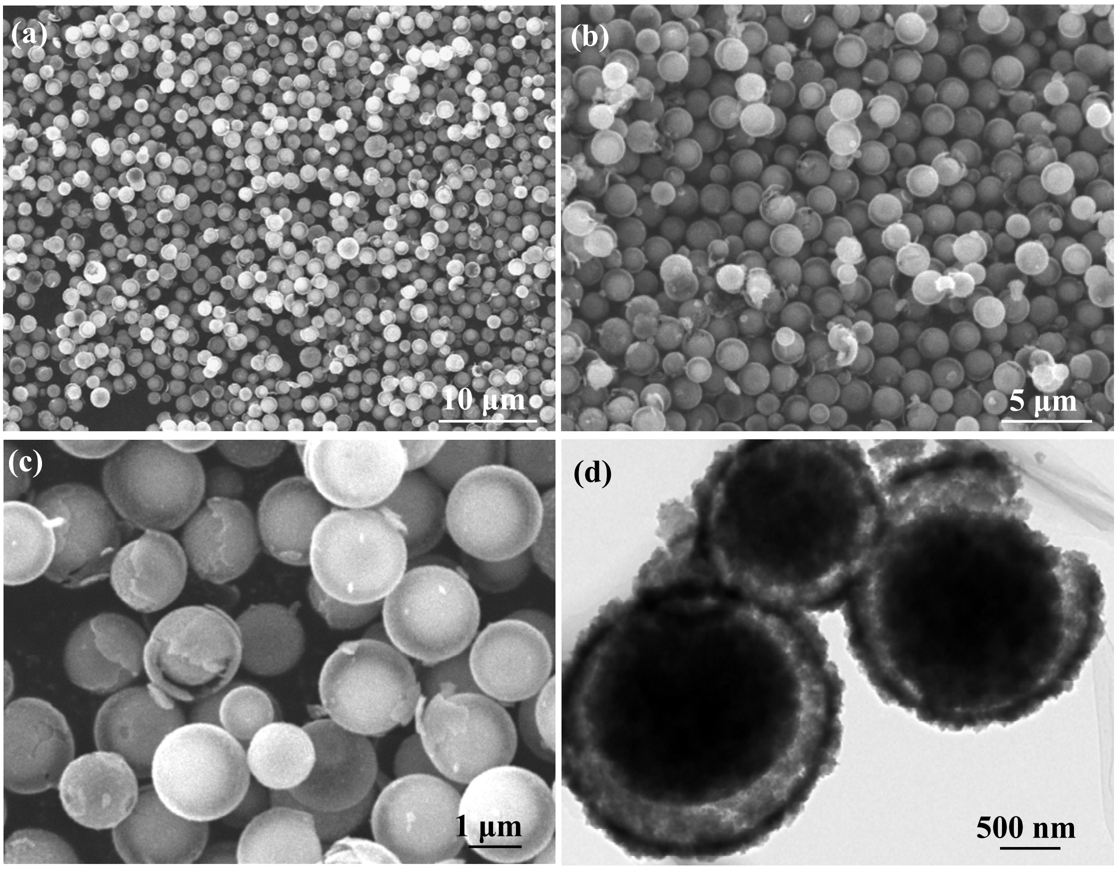

Fig. S2 Different magnification SEM (a–c) and high-magnification TEM (d) images of yolk-shell V_2O_5 microspheres. From Fig. S2a–c, it can be seen that these uniform yolk-shell V_2O_5 microspheres all have a solid core. High-magnification SEM (Fig. S2c) and TEM (Fig. S2d) images clearly shows that these solid cores of yolk-shell V_2O_5 microspheres are not detached completely from the outside wall, and there are connections (relatively loosely packed nanoparticles) between porous cores and shells (Fig. S2d).

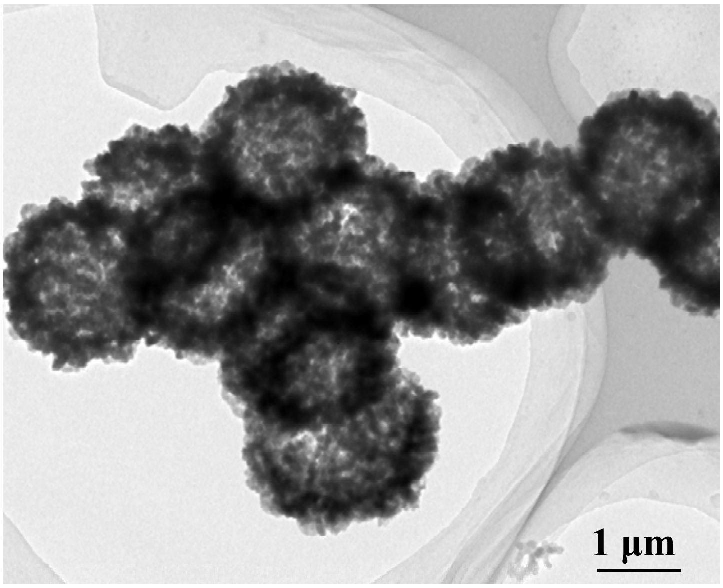

Fig. S3 TEM image of completely hollow structured V_2O_5 microspheres obtained via extending the solvothermal reaction time.

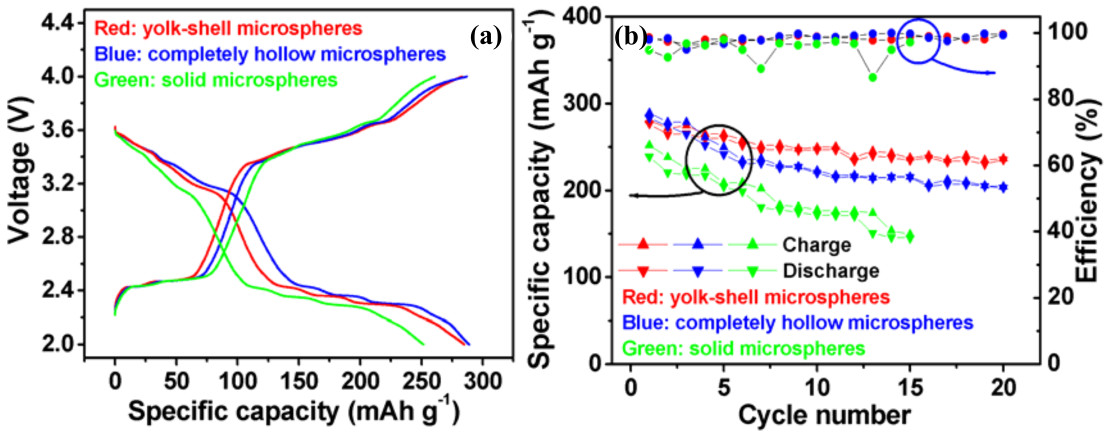

Fig. S4 Electrochemical performances of yolk-shell (red), completely hollow (blue) and solid (green) V_2O_5 microspheres: (a) voltage-capacity curves at 0.2C rate; (b) cycling performance (0.2C) at the voltage range of 2.0–4.0 V. It can be seen that the cycling performance of yolk-shell V_2O_5 microspheres is higher than that of completely hollow and solid V_2O_5 microspheres. Despite the specific capacity of initial discharge/charge processes of completely hollow microspheres is higher than that of yolk-shell microspheres, only a specific capacity of 204 mAh g^{-1} can be achieved after 20 cycles (236 mAh g^{-1} for yolk-shell microspheres). During these cycles, the Coulombic efficiency of yolk-shell microspheres is nearly approaching that of complete hollow microspheres and higher than that of solid microspheres (Fig. S4b).

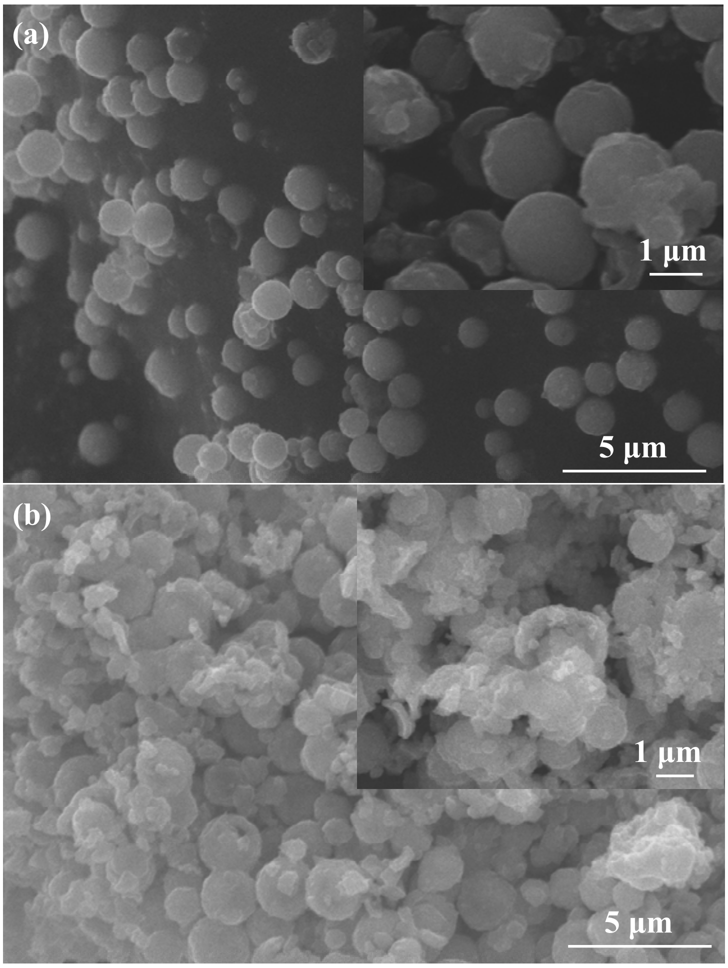

Fig. S5 Tracking the volume changes in yolk-shell (a) and complete hollow (b) V_2O_5 microspheres after 20 cycles. As shown in these SEM images, the microsphere configuration of most yolk-shell V_2O_5 was preserved (Fig. S5a), while most of hollow V_2O_5 microspheres collapsed (Fig. S5b), which indicates that the structure stability of yolk-shell microspheres is higher than that of completely hollow microspheres.