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Supporting Information

Experimental:

<u>Preparation of bulk VO₂(B):</u>

 $VO_2(B)$ was prepared from NH_4VO_3 (Aldrich) solution dissolved in oxalic acid by hydrothermal technique similar to previously reported by Xie and the co-workers.¹ In typical procedure 1 mmol of NH_4VO_3 was dissolved in 15 ml of deionized water, then 1 M oxalic acid (Aldrich) was added dropwise until pH 1.3. The mixture was then placed in a 23 ml Teflon lined autoclave with stainless steel shell and kept for 1 day at 200 °C. After cooling down to room temperature the product was washed with deionized water and pure ethanol at least three times to remove any impurities. Finally, the $VO_2(B)$ was dried in air at 60 °C for 2-3 h.



Figure S1: (a) Powder XRD patterns for commercial VO₂ (which matches well with the standard pattern for VO₂(M), (JCPDS No. 082-0661)), compared with that after 6 days of reflux in water at 60 °C; inset in (a) shows the SEM image of the exfoliated V₂O₅.nH₂O material obtained from VO₂(M) after 6 days of reflux. (b) XPS spectrum for V₂O₅.0.55H₂O nanosheets; inset in (b) shows the deconvolution of V 2p_{3/2} peak.



Figure S2. (a) Vanadium K-edge XANES spectra of $V_2O_5 \cdot 0.55H_2O$ nanosheets (red line) and $VO_2(B)$ (black line); (b) Vanadium K-edge XANES spectra of standard commercial V_2O_5 (red line) and VO_2 (black line).



Figure S3: Powder XRD patterns for $VO_2(B)$ after refluxing for 24h at room temperature in pure deionized water, 0.8 M NaCl solution, and 0.8 M LiCl solution.



Figure S4: (a) Powder XRD patterns for $VO_2(B)$ after refluxing in water for 5 days at 22 °C, compared with that refluxed in water for the same period at 40, and 60 °C; (b) powder XRD patterns for bulk $VO_2(B)$, compared with that refluxed in water for 1 and 2 days at 60 °C; and (c) powder XRD patterns for $VO_2(B)$ after refluxing in water for 6 days at 60 °C, compared with that refluxed in water for 4 days at 60 °C and 2 days at 22 °C.



Figure S5: (a) Powder XRD pattern of uncoated MW-CNT and that coated with our exfoliated material using diluted suspension, (b) and (c) SEM images of the coated MW-CNT at different magnification. (d) SEM images of cross-section of the four electrodes used in our study.



Figure S6: (a) TEM image and (b) the corresponding SAED pattern of $V_2O_5.0.55H_2O$ nanosheets obtained from electrode VO-45 after the electrochemical cycling for 20 cycles. (c) Simulated powder pattern obtained from the SAED pattern of $V_2O_5.0.55H_2O$ before and after cycling (simulation done using CRISP 2.2 program).²



Figure S7: Cyclic voltammograms of the uncoated MW-CNT paper and electrode VO-4 (MW-CNT paper coated with the exfoliated vanadium oxide).



Figure S8: Electrochemical impedance spectroscopy (EIS) data collected for electrodes VO-45 and VO-4 at various voltages during discharge (a) and charge (b). The Nyquist plots shown above indicate that the electrode with a thicker oxide film (VO-45) is more resistive as compared to electrode VO-4.

Electrode Material Description	Morphology	Capacity ∕ mAhg⁻¹	C-rate or current density / mAg ⁻¹	Potential range / V	Reference
V ₂ O ₅ .nH ₂ O / CNT paper	Ultrathin nanosheets	280	200	1.7-3.9	This work
$V_2O_5.nH_2O$ / CNT	Nanobelts	241	200	2.0-4.0	Xianhong Rui <i>et.al.</i> ³
V ₂ O ₅ .nH ₂ O xerogel / graphene	Ribbons	239	30	1.5-4.0	Guodong Du <i>et.al.</i> ⁴
$V_2O_5.nH_2O$ xerogel	2D flakes composed of thin acicular nanowires	300	200	1.5–4.0	Qiulong Wei <i>et.al.</i> ⁵
V ₂ O ₅ .nH ₂ O xerogel	Network of long ribbons	250	0.1 C	1.5-3.6	Qi Liu <i>et.al.</i> ⁶
V ₂ O ₅ .nH ₂ O xerogel / 2% reduced graphene oxide	Network of long ribbons	419	0.1 C	1.5-3.6	Qi Liu <i>et.al</i> . ⁶
V_2O_5 aerogel	Network of ribbons	291	0.25 C	1.5-4.0	Arianna Moretti <i>et.al.</i> 7

Table S1: Comparison of the morphology and electrochemical performance of V_2O_5 .nH₂O reported in this study and previously reported work.

References:

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