## **Electronic Supplementary Information**

Hierarchical *T*-Nb<sub>2</sub>O<sub>5</sub> nanostructure with hybrid mechanisms of intercalation and pseudocapacitance for potassium storage and high-performance potassium dual-ion battery

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## **Materials and Methods**

*Materials*. NbCl<sub>5</sub>, oxalic acid dehydrate, hexamethylenetetramine (HMTA) were purchased from Sigma. Expanded graphite (EG), polypropylene separator (Celgard 2400), conductive carbon black (Timcal Super P), polyvinylidene fluoride (PVDF), and N-methyl-2-pyrrolidone (NMP) were purchased from Shenzhen Kejingstar Technology Ltd. Electrolyte 0.8 KPF<sub>6</sub> in ethylene carbonate (EC) : propylene carbonate (PC) : dimethyl carbonate (DMC) : ethyl methyl carbonate (EMC) = 2:2:3:3 (v/v/v/v) was purchased from Dodochem. All materials were used directly without further purification.

*Synthesis of urchin-like T-Nb*<sub>2</sub>*O*<sub>5</sub> *nanowires.* The urchin-like T-Nb<sub>2</sub>O<sub>5</sub> nanowires were prepared by hydrothermal method. Typically, NbCl<sub>5</sub> (0.8 mmol) was added into 20 ml deionized water and stirred vigorously to obtain a white floc. Then oxalic acid dehydrate (4.0 mmol) was added into the above suspension and stirred until it turned into transparent. After further adding HMTA (2.0 mmol) into the above solution, it was transferred into a 50 ml Teflon lined autoclave and kept at 180 °C for 14 h. The product was centrifuged and washed with water and ethanol for several times and vacuum dried at 60 °C for 12 h. Finally, it was annealed at tubular furnace at 600 °C for 3 h under air, and urchin-like *T*-Nb<sub>2</sub>O<sub>5</sub> nanowires were obtained.

*Characterization.* The morphology and structure of the obtained *T*-Nb<sub>2</sub>O<sub>5</sub> was characterized by field emission scanning electron microscopy (FESEM, ZEISS SUPRA<sup>®</sup>55), transmission electron microscopy (TEM, Tecnai G2 F30 U-TWIN), X-ray diffraction (XRD, Rigaku D/Max-2500 diffractometer with Cu K $\alpha$  radiation), and X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Thermo Fisher, with monochromatic aluminum K $\alpha$  radiation). Ex-situ X-ray diffraction (XRD) analyses of the EG cathode were performed at a 2 $\theta$  step of 2° min<sup>-1</sup> over the range of 20-35°. Ex-situ Raman spectroscopy of the EG cathode was analyzed using a LabRAM HR Raman spectrometer (633 nm). All the cathode and anode for ex-situ SEM, XRD, Raman and XPS measurements were washed with DMC and dried in the glove box before test.

Electrochemical Characterization. Electrochemical characterizations of the T-Nb<sub>2</sub>O<sub>5</sub>/K half cell and the potassium-based dual-ion battery were studied in 2032 coin-type cells that assembled in Ar-filled glove box. For preparing T-Nb<sub>2</sub>O<sub>5</sub> anode, 70 wt% T-Nb<sub>2</sub>O<sub>5</sub>, 20 wt% conductive carbon black, and 10 wt% PVDF were mixed with several drops of NMP solvent together to form a uniform slurry. The slurry was dipped onto a nickel foam, dried at 80 °C in vacuum for 12 h and punched into circular sheets (12 mm in diameter). For preparing EG cathode, 80 wt% EG, 10 wt% conductive carbon black, and 10 wt% PVDF were mixed with several drops of NMP solvent together to form a uniform slurry. The slurry was coated onto an Al foil and dried at 80 °C in vacuum for 12 h and punched into circular sheets (10 mm in diameter). For half-cell characterization, T-Nb2O5, K foil, and glass fiber were used as cathode, counter electrode/anode, and separator, respectively. For full-cell characterization, EG, T-Nb<sub>2</sub>O<sub>5</sub>, and glass fiber were used as cathode, anode, and separator, respectively. The electrolyte with composition of 0.8 KPF<sub>6</sub> in EC:PC:DMC:EMC = 2:2:3:3 (v/v/v/v) was used in both half cells and full cells. The mass loading of the anode and cathode are  $2 \text{ mg cm}^{-2}$  and 1 mg cm<sup>-2</sup> respectively with ratio of 2:1. Galvanostatic charge-discharge measurements and galvanostatic intermittent titration technique (GITT) measurements were performed on a NEWARE battery testing system. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were conducted on an Autolab (PGSTAT302N, Switzerland) electrochemical workstation. Before the GITT test, the assembled T-Nb<sub>2</sub>O<sub>5</sub>/K half cell was first discharged and charged at 50 mA g<sup>-1</sup> over the voltage range of 0.01-3 V for one cycle and then stayed for 1 h to stabilize the cell. Then it was discharged by applying a series of pulse current of 20 mA g<sup>-1</sup> for 10 min followed by a relaxation interval of 10 min for each pulse.



**Fig. S1** CV curves of the T-Nb<sub>2</sub>O<sub>5</sub> electrode with separation of capacitive and diffusion currents at different scan rates.



Fig. S2 Ex-situ XRD patterns of the T-Nb<sub>2</sub>O<sub>5</sub> electrode in the K half cell at fully charged/discharged states.



**Fig. S3** Cycling performance of the *T*-Nb<sub>2</sub>O<sub>5</sub>/K half cell for 400 cycles at 0.4 A  $g^{-1}$ .



**Fig. S4** CV curves of the KDIB at 5 mV  $s^{-1}$  in the initial five cycles.



**Fig. S5** Ex-situ XPS profiles of Nb and K elements in the *T*-Nb<sub>2</sub>O<sub>5</sub> anode in the KDIB at fully charged/discharged states.



Fig. S6 CV curves of the KDIB at different scan rates from 2 to 20 mV s<sup>-1</sup>.



**Fig. S7** Nyquist plots of the KDIB after different cycle numbers in the frequency range of 100 kHz to 10 mHz.