Supporting information for

Template-Free Synthesis of Hierarchical Hollow V_2O_5 Microspheres with Highly Stable Lithium Storage Capacity

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~~Experimental section~~

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Sample preparation: In a typical procedure, 0.0125 mol V_2O_5 (99.6%) were dissolved in 75 mL of deionized water under vigorous stirring at room temperature for 30 mins, then 0.025 mol citric acid (99.7%) was added. After 12 hours continuous stirring, a clear blue solution was obtained, which indicated the formation of $VO(C_6H_6O_7)$ (0.33 M).[1,2] Finally, 5 ml of as-prepared $VO(C_6H_6O_7)$ solution was mixed with 13 ml isopropanol (IPA, AR) or ethylene glycol (EG, AR) before being transferred into a 25 mL Teflon-lined stainless steel autoclave and kept in an oven at 200°C for 24 h. For comparison, the vanadium sources were changed to $VO(C_2O_4)$ (prepared from V_2O_5 and $H_2C_2O_4$)[3] or V_2O_5 sol (prepared from V_2O_5 and H_2O_2)[4] solution while other conditional parameters were kept the same. To study the time- and concentration- dependent structural evolutions of the precursors, the samples with different reaction times (6 h, 12 h, 18 h, and 24 h) and $VO(C_6H_6O_7)$ concentrations (0.066 M, 0.11 M, 0.165 M, and 0.264 M) were also fabricated, respectively. The synthesized precursors (designated as P-IPA and P-EG for isopropanol ethylene glycol cases, respectively) from the solvothermal reaction were washed with deionized water three times and then dried using a freeze dryer. Finally, the hollow V_2O_5 spheres were prepared by annealing the precursors at 350°C for 1 h with a heating rate of 1°C/min.

Materials characterization: The X-ray powder diffraction data were collect using a D8 Advanced Diffractometer (Bruker AXS) operated at 40 kV and 40 mA with Cu Kα radiation at room temperature. The Hitachi S-4800 scanning electron microscopy was applied for morphological observation and energy dispersive spectroscopy (EDS) mapping. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were performed on a FEI Tecnai G2 20 S-TWIN Scanning Transmission Electron Microscope.

The N_2 adsorption–desorption isotherms were measured on Micromeritics ASAP 2460 at 77 K.

Electrochemical measurements: The electrochemical measurements were conducted using a coin cell (CR2032) with lithium metal as the anode. The cathode slurry was fabricated by mixing the V_2O_5 products, acetylene black and polyvinylidene fluoride (PVDF) in a weight ratio of 7:2:1 in N-methyl-2-pyrrolidone (NMP) solution. Then the slurry was coated on the aluminum foil and dried in vacuum at 110^{o}C overnight. Finally, the coin cells were assembled in an Ar-filled glove box using a 1 M $LiPF_6$ in a 1:1:1 (vol.%) mixture of ethylene carbonate, dimethyl carbonate and diethyl carbonate as electrolyte. The cyclic voltammetry (CV) curves were obtained on a ZAHNER-IM6ex electrochemical workstation at a rate of 0.1 mV/s in the voltage range of 2.5-4 V (vs. Li/Li^+). The galvanostatic charge/discharge performances of the electrodes were measured at room temperature using a Land Battery tester (Land CT 2001 A, Wuhan, China). The loading mass of the active materials in the electrodes were about 0.6 to 0.7 mg/cm^2.

Figures and Captions

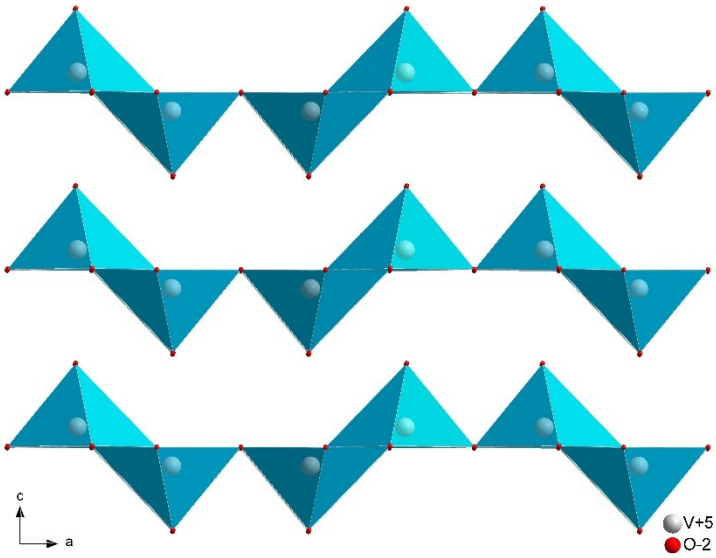

Fig. S1. Crystal structure projection of V_2O_5 along the [010] direction.

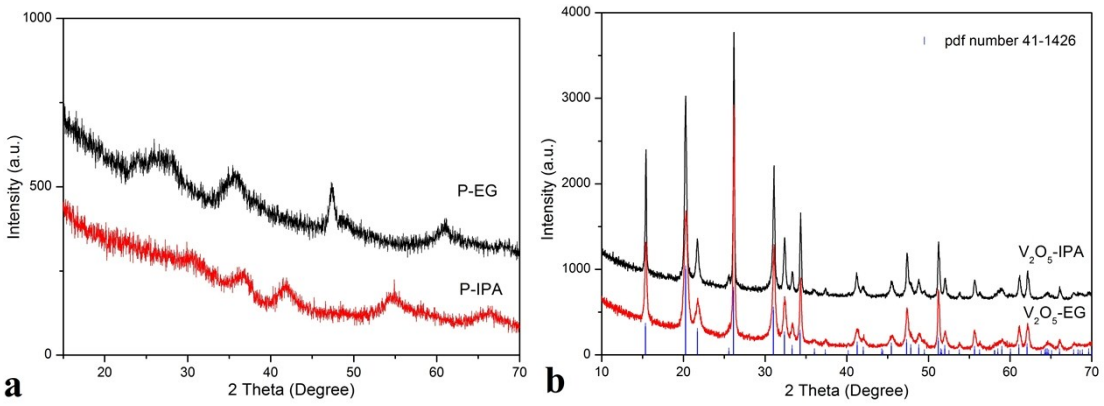

Fig. S2. XRD patterns of the precursors (a) obtained from IPA and EG solvents and the final products after calcination (b).

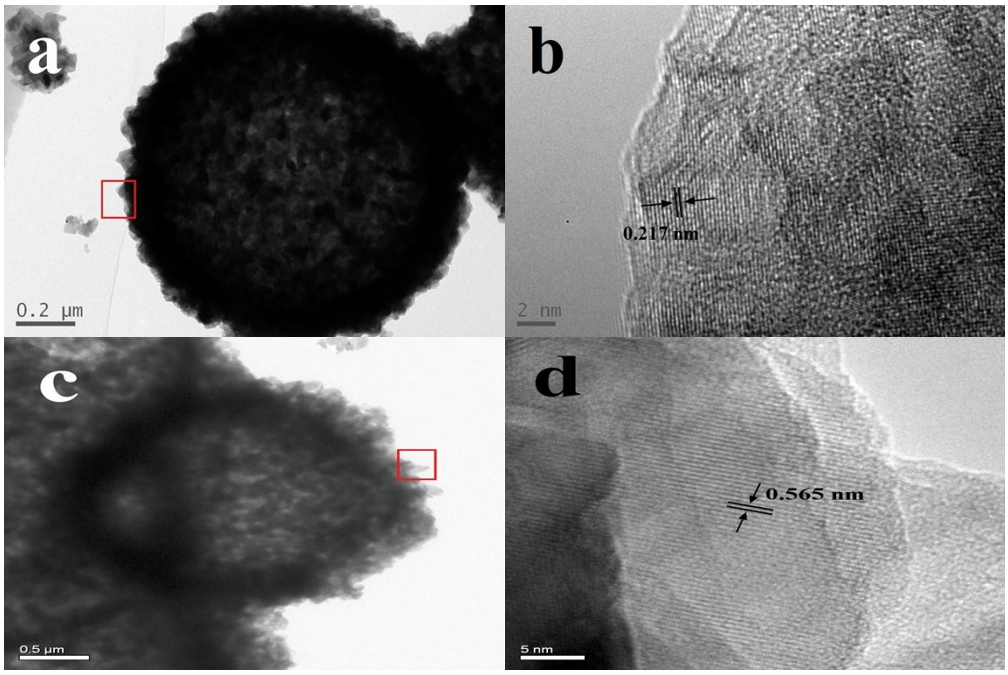

Fig. S3. TEM and HRTEM images of the V_2O_5-IPA (a and b) and V_2O_5-EG (c and d) microspheres.

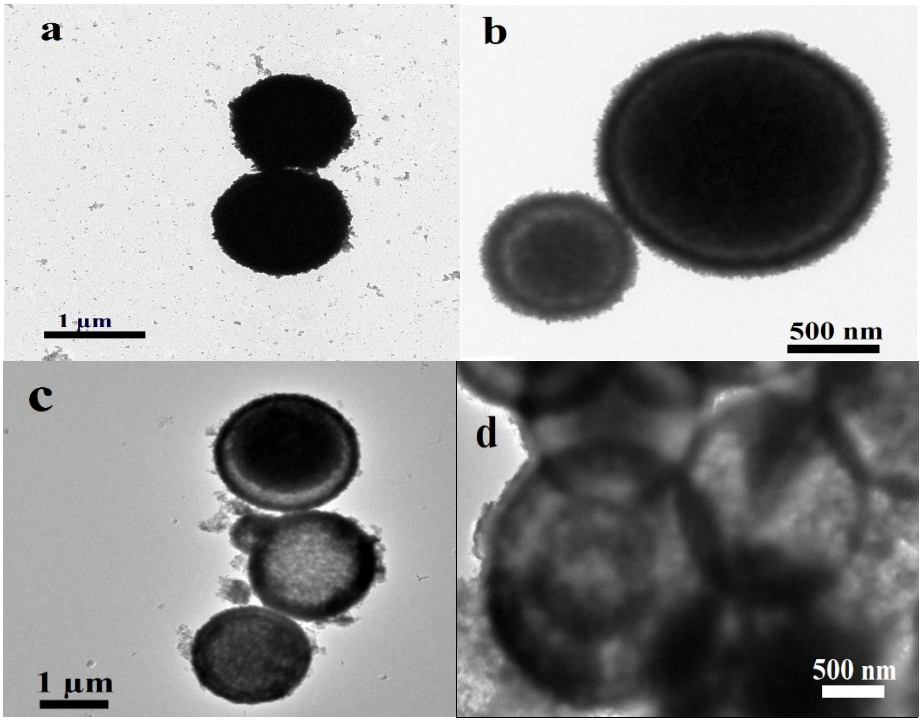

Fig. S4. TEM images of the as-prepared precursors in IPA at different reaction times: (a) 6 h, (b) 12 h, (c) 18 h and (d) 24 h.

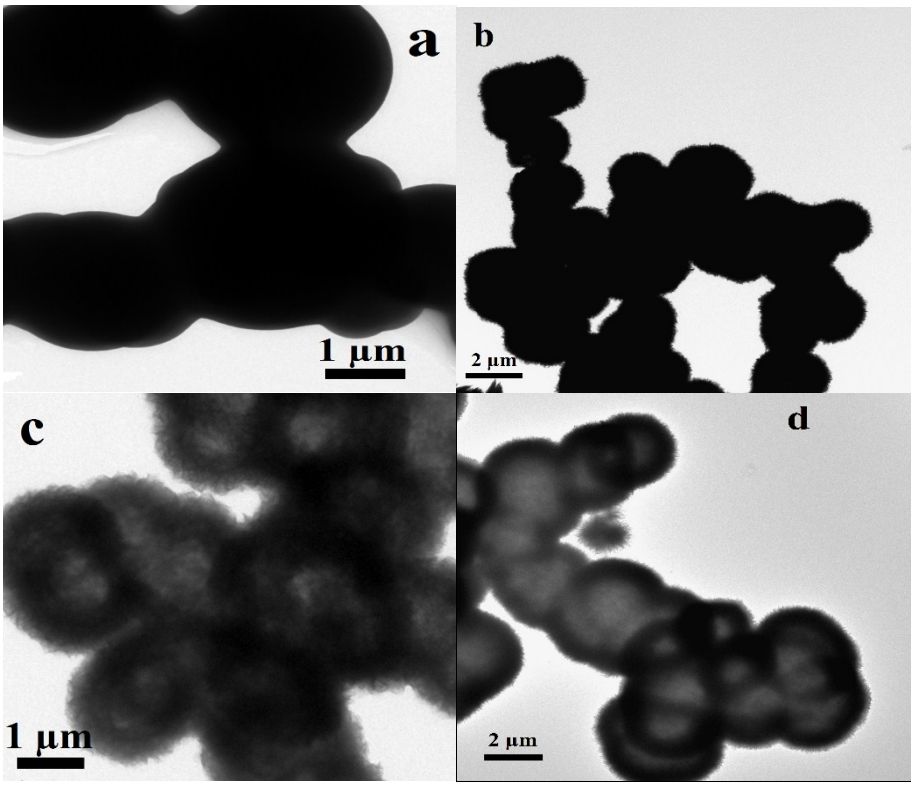

Fig. S5. TEM images of the as-prepared precursors in EG at different reaction times: (a) 6 h, (b) 12 h, (c) 20 h and (d) 24 h.

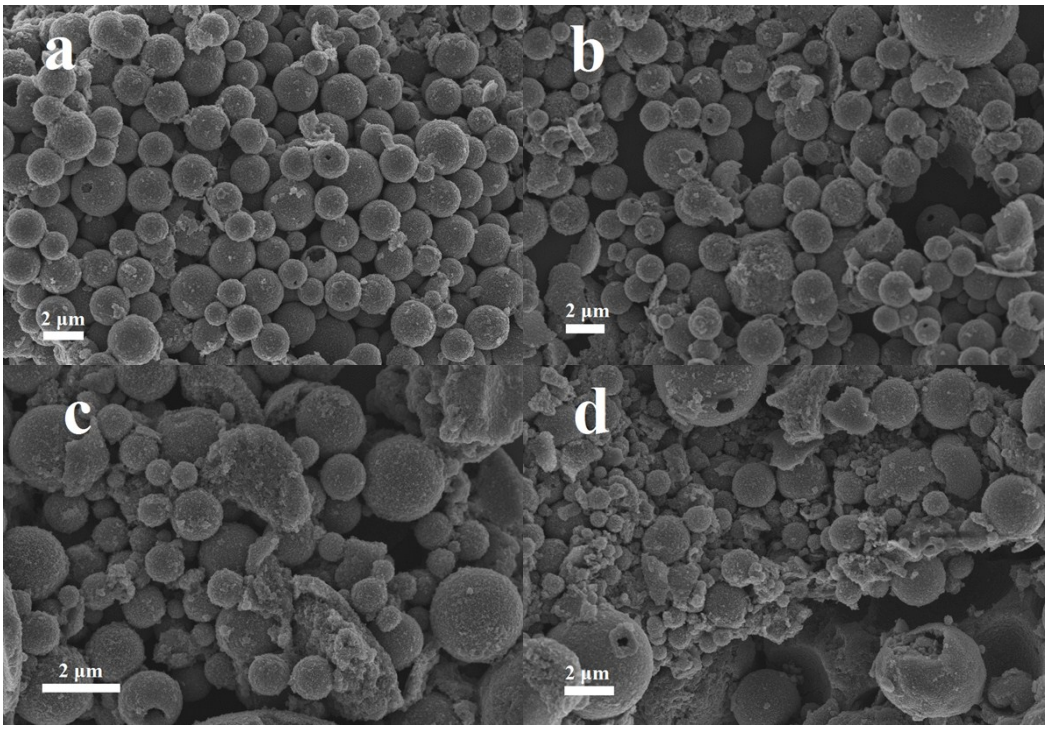

Fig. S6. SEM images of the precursors prepared from 5 ml of $VO(C_6H_6O_7)$ solution with concentrations of 0.264 M (a), 0.165 M (b), 0.11 M (c), and 0.066 M (d) in isopropanol.

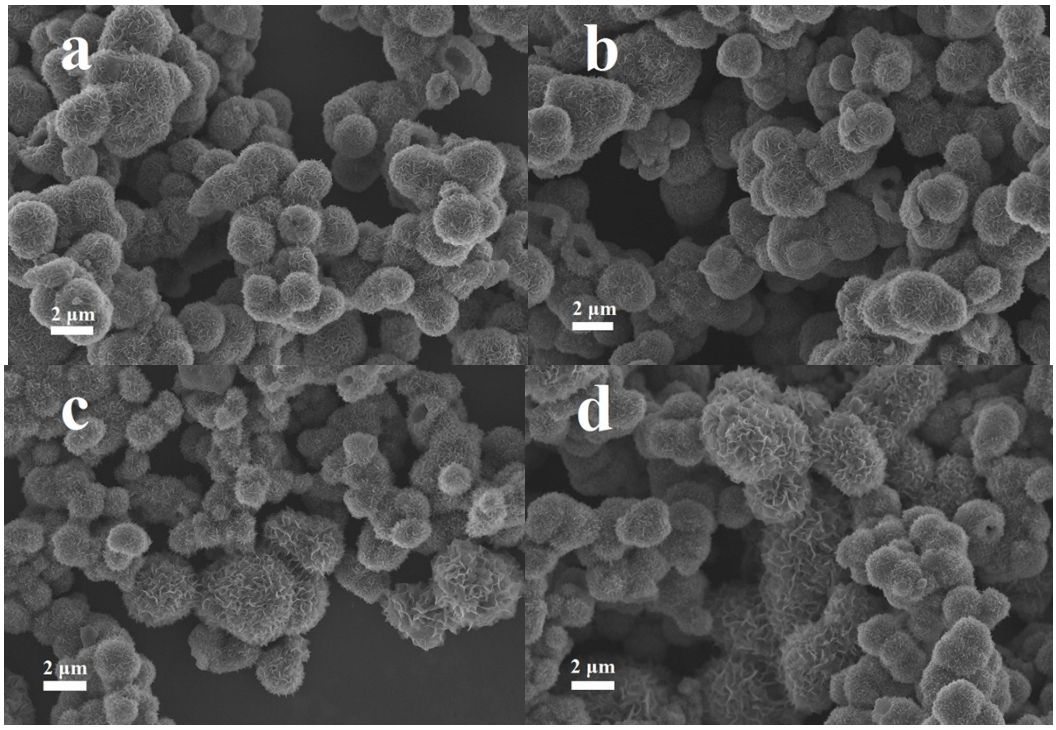

Fig. S7. SEM images of the precursors prepared from 5 ml of $VO(C_6H_6O_7)$ solution with concentrations of 0.264 M (a), 0.165 M (b), 0.11 M (c), and 0.066 M (d) in ethylene glycol.

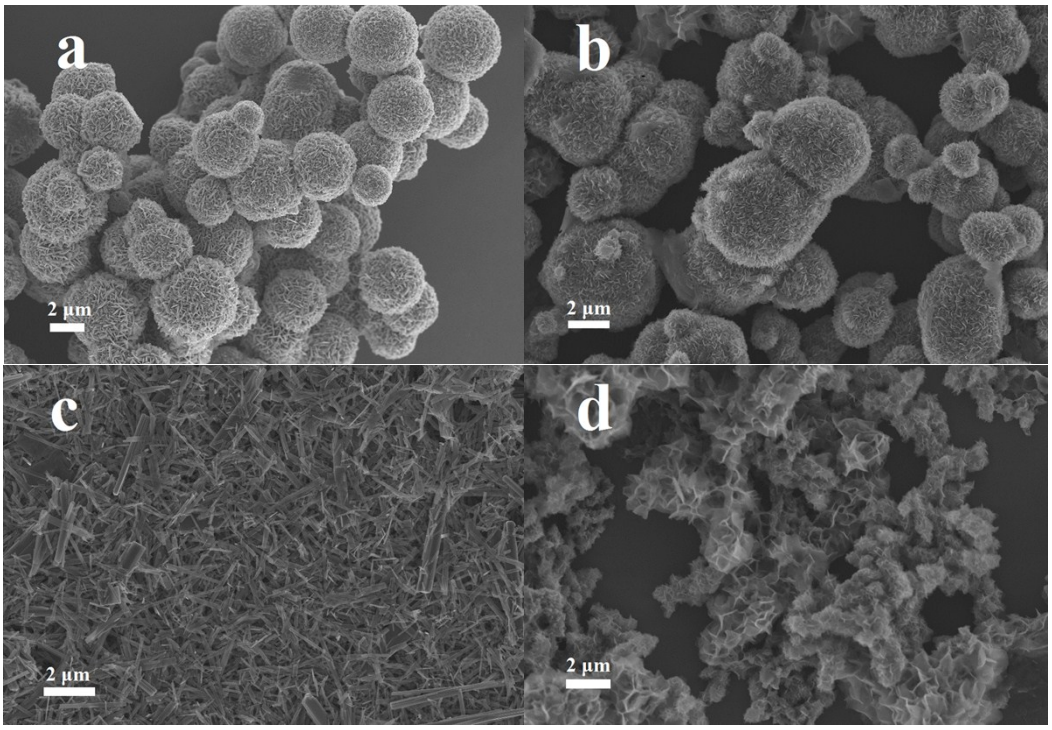

Fig. S8. SEM images of the precursors prepared from $VO(C_2O_4)$ and V_2O_5 sol solution in isopropanol (a and c) and ethylene glycol (b and d), respectively.

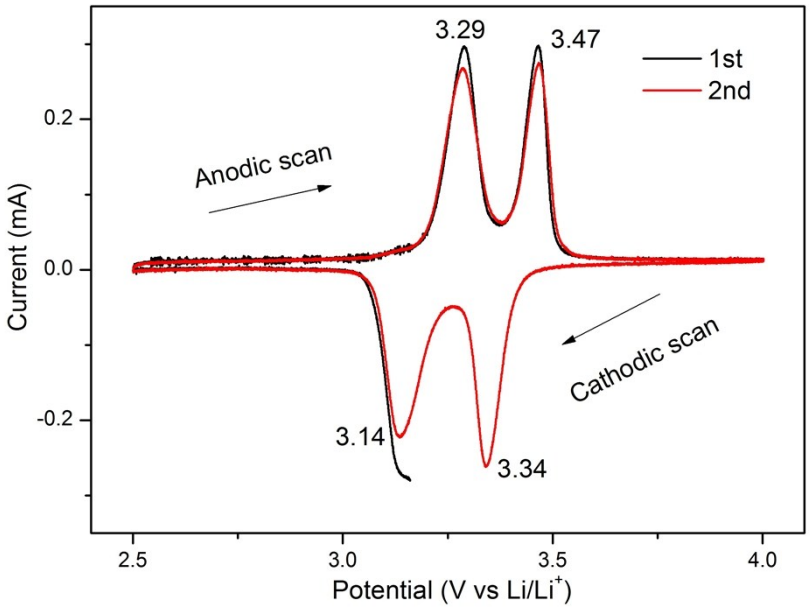

Fig. S9. CV curves of V_2O_5-EG electrode.

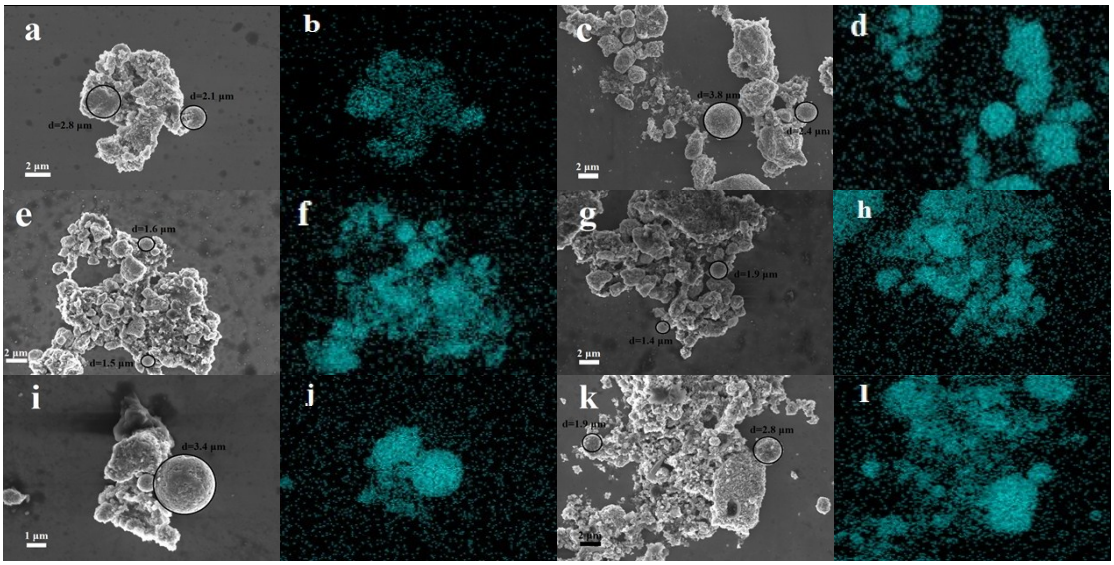

Fig. S10. SEM images and corresponding elemental mapping of V for V_2O_5-IPA electrodes under different charge/discharge states (from OCV (a and b) to 3.25 V (c and d), 2.5 V (e and f), then to 3.35 V (g and h) and 4 V (i and j)) or after 300 cycles (k and l).

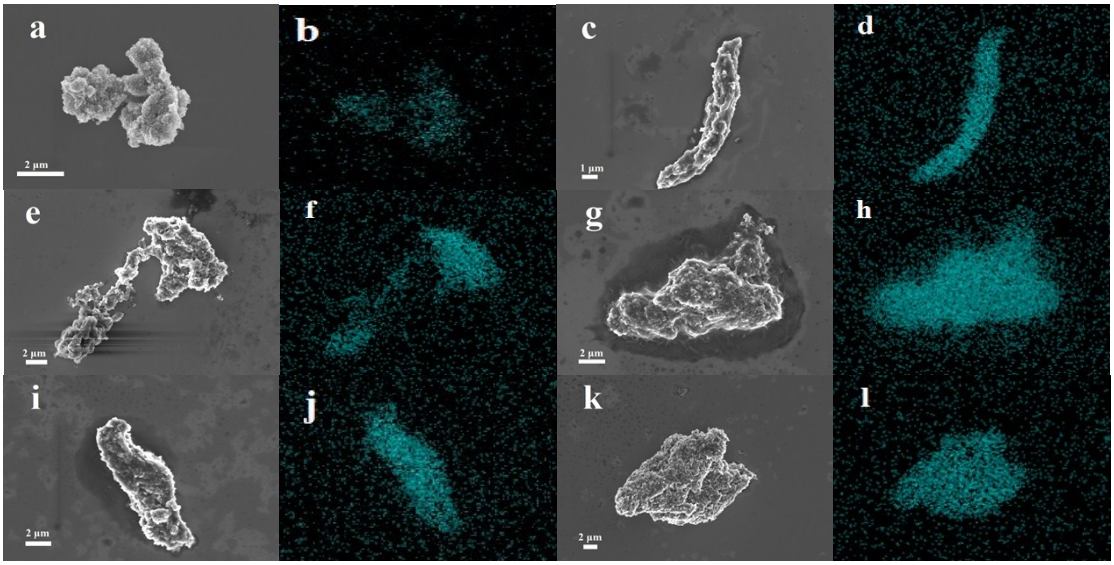

Fig. S11. SEM images and corresponding elemental mapping of V for V_2O_5-EG electrodes under different charge/discharge states (from OCV (a and b) to 3.25 V (c and d), 2.5 V (e and f), then to 3.35 V (g and h) and 4 V (i and j)) or after 300 cycles (k and l).

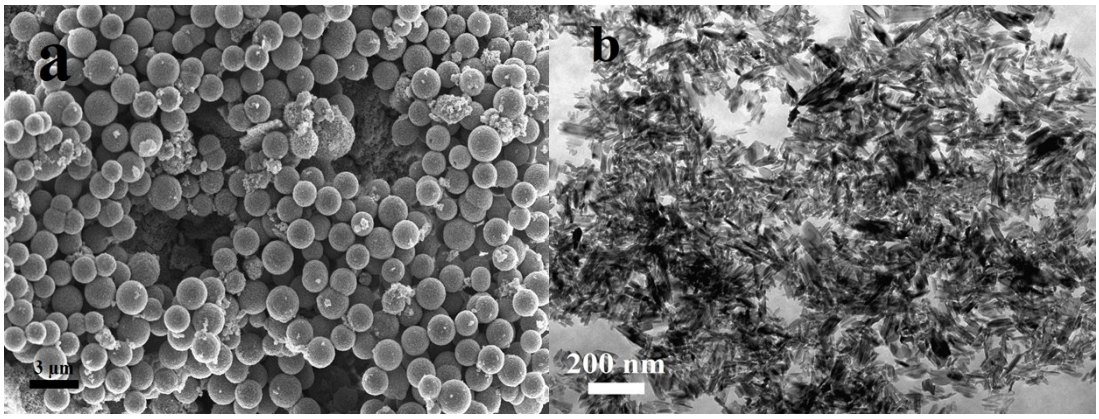

Fig. S12. the V_2O_5-IPA (a) and V_2O_5-EG (b) microspheres after dispersing in ethanol for one month, respectively.

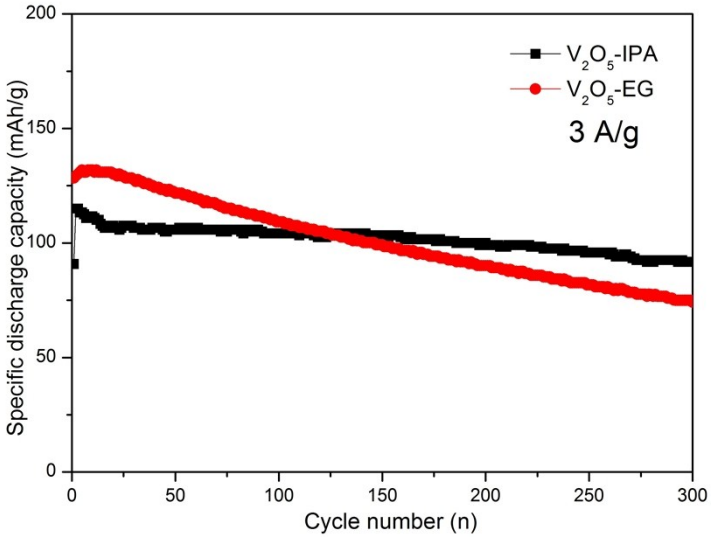

Fig. S13. Cycling performance of V_2O_5-IPA and V_2O_5-EG electrodes at 3 A/g.

Table and Caption

Table S1 The cycling performance of the reported V_2O_5 electrodes

Materials	Voltage range	Current density	Initial or maximum capacity (mAh/g)	Capacity (mAh/g) (cycle number)
Rigid hollow microspheres[a]	2.5-4 V	1000 mA/g	128	118 (500)
		3000 mA/g	115	92 (300)
Nanosheet-assembled hollow microspheres[a]		300 mA/g	140	122 (300)
Ultra-large nanosheets[4]	2.5-4 V	300 mA/g	135	127 (200)
3D porous hierarchical octahedrons[5]	2.4-4V	2000 mA/g	96	93 (500)
3D Interconnected Nanonetwork[6]	2.4-4 V	1000 mA/g	110	106 (1000)
Hollow microflowers[7]	2.5-4 V	300 mA/g	140	120 (100)
Nanosheet-assembled hollow microspheres[8]	2.5-4 V	300 mA/g	137	128 (50)
Nanorod-assembled hollow microspheres[9]	2.5-4 V	294 mA/g	143	128.8 (200)
3D porous hierarchical microplates[10]	2.4-4 V	1000 mA/g	130	123 (100)

a: this work

References

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