

## Ultra-Expanded Interlayer Spacing of Vanadium Oxide Nanowires Intercalated with Ploy (3,4-ethylene dioxythiophene) for Organic Ammonium Ion Batteries

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### Experimental Section

*Synthesis of VO-P-x:* 3.5 g commercial V<sub>2</sub>O<sub>5</sub> power was dispersed in 100 ml de-ionized water. x ml (x=0, 0.5, 1.0, 1.5 and 2.0) 3,4-ethylenedioxythiophene (EDOT, macklin) was added dropwise into the solution at a rate of 0.5 ml min<sup>-1</sup> under vigorous stirring. The solution was stirred for 144 hours at room temperature. Then the solution was diluted with de-ionized water to 1000 ml and sonicated for 10 hours. After centrifuged at 3000 rpm, the supernatant was taken and centrifuged at 12000 rpm to obtain the precipitate. Finally, the VO-P-x power was obtained by freeze-drying the precipitate for 10 hours. Commercial V<sub>2</sub>O<sub>5</sub> power was purchased from Aladdin.

*Synthesis of PEDOT:* 0.8 ml EDOT was dropwise into the 40 ml 1 mol L<sup>-1</sup> Ammonium persulphate solution at a rate of 0.2 ml min<sup>-1</sup> under vigorous stirring. After stirring for 24 hours, the solution was centrifuged to obtain precipitate. Commercial EDOT was purchased from Aladdin.

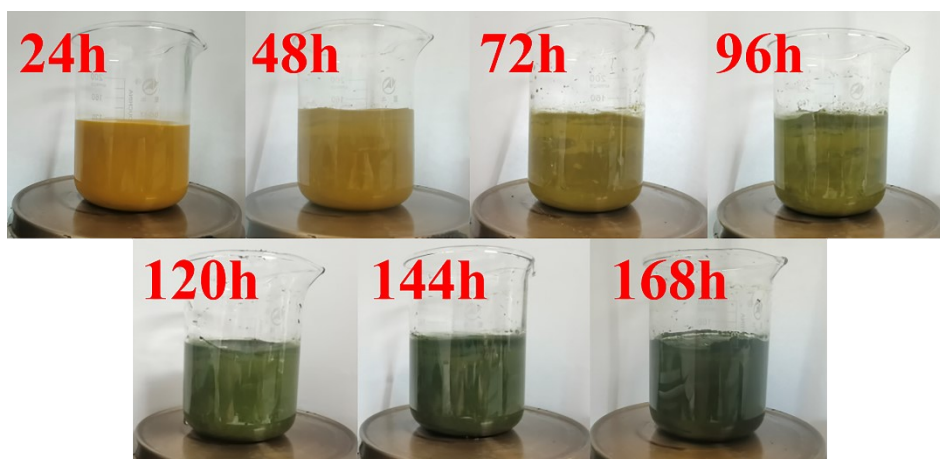
Commercial 3,4,9,10-perylenetetracarboxylic diimide (PTCDI) was purchased from Aladdin.

*Materials Characterization:* The crystal structures of VO-P-x and VO were characterized by a Rigaku MiniFlex 600 X-Ray Diffractometer with Cu K $\alpha$  radiation ( $\lambda=1.5404$  Å) in the range of 15-50°. Thermogravimetric analysis (TGA) was

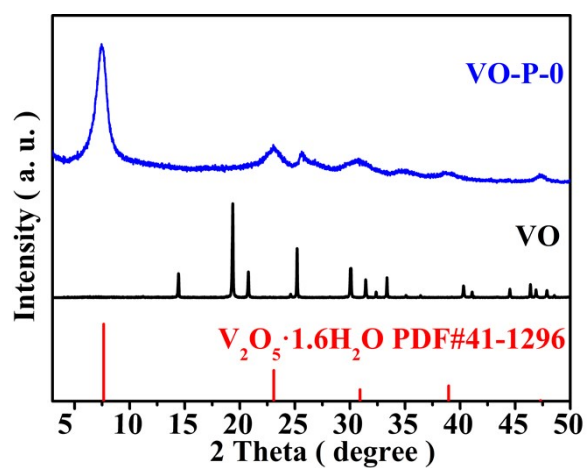
performed by an integrated thermal analyzer STA449F3 in air at a temperature ramp of  $10\text{ }^{\circ}\text{C min}^{-1}$  from room temperature to  $1000\text{ }^{\circ}\text{C}$ . X-ray Photoelectron Spectroscopy (XPS) spectra were tested on a Thermo Fisher Scientific ESCALAB 250Xi photoelectron spectrometer. Transmission electron microscopy (TEM, JEM-2100F) and Scanning electron microscopy (SEM, JSM-7500F) were conducted for morphology analysis. Fourier transform infrared (FTIR) spectra were recorded on a Thermo Scientific Nicolet 6700 infrared spectrophotometer.

*Electrochemical Measurements:* The preparation of electrodes: 70 wt.% of active mass, 20 wt.% of ketjenb black and 10 wt.% of polyvinylidene fluoride (PVDF) were mixed and grinded with isopropanol to obtain a homogenous slurry. The slurry was cast on an Al foil and dried in a vacuum oven for 12 hours. Then the electrodes were cut to obtain circular electrodes with a diameter of 8 mm. The active mass loading was  $\sim 1.75\text{ mg cm}^{-2}$ . Ag/Ag<sup>+</sup> electrode with  $10\text{ mmol L}^{-1}$  AgNO<sub>3</sub> in acetonitrile works as the reference electrode. The electrochemical performance of the half-cell was tested in a swagelok three-electrode cell, which comprises  $1.0\text{ mol L}^{-1}$  bis(trifluoromethanesulphonyl)imide ammonium (NH<sub>4</sub>TFSI) in tetraethylene glycol dimethyl ether (TEGDME) as electrolyte. The electrochemical performance of the full cell was tested using 2032 coin-cells. The mass ratio of cathode and anode was  $\sim 1:1$ .  $1.0\text{ mol L}^{-1}$  NH<sub>4</sub>TFSI in TEGDME served as the electrolyte. The cyclic voltametric (CV) tests and electrochemical impedance spectroscopy (EIS) were performed on a CHI 660E electrochemical workstation (Chenhua). The galvanostatic charge/discharge (GCD) and cycling tests were carried out on a Land CT2001A battery test system.

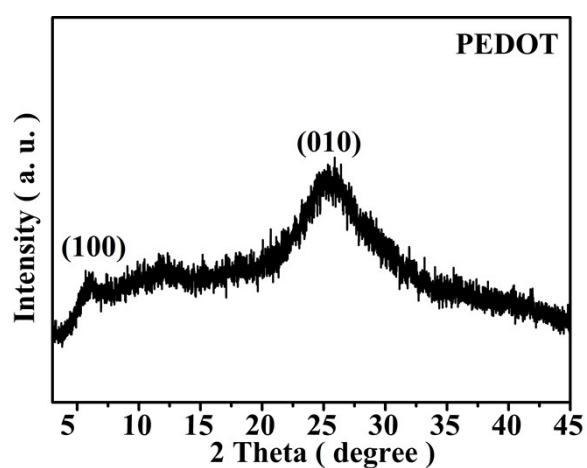
## **Supplementary Figures**



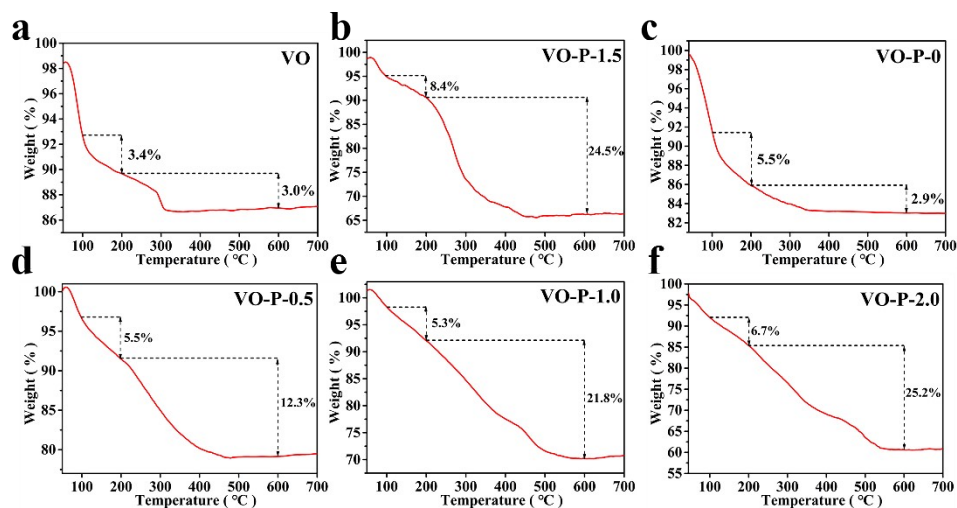
**Fig. S1** The color change of the solution with 1.5 ml EDOT in 168 hours.



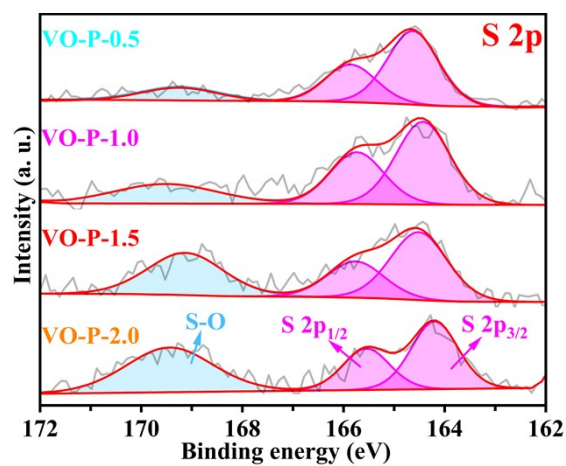
**Fig. S2** The XRD patterns of VO and VO-P-0.



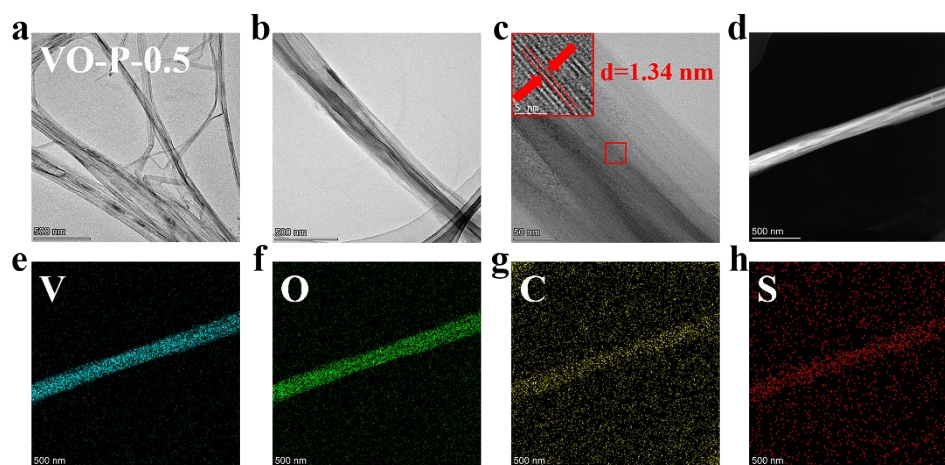
**Fig. S3** The XRD patterns of PEDOT.



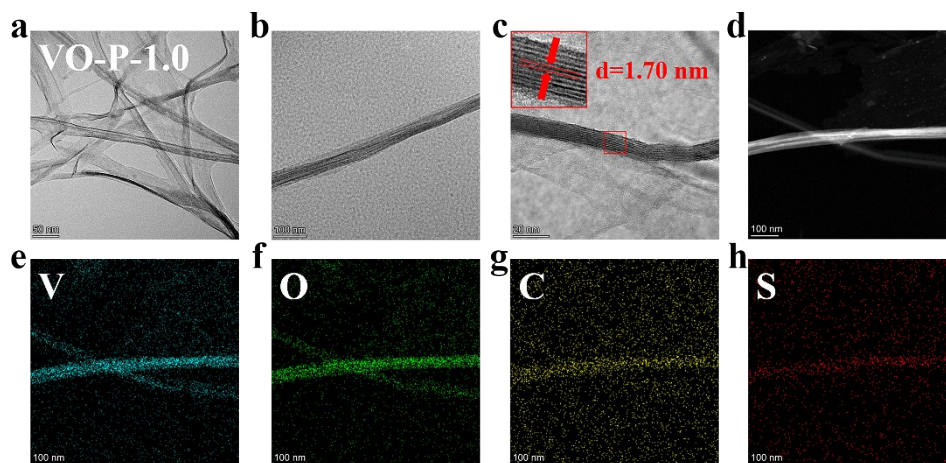
**Fig. S4** The TGA curves of VO and VO-P-x (x=0, 0.5, 1.0, 1.5 and 2.0)



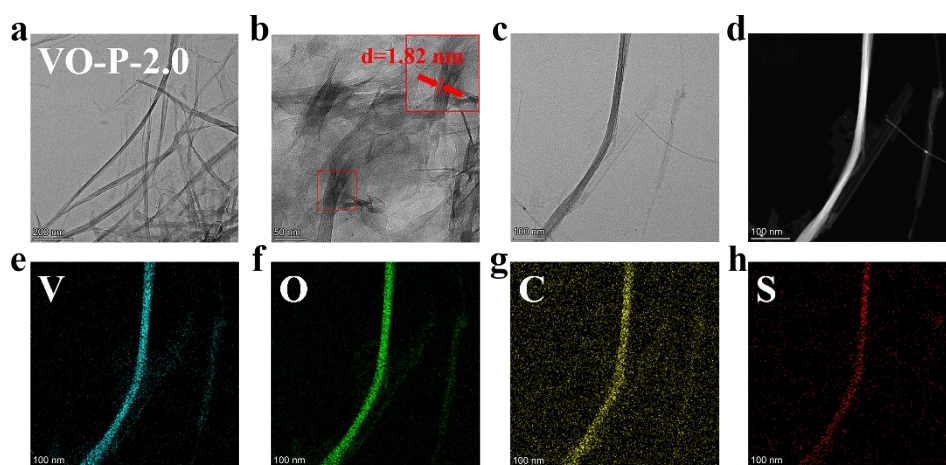
**Fig. S5** The XPS spectra of S 2p region of VO-P-x (x= 0.5, 1.0, 1.5 and 2.0)



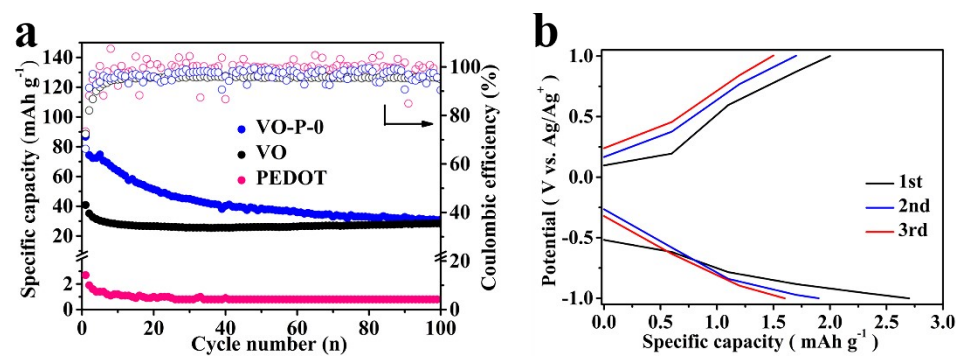
**Fig. S6** a-b) The TEM images c) HRTEM image and d) Dark field image of the VO-P-0.5. The EDS mappings of e) V, f) O, g) C, and h) S elements.



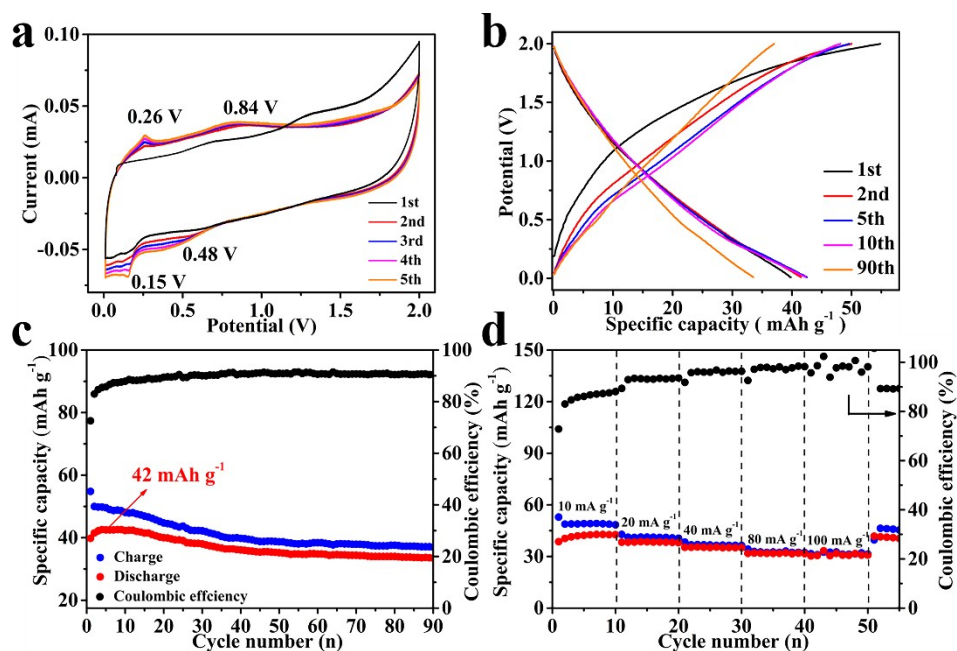
**Fig. S7** a-b) The TEM images c) HRTEM image and d) Dark field image of the VO-P-1.0. The EDS mappings of e) V, f) O, g) C, and h) S elements.



**Fig. S8** a-b) The TEM images c) HRTEM image and d) Dark field image of the VO-P-2.0. The EDS mappings of e) V, f) O, g) C, and h) S elements.



**Fig. S9** a) The cycling performances of VO, VO-P-0 and PEDOT at  $200 \text{ mA g}^{-1}$ . b) The GCD curves of PEDOT from  $-1.0 \text{ V}$  vs.  $\text{Ag}/\text{Ag}^+$  at  $200 \text{ mA g}^{-1}$ .



**Fig. S10** The performance of the full cell. a) The CV curves from 0 to 2.0 V. b) The GCD curves from 0 to 2.0 V vs at 10 mA g<sup>-1</sup>. c) The cycling performance at 10 mA g<sup>-1</sup>. d) The rate performance at different current densities.

**Table S1.** The stretching vibrations of PEDOT, VO-P-1.0 and 1.5.

	C-C (cm <sup>-1</sup> )	C-O-C (cm <sup>-1</sup> )	C-S-C (cm <sup>-1</sup> )
PEDOT	1477.2	1141.6	688.5
VO-P-1.0	1467.5	1133.9	692.3
VO-P-1.5	1469.5	1135.8	693.2

**Table S2.** The electrochemical performance of VO-based materials in NH<sub>4</sub><sup>+</sup> ion batteries.

Host material	Electrolyte	Working window (V. vs Ag/AgCl)	Capacity (mAh g <sup>-1</sup> )	Initial coulombic efficiency (%)	Ref.
Bi-layered V <sub>2</sub> O <sub>5</sub>	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	-0.2—0.8	100 (0.1 A g <sup>-1</sup> )	/	[18]
PANI-V <sub>2</sub> O <sub>5</sub>	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	-0.5—0.9	150 (5.0 A g <sup>-1</sup> )	/	[19]
PANI-V <sub>2</sub> O <sub>5</sub>	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	-0.5—1.0	192 (1.0 A g <sup>-1</sup> )	/	[37]
V <sub>2</sub> O <sub>5</sub> /polypyrrole	CH <sub>3</sub> COONH <sub>4</sub>	-0.9—0 (V. vs SCE)	90 (1.0 A g <sup>-1</sup> )	/	[38]

Co-doped V <sub>2</sub> O <sub>5</sub>	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	-0.8—0.7 (V. vs Ag/AgCl)	141 (1.0 A g <sup>-1</sup> )	/	[11]
V <sub>2</sub> O <sub>5</sub> -PEDOT	NH <sub>4</sub> TFSI	-1.0—1.0 (V. vs Ag <sup>+</sup> /Ag)	163 (0.2 A g <sup>-1</sup> )	91%	This work

**Table S3.** The fitting results of the EIS curves.

	VO	VO-P-1.5	VO-P-2.0
R <sub>s</sub> (ohm)	13.4	1.2	13.1
R <sub>ct</sub> (ohm)	62.0	19.4	24.1