## Supporting Information

## Ultrathin Single-Crystalline Vanadium Pentoxide Nanoribbons Constructed 3D Networks for Superior Energy Storage

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**Figure S1.** (a) Schematic illustration for the fabrication of 3D V<sub>2</sub>O<sub>5</sub>@PPy networks by a combined hydrothermal synthesis, freeze-drying and subsequent PPy coating. The optical photos of (b) commercial V<sub>2</sub>O<sub>5</sub> particles, (c) as-prepared V<sub>2</sub>O<sub>5</sub> nanoribbon gelatin, (d) pure 3D V<sub>2</sub>O<sub>5</sub> network gel produced by freeze-drying process, and (e) 3D V<sub>2</sub>O<sub>5</sub>@PPy network produced by PPy nanocasting process.



**Figure S2.** (a) and (b) SEM images with different magnifications for  $V_2O_5$  sample obtained by normal drying method, demonstrating that the  $V_2O_5$  nanoribbons are strongly aggregated and compactly stacked together without using freeze-drying process.



**Figure S3.** (a) and (b) HRTEM images of  $V_2O_5$ @PPy ribbon with different magnifications. (a) HRTEM image shows the incontinuous structure of PPy on the surface of  $V_2O_5$  wellcrystalline ribbon (marked by white dot line). (b) HRTEM image discloses the interfaces between PPy nanograins and well-defined  $V_2O_5$  (marked by red dot line) (scale bar, 2 nm).



**Figure S4.** (a) XRD patterns of 3D V<sub>2</sub>O<sub>5</sub>@PPy network, showing a main peak at 6.1°, and three small peaks at 12.2°, 18.3° and 24.4°, well consistent with those of pure 3D V<sub>2</sub>O<sub>5</sub> network. (b) XPS surveys of 3D V<sub>2</sub>O<sub>5</sub>@PPy network and pure 3D V<sub>2</sub>O<sub>5</sub> network. High resolution spectra of (c) C1s, (d) N1s, (e) V2p3 and (f) O1s, respectively.



**Figure S5.** The Fourier transform infrared spectroscopy (FTIR) spectra of  $PP_y$ , 3D V<sub>2</sub>O<sub>5</sub> network and V<sub>2</sub>O<sub>5</sub>@PP<sub>y</sub> network. There is a band at 1556 cm<sup>-1</sup>, attributed to the fundamental vibration of pyrrole ring, and another band at 1173 cm<sup>-1</sup> is characteristic of the C-N stretching vibration, demonstrating the presence of PP<sub>y</sub> in our 3D V<sub>2</sub>O<sub>5</sub>@PP<sub>y</sub> network.



**Figure S6.** Nitrogen adsorption/desorption isothermal of the 3D pure  $V_2O_5$  network and  $V_2O_5@PP_y$  network, showing the surface area of 130 and 35 m<sup>2</sup>g<sup>-1</sup>, respectively. Insert was the pore size distribution of 3D pure  $V_2O_5$  network.



**Figure S7.** The electrochemical performances of a symmetric supercapacitor using 3D  $V_2O_5@PP_y$  network as electrode material. (a) CV curves at various scan rates from 5 to 100 mV s<sup>-1</sup>, (b-c) Galvanostatic charge-discharge curves at different current densities from 0.25 to 10 A g<sup>-1</sup>.



**Figure S8.** The influence of of  $PP_y$  content on the cyclic voltammetry (CV) curves of 3D  $V_2O_5@PP_y$  networks. The shape of the CV curve become distinctly distorted with increasing  $PP_y$  content from 5 wt% to 40 wt% at the scan rate of 20 mV s<sup>-1</sup> in 1.0 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution.



**Figure S9.** The influence of  $PP_y$  content on rate capabilities of 3D V<sub>2</sub>O<sub>5</sub>@PP<sub>y</sub> networks at different current densities. The specific capacitances calculated from charge-discharge curves largely decreases with increasing  $PP_y$  coating amount (from 5 wt% to 40 wt%).



Figure S10. The equivalent circuit diagram used for fitting the EIS profiles of 3D  $V_2O_5@PP_y$ network, pure 3D  $V_2O_5$  network and  $V_2O_5$  particles@PP<sub>y</sub>.



**Figure S11.** (a) A series of CV measurements at 100 mV s<sup>-1</sup>, while the operating potential is extended to 2.0 V, a distinct peak appears at the end of CV (select area in (a)), ascribed to the evolution of oxygen. (b) Galvanostatic charge/discharge plots at 1A g<sup>-1</sup> with the potential window between 1.0 and 2.0 V, when the voltage reach 2.0 V, the charge-discharge curve is no longer symmetric (select area in (b)) indicating non-capacitive behavior.



Figure S12. Galvanostatic charge/discharge plots of 3D V<sub>2</sub>O<sub>5</sub>@PPy network// 3D rGO asymmetric supercapacitor at high current densities between 2 and 10 A  $g^{-1}$  under the potential window of 1.8 V.



Figure S13. Specific capacitance of  $V_2O_5@PP_y$  network// 3D rGO asymmetric supercapacitorl under different current densities (from 0.25 to 10 A g<sup>-1</sup>) calculated from galvanostatic charge/discharge plots.

**Table 1.** The kinetics parameters of 3D  $V_2O_5$ @PPy network, pure 3D  $V_2O_5$  network and  $V_2O_5$ particles@PPy.

Electrodes	$R_{\rm s}\left(\Omega ight)$	$R_{\rm ct}\left(\Omega\right)$
$3D V_2O_5@PP_v$ network	0.6	5.1
Pure 3D $V_2O_5$ network	0.7	7.4
$V_2O_5@PP_y$ particles	1.0	8.6