Supporting Information

Triple conductive wiring by electron doping, chelation coating and electrochemical conversion in fluffy Nb$_2$O$_5$ anodes for fast-charging Li-ion batteries

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Experimental Section
**Materials and Reagents:** NbCl$_5$ (Aladdin, 99.9%), Co(NO$_3$)$_2$·6H$_2$O (Aladdin, 99.99%), Mn(NO$_3$)$_2$·6H$_2$O (Aladdin, 98%), isopropanol (Aladdin, 99.5%), glycerol (Sinopharm, 99%), tris(hydroxymethyl)methyl aminomethane (Tris, Aladdin, 99.9%), HCl (Sinopharm, 36% - 38%), dopamine hydrochloride (Aladdin, 99.9%), anhydrous ethanol, deionized water.

**Synthesis of Co-NbO:** 0.5 mmol NbCl$_5$ and 0.05 mmol Co(NO$_3$)$_2$·6H$_2$O (or Mn(NO$_3$)$_2$·6H$_2$O) were thoroughly dissolved in the isopropanol (30 ml) and ethanol (10 ml) solution with the assistance of agitation. 8 ml glycerol was added under vigorous stirring for 30 min to promise the homogeneous dispersion. Then the solution was transferred into a 50 ml Teflon-sealed autoclave and heated at 180 °C for 24 h in a drying oven. After naturally cooling down to room temperature, the obtained precipitation was washed with anhydrous ethanol/deionized water for three times and dried at 60 °C overnight. The dried powder was calcined at 600 °C in air for 3 h with a heat rate of 3 °C/min. Finally, the obtained light blue powder was denoted as Co-NbO (or Mn-NbO). In comparison, the pristine Nb$_2$O$_5$ powder was synthesized based on the same procedure without the use of cobalt precursor, denoted as P-NbO.

**Synthesis of PDA coated Co-NbO:** The obtained Co-NbO powder (200 mg) was dispersed in 200 mL 10 mM Tris/deionized water solution with violent agitation. The PH value was adjusted to 8.5 with 1 M HCl. 50 mg dopamine hydrochloride was added and stirred dramatically for 24 h to promise the conformal coating of polydopamine (PDA) on the surface of Co-NbO particles. The PDA coated Co-NbO particles were collected by vacuum filtration and washed with anhydrous ethanol for 3 times, followed by annealing at 450 °C in N$_2$ for 3 h with a heat rate of 3 °C/min. The obtained gray powder was denoted as PDA-Co-NbO.

**Physical characterizations:** The crystal structures and phase compositions of P-NbO, Co-NbO and PDA-Co-NbO were identified by X-ray powder diffractometer (XRD, Bruker, D8 Discover, Cu Kα) with 2θ ranging from 10° to 80°. The morphologies and microstructures were characterized by scanning electron microscopy (SEM, Magellan 400L, FEI, operated at 2.0 kV). Element distribution in PDA-Co-NbO powder was exhibited by using the energy dispersive X-ray spectrometer on SEM. Transition
electron microscopy (TEM, JEOL JSM-6700F, operated at 200 kV) was used to collect the common TEM images and high-resolution TEM (HRTEM) images of PDA-Co-NbO. The elemental composition and corresponding valence state on the surface of PDA-Co-NbO particles were analyzed by X-ray photoelectron spectroscopy (XPS, ESCAlab-250). Raman spectra were collected in the scope of 50-990 cm\(^{-1}\) on a Renishaw InVia Reflex using a 532 nm laser as the excitation source. Electron paramagnetic resonance (EPR) spectra were collected by a JEOL-FA200 instrument with a magnetic field strength from 310 mT to 360 mT.

**Measurements of electrochemical performance:** For the rate and cycling performance tests, CR2032-type coin cells were assembled in argon-filled glovebox (with water and oxygen contents below 0.1 ppm) by taking P-NbO, Co-NbO or PDA-Co-NbO as working electrode and lithium foil as counter electrode. All three working electrodes were fabricated by blending active material powder, carbon black and poly(vinylidene fluoride) (PVDF, dissolved in 1-methyl-2-pyrrolidinone in a ratio of 1 mg/20 \(\mu\)L) with a weight ratio of 7:2:1. The uniform slurry dispersed by mortar and pestle was casted onto copper foil followed by drying in vacuum oven at 60 °C for 18 h. Then, the electrodes were cut into small disks with a diameter of 10 mm, with a mass loading of 1.5-1.8 mg/cm\(^2\) if no special notation. 150 \(\mu\)L commercial electrolyte (Sigma-Aldrich) was employed, and it consists of 1 M lithium hexafluorophosphate (LiPF\(_6\)) dissolved in ethylene carbonate (EC) and diethyl carbonate (DEC) with a volume ratio of 1:1. Glass fiber (Whatman) was adopted as separator for the assembly of Li/P-NbO, Li/Co-NbO and Li/PDA-Co-NbO cells. Galvanostatic charge/discharge measurements were performed in the potential scope of 0.4-3.0 V versus Li\(^+\)/Li, under different current densities from 0.2 to 10 A/g (i.e. from 1 C to 50 C, 1 C = 200 mA/g) on Land multichannel battery testing system (CT2001A) at room temperature. For the assembly of full cells, the lithiated PDA-Co-NbO or Co-NbO electrode (precycled at 200 mA/g for 5 cycles and disassembled from Li/PDA-Co-NbO or Li/Co-NbO cells) and LiNi\(_{1/3}\)Co\(_{1/3}\)Mn\(_{1/3}\)O\(_2\) or LiFePO\(_4\) electrode (on aluminum foil as current collector) were adopted as anode and cathode, respectively. Galvanostatic intermittent titration technique (GITT) was
performed at a small current density of 20 mA/g for 1 h with subsequent static interval of 6 h. Electrochemical impedance spectroscopy (EIS) measurements of Li/P-NbO, Li/Co-NbO and Li/PDA-Co-NbO cells before cycling were performed with Solartron frequency analyzer (1260-1296), ranging from 1 MHz to 0.01 Hz. Cyclic voltammetry (CV) measurements were finished by using an electrochemical workstation (VersaSTAT3, AMETEK Scientific Instruments) in the potential scope of 0.4-3.0 V at stepwise increasing scan rates from 0.1 to 5 mV/s.

Simulation and calculation: Our calculations were performed using the plane wave basis Vienna ab initio simulation package (VASP),\textsuperscript{[1,2]} implementing the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof form.\textsuperscript{[3]} The interaction between ions and electrons is described by the projector augmented wave (PAW) method,\textsuperscript{[4,5]} with plane waves up to a cutoff energy of 600 eV. The Brillouin-zone integrations were performed on the grid of Monkhorst-Pack procedure.\textsuperscript{[6]} The convergence of the total energy with respect to the kinetic energy cutoff and k-point sampling has been carefully examined.

Measurements of in situ XRD and in situ Raman: In situ XRD measurement of PDA-Co-NbO was performed by X-ray diffractometer (Bruker, D8 Discover, Cu Ka) in the scope of 20°-60° with a scan rate of 3 °C/min. XRD data were collected with a charge/discharge interval of 10 min. Corresponding charge/discharge process was operated with an electrochemical window of 0.4-3.0 V at a current density of 100 mA/g on Land test system (CT2001A). The electrode slurry was fabricated by mixing PDA-Co-NbO, carbon black and PVDF in a mass ratio of 7:2:1 and casted on Beryllium plate, with an average loading of 3 mg/cm². The same electrolyte (1 M LiPF₆ in EC/DEC with a volume ratio of 1:1) used in coin cells was adopted to ensure the identical conditions. In-situ Raman spectra was collected in the scope of 100-600 cm⁻¹ on a Renishaw InVia Reflex (3 mW) using a 524 nm laser as excitation source and the corresponding electrochemical test conditions are the same as those of in-situ XRD measurement.

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**Formula S1**

\[ I_p = 2.69 \times 10^5 n^{3/2} A (D_{Li})^{1/2} v^{1/2} \Delta C_0 \]

\( I_p \) is the peak current, \( n \) refers to the number of electrons participating in reaction, \( A \) is equal to the electrode area immersed in electrolyte, \( D_{Li} \) is \( Li^+ \) diffusion coefficient in electrode, \( v \) is the sweep rate and \( \Delta C_0 \) is the driving concentration difference of \( Li^+ \) in lattices before and after the corresponding electrochemical process.

**Supplementary Figures**

![Figure S1](image_url)

**Figure S1.** (a) Typical charge/discharge curves of T-Nb_2O_5 within a voltage range of 1-3 V. (b) Capacity contribution of carbon black in the 1\textsuperscript{st} and 2\textsuperscript{nd} cycles in T-Nb_2O_5 electrode within the voltage range of 0.4-3 V.
Figure S2. Crystallographic structures of (a) T-Nb$_2$O$_5$ and (b,c) Coalt substituted T-Nb$_2$O$_5$ with NbO$_n$ and CoO$_n$ polyhedrons in green and blue respectively. Nb atoms in green, oxygen atoms in red, cobalt atoms in blue.

Figure S3. (a) TEM image and (b, c) HRTEM images of PDA-Co-NbO.

Figure S4. (a) Charge/discharge curves of PDA-Co-NbO at different current densities from 0.2 to 10 A/g in a potential scope of 0.4-3.0 V. (b) Charge/discharge curves of PDA-Co-NbO during the 1$^{st}$ cycle.
Figure S5. CV curves of (a) P-NbO and (b) Co-NbO at different scan rates from 0.1 mV/s to 5.0 mV/s.

Figure S6. (a) GITT curves of PDA-Co-NbO during lithiation and delithiation. (b) Adjacent charging/standing voltage curves (versus time) for the interpretation of parameters in the calculation of Li$^+$ diffusion coefficient. (c) Plots of linear relationship between the square root of time and potential in the charge process of PDA-Co-NbO.
Figure S7. (a) b-value determination from the relationship between peak current and scan rate in cathodic process for P-NbO, Co-NbO and PDA-Co-NbO based on \( \log i(V) = b \log v + \log \alpha \). CV curves of (b) P-NbO and (c) Co-NbO at a scan rate of 1 mV/s with gray and orange areas assigned for pseudocapacitive current contribution estimated according to the formula of \( i(V) = k_1v + k_2v^{1/2} \).
**Figure S8.** Nyquist plots of (a) P-NbO and (b) Co-NbO based cells at different temperatures fitted with the equivalent circuit in the inset. (c) Scatter plots of imaginary impedance as a function of frequency ranging from 0.1 MHz to 0.01 Hz at different temperatures for PDA-Co-NbO. Column graphs of (d) SEI resistance and (e) total resistance ($R_{SEI} + R_{CT}$) at different temperatures for P-NbO, Co-NbO and PDA-Co-NbO.

**Figure S9.** (a) Calculated XRD patterns of NbO and T-Nb$_2$O$_5$ structures from PDOS analysis. (b) In situ Raman curves of PDA-Co-NbO during the second charge/discharge process.
**Figure S10.** Average voltage estimation from the (a) charge and (b) discharge profiles of NCM811 cathode. Average voltage estimation from the (c) charge and (d) discharge profiles of Co-NbO anode. Average voltage estimation from the (e) charge and (f) discharge profiles of Co-NbO/NCM811 full cell.
**Figure S11.** (a) Charge/discharge voltage profiles of Co-NbO anode at 200 mA/g and LiFePO$_4$ cathode at 170 mA/g. (b) Charge/discharge curves of Co-NbO/LiFePO$_4$ full cell at different cycling stages. (c) Cycling performance of Co-NbO/LiFePO$_4$ full cell at 0.2 C (1 C = 170 mA/g). (d) Rate performance of Co-NbO/LiFePO$_4$ full cell at different rates from 0.2 C to 2 C.

**Figure S12.** Average voltage estimation from the (a) discharge profile of LiFePO$_4$ cathode, (b) charge profile of Co-NbO anode and (c) discharge profile of Co-NbO/LiFePO$_4$ full cell. Average voltage estimation from the (d) charge profile of LiFePO$_4$ cathode, (e) discharge profile of Co-NbO anode and (f) charge profile of Co-NbO/LiFePO$_4$ full cell.