Supporting Information

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

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Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A. This journal is © The Royal Society of Chemistry 2014
Figure S1. (a) Schematic illustration for the fabrication of 3D V₂O₅@PPy networks by a combined hydrothermal synthesis, freeze-drying and subsequent PPy coating. The optical photos of (b) commercial V₂O₅ particles, (c) as-prepared V₂O₅ nanoribbon gelatin, (d) pure 3D V₂O₅ network gel produced by freeze-drying process, and (e) 3D V₂O₅@PPy network produced by PPy nanocasting process.
**Figure S2.** (a) and (b) SEM images with different magnifications for V$_2$O$_5$ sample obtained by normal drying method, demonstrating that the V$_2$O$_5$ nanoribbons are strongly aggregated and compactly stacked together without using freeze-drying process.

**Figure S3.** (a) and (b) HRTEM images of V$_2$O$_5$@PPy ribbon with different magnifications. (a) HRTEM image shows the incontinuous structure of PPy on the surface of V$_2$O$_5$ well-crystalline ribbon (marked by white dot line). (b) HRTEM image discloses the interfaces between PPy nanograins and well-defined V$_2$O$_5$ (marked by red dot line) (scale bar, 2 nm).
Figure S4. (a) XRD patterns of 3D V$_2$O$_5$@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$_2$O$_5$ network. (b) XPS surveys of 3D V$_2$O$_5$@PPy network and pure 3D V$_2$O$_5$ 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 PPy, 3D V_{2}O_{5} network and V_{2}O_{5}@PPy network. There is a band at 1556 cm\(^{-1}\), attributed to the fundamental vibration of pyrrole ring, and another band at 1173 cm\(^{-1}\) is characteristic of the C-N stretching vibration, demonstrating the presence of PPy in our 3D V_{2}O_{5}@PPy network.

**Figure S6.** Nitrogen adsorption/desorption isothermal of the 3D pure V_{2}O_{5} network and V_{2}O_{5}@PPy network, showing the surface area of 130 and 35 m\(^{2}\)g\(^{-1}\), respectively. Insert was the pore size distribution of 3D pure V_{2}O_{5} network.
Figure S7. The electrochemical performances of a symmetric supercapacitor using 3D V$_2$O$_5$@PP$_y$ network as electrode material. (a) CV curves at various scan rates from 5 to 100 mV s$^{-1}$, (b-c) Galvanostatic charge-discharge curves at different current densities from 0.25 to 10 A g$^{-1}$.

Figure S8. The influence of PP$_y$ content on the cyclic voltammetry (CV) curves of 3D V$_2$O$_5$@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$^{-1}$ in 1.0 M Na$_2$SO$_4$ aqueous solution.
Figure S9. The influence of PP_y content on rate capabilities of 3D V_2O_5@PP_y 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_y.
Figure S11. (a) A series of CV measurements at 100 mV s\(^{-1}\), 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\(^{-1}\) 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\(_2\)O\(_5\)@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$_2$O$_5$@PP$_y$ network//3D rGO asymmetric supercapacitorl under different current densities (from 0.25 to 10 A g$^{-1}$) calculated from galvanostatic charge/discharge plots.

Table 1. The kinetics parameters of 3D V$_2$O$_5$@PP$_y$ network, pure 3D V$_2$O$_5$ network and V$_2$O$_5$ particles@PP$_y$.

<table>
<thead>
<tr>
<th>Electrodes</th>
<th>$R_s$ (Ω)</th>
<th>$R_{ct}$ (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3D V$_2$O$_5$@PP$_y$ network</td>
<td>0.6</td>
<td>5.1</td>
</tr>
<tr>
<td>Pure 3D V$_2$O$_5$ network</td>
<td>0.7</td>
<td>7.4</td>
</tr>
<tr>
<td>V$_2$O$_5$@PP$_y$ particles</td>
<td>1.0</td>
<td>8.6</td>
</tr>
</tbody>
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