Experimental details

Synthesis of VOOH and V$_2$O$_5$ hollow microspheres: The V(OH)$_2$NH$_2$ solid precursors were first prepared according to the method reported in literature with minor modification.[30] Briefly, 2 mmol of NH$_4$VO$_3$ and 1 mL of HCl (1 mol·L$^{-1}$) were dissolved in 45 mL of H$_2$O to obtain a yellow transparent solution. Subsequently, 3 mL of hydrazine (N$_2$H$_4$·H$_2$O) was introduced into the above solution dropwise, which was further stirred at room temperature for 30 min. The yellow transparent solution became gray and turbid. At last, the V(OH)$_2$NH$_2$-containing suspensions were directly transferred into an autoclave and hydrothermally treated at 120°C for 4h. The VOOH precipitate was collected by centrifuging and washing. High crystalline V$_2$O$_5$ hollow microspheres were obtained via calcination of VOOH at 350°C in air for 3h.

Characterization methods: The morphology, microstructure, and composition of the materials were investigated by FE-SEM (Hitachi SU8000), TEM (Philips EM 420), XRD (Bruker D4), XPS (VG ESCA 2000), and FTIR (Nicolet 730).

Electrochemical testing: The working electrode slurry was prepared by dispersing the
A mixture of VOOH or V₂O₅, Super P-Li, and poly(vinylidene fluoride) (PVDF) binder with a weight ratio of 7/2/1 in N-methylpyrrolidone. The slurry was spread onto aluminum foil disks and dried in a vacuum oven at 120 °C overnight. The mass loading of active material on each electrode is about 1 mg cm⁻². Na foil as the counter and reference electrodes, and 1 mol L⁻¹ NaClO₄ dissolved in propylene carbonate (PC) solvent as the electrolyte, Celgard 2500 as the separator, were used to assemble a CR2032 coin cell. Galvanostatic discharge and charge tests were performed with a cycle tester from LAND Electronic Co. The cyclic voltammograms were obtained using ZAHNER Electrochemical Workstation IM6.

Supplementary figures

Figure S1 XRD patterns of VOOH hollow microspheres prepared at different hydrothermal conditions or using different vanadium sources.
Figure S2 TEM images of high crystallinity V$_2$O$_5$ hollow microspheres.

Figure S3 Coulombic efficiency of the VOOH microspheres electrode during long-term cycles.
Figure S4 Survey XPS spectra of VOOH electrodes after cycling.