Supporting Information

Template-free bottom-up synthesis of yolk-shell vanadium oxide as high performance cathode for lithium ion batteries

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Experimental section

Preparation

The unique yolk-shell vanadium oxide was prepared by a facile one-pot hydrothermal method. In a classic synthesis, 100 μL vanadium oxytriisopropoxide (purchase from Sigma-Aldrich) was mixed with 20 mL 2-propanol with vigorous stirring for half an hour at ambient temperature. Subsequently, deionized water (3:1 molar ratio to VIP) was carefully dropped with continuous stirring for another 20 minutes. And then the mixture was transferred into 50 mL capacity Teflon-lined stainless steel autoclave, sealed and heated at 180 °C for 20 h. The black precipitated powders were filtered, washed thoroughly with absolute ethanol, dried at 100 °C for 48 h. The yellow V_2O_5 product with preserved microstructure can be easily obtained through calcination of black precursor at 500 °C for half an hour.

Characterization

The morphology of the yolk-shell product was tested by field-emission scanning electron microscope (FE-SEM, JSM-6700F) and transmission electron microscope (TEM, Tecnai G^2 20 instrument). The line-scan energy-dispersive X-ray spectroscopy (EDX) was also measured by Tecnai G^2 20 instrument. The XRD pattern was conducted using Rigaku D/max 2400 X-ray diffractometer equipped with graphite monochromatized Cu Kα radiation (λ=1.5406 Å). A scan rate of 0.02 $^{\circ}\cdot s^{-1}$ was applied to record the pattern in the 2θ range from 10 ° to 60 °. Measurement of surface area and analysis of pore size for the V_2O_5 sample are conducted by testing N_2 adsorption-desorption isotherms with a Micromeritics ASAP 2010 system.

Electrochemical Measurements

The electrochemical tests were carried out using two electrode Swagelok-type cells with pure lithium foil as the counter and also the reference electrode at room temperature. The working electrode was made of a mixture containing the active material (yolk-shell V_2O_5), conducting carbon black (Super-P-Li), and an organic binder (poly(vinylidene difluoride)) in a weight ratio of 70:20:10. 1 M LiPF6 in a 50:50 w/w mixture of ethylene carbonate and diethyl carbonate was employed as the electrolyte. Cells were assembled in an argon-filled glovebox with the moisture and oxygen contents maintained below 1 ppm. The cyclic voltammetry (CV) and galvanostatic charge-discharge properties were tested using a CHI-660D electrochemical workstation and a NEWARE battery tester, respectively.

The Fig. S1 clearly shows that the subunit nanoparticles attached together to form 200-300 nm balls (cores) by the first step of hydrolysis of VIP. And less than 50 nm of subunits in the ball can also be observed based on the enlarged SEM image (Fig. S1A, inset). With the reaction being prolonged > 2 h, yolk-shell structure could be obtained. This growth mechanism of nanoparticles self-assembly into a hierarchical yolk-shell structure is remarkably distinct from Ostwald repining process which involves mass diffusion from inner dense core to outer shell (The typical process of Ostwald repining is not observed throughout the whole reaction process.).

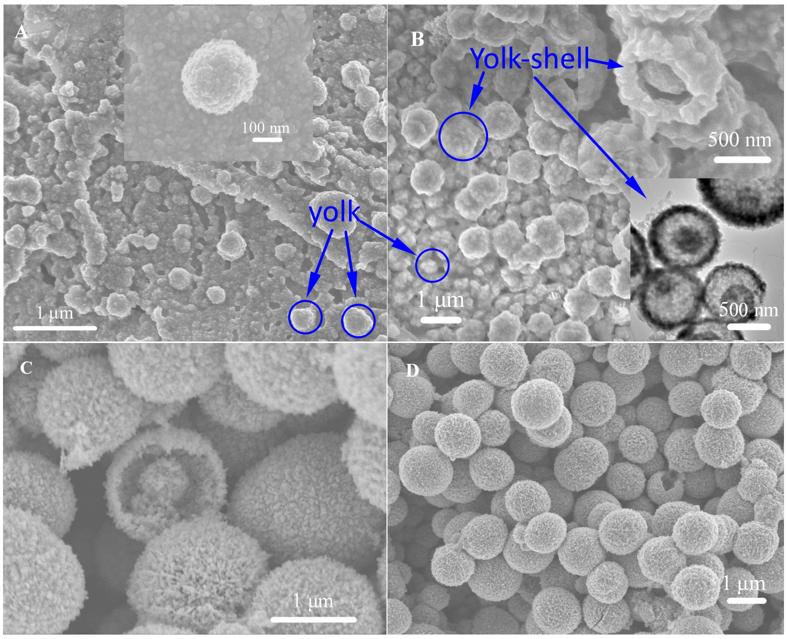

Fig. S1. SEM images (A) and inset, (B) and inset, (C) and (D) of the samples prepared by solvent-thermal reaction at 180 °C for 1 h, 2 h, 5 h and 10 h, respectively.

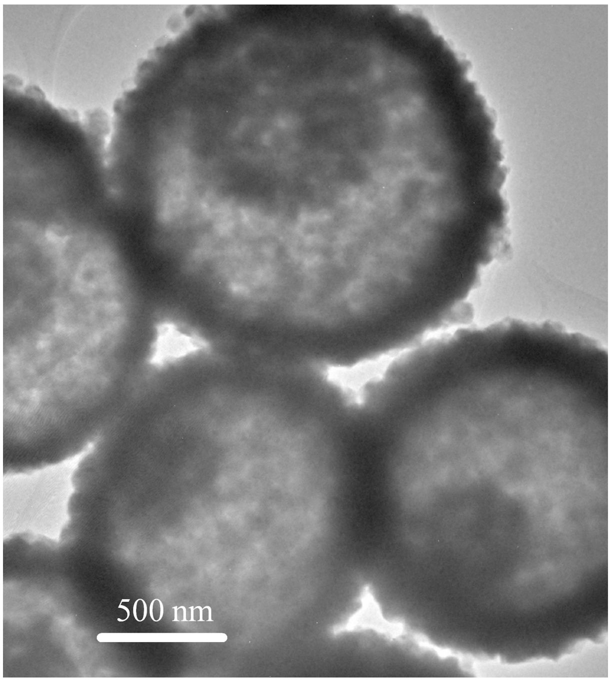

Fig. S2. TEM image of as-prepared precursor sample corresponding to the same one measured as Fig. 2B.

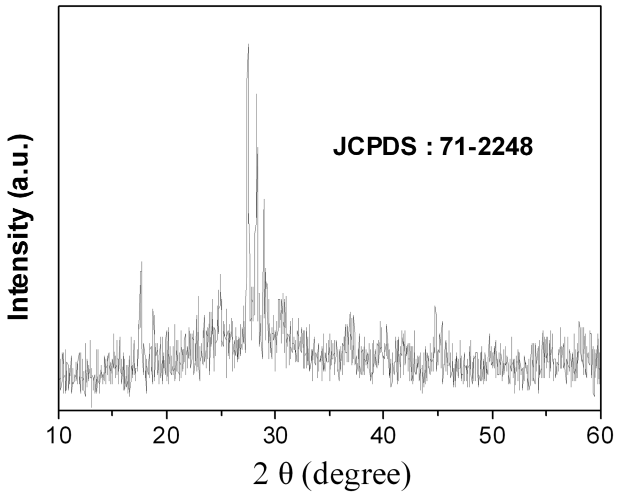

Fig. S3. XRD pattern of the yolk-shell precursor prepared by hydrolysis of VIP.

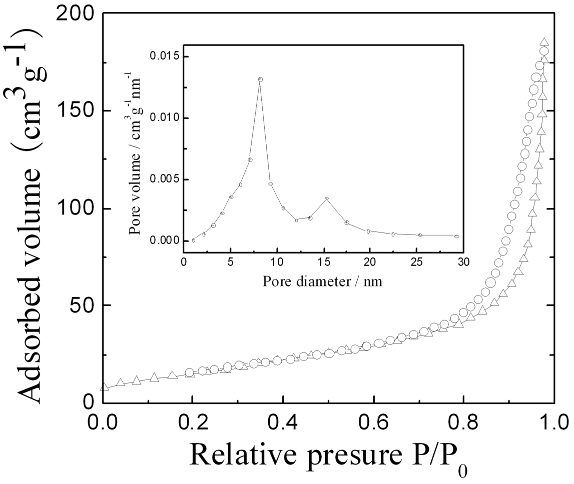

Fig. S4. Nitrogen sorption isotherm and pore size distribution (inset) of the yolk-shell V_2O_5.

The mechanism of lithium ion intercalation into V_2O_5 crystal has been discussed in previous literature.[1] Diffusion mechanism of Li^+ in yolk-shell nanostructure would be emphasized here: Electrolyte can penetrate free into the interstitial space between nanoparticles and into the space between the core and the shell. Besides, the nanoparticle subunits are small enough to short Li^+ diffusion path. The intrinsic layered lattice matrices of V_2O_5 crystals might supply space for Li^+ intercalation.

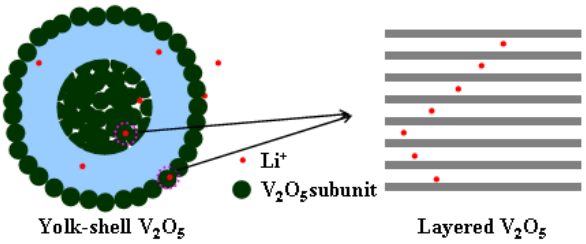

Fig. S5. Schematic illustration of diffusion and intercalation of lithium ion in yolk-shell V_2O_5 based cathode.

After 100 cycles, Fig. S6 showed that the yolk-shell structure of vanadium oxide could be still preserved very well. Furthermore, the primary nanoparticles did not agglomerated into bulk particles, indicating that well-defined yolk-shell structure might inhibit aggregation of nanoparticles and retain the integrity of microstructure by reducing stress suffered from Li^+ insertion/extraction.

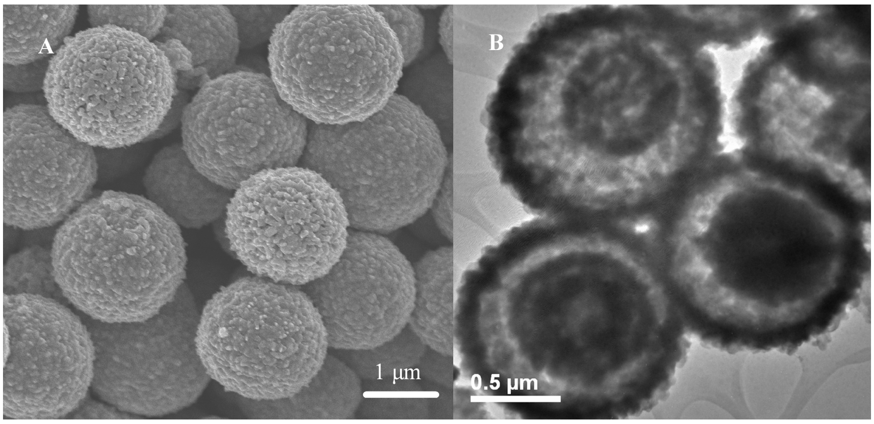

Fig. S6. (A) SEM image and (B) TEM image of the sample corresponding to the same one measured in stability test after 100 cycles shown in Figure 4c.

Reference
1. Y. Wang, G. Z. Cao, *Adv. Mater.* 2008, 20, 2251.