**Supporting Information**

**Crystal structure regulation boosts the conductivity and redox chemistry of T-Nb2O5 anode material**

Jinghui Chen1,2, Jiashen Meng3, Kang Han1, Fang Liu4, Weixiao Wang1, Qinyou An1,2\* and Liqiang Mai1,2\*

1 State Key Laboratory of Advanced Technology for Materials Synthesis and Processing,Wuhan University of Technology, Wuhan 430070, P. R. China

2 Hainan Institute, Wuhan University of Technology, Sanya 572000, China

3 Beijing Key Laboratory of Theory and Technology for Advanced Batteries Materials, School of Materials Science and Engineering, Peking University, Beijing, 100871, China

4 NRC (Nanostructure Research Centre) ,Wuhan University of Technology, Wuhan 430070, P. R. China

\* Corresponding authors.

*E-mail addresses*: [anqinyou86@whut.edu.cn](mailto:anqinyou86@whut.edu.cn) (Prof. Q. Y. An), [mlq518@whut.edu.cn](mailto:mlq518@whut.edu.cn) (Prof. L. Q. Mai)

**Experimental section**

***Synthesis of* Co-Nb2O5 *and* Nb2O5**

*Materials Synthesis*: The Co-Nb2O5 particles were synthesized by a simple calcination process after obtaining a precursor by simple heat treatment. First, 2 g of terephthalic acid (H2BDC) was dissolved in 80 ml of N, N-dimethylformamide after magnetic stirring 1 h at room temperature. Second, 4 mmol of niobium pentachloride (NbCl5) and 2% of cobaltous chloride (CoCl2, 99.7%) were dissolved in previous solution with vigorous stirring at room temperature for another 1 h. Then, the solution was transferred into a 100 mL Teflon-autoclave and allowed to stand for 12 h in an oven with the temperature of 200 °C. After the autoclave was naturally cooled down to room temperature, the interior mixture was centrifuged to obtain the precipitate, which was subsequently washed with ethanol for 3 times and then dried in an oven at 70 °C for 12 h. The dried light blue powder by the previous steps (named as Co-Nb-BDC) was sintered under air at 800 °C for 2 h. The heating rate of the muffle furnace is 5 °C min−1. As a comparison, the Nb2O5 and Co-Nb2O5-2 were synthesized using the same processes, without CoCl2 and with 4% cobaltous chloride, respectively. Additionally, the precursor of Nb2O5, white powder, is named as Nb-BDC.

***Material characterization***

The XRD patterns to investigate the crystallographic structure were performed by powder X-ray diffraction using a D8 Discover X-ray diffractometer, with Cu Kα radiation (λ = 1.5418 Å). TOPAS 4.2 software was used to perform XRD Rietveld refinement. Scanning electron microscopy (SEM) images and energy dispersive X-ray spectra (EDS) were obtained using a JEOL JSM-7100F SEM/EDS microscope at an acceleration voltage of 20 Kv. Transmission electron microscopy (TEM), high resolution TEM (HRTEM) and selected area electron diffraction (SAED) images were collected by a JEM-2100F/Titan G2 60-300 microscope. ICP measurement was recorded with a PerkinElmer Optima 4300DV spectrometer. X-ray photoelectron spectroscopy (XPS) analysis was performed using a VG Multilab 2000 instrument. Raman spectra were obtained using a Renishaw INVIA micro-Raman spectroscopy system. The I-V curve tests were carried out by using probe station (Lake Shore, TTPX). UV-Vis diffuse reflectance spectra were acquired by Lambda 750 S.

***Electrochemical properties***

The electrochemical properties were characterized by assembling 2016 coin cells in a glove box (O2 ≤ 0.01 ppm and H2O ≤ 0.01 ppm), and a Li metal (99.5%, Sigma-Aldrich) of 200 µm in thickness was used as the reference electrode. 1 M LiPF6 in 1:1 ratio v/v ethylene carbonate/dimethyl carbonate (EC/DMC; Sigma-Aldrich, battery grade) (140 µl) was used as the electrolyte, and the separator was Celgard 2400 microporous membrane. To obtain the anodes, 70% as-synthesized active materials, 20% acetylene black and 10% polyvinylidene fluoride (PVDF) were mixed in N-methyl-2-pyrrolidone (NMP). The copper foil coated with active materials was dried at 70 °C in a vacuum oven overnight. The loading of the active material was 1.2-2.0 mg cm−2. The cathode was obtained by casting slurry containing LiFePO4 (70 wt%), acetylene black (20 wt%), and PVDF (10 wt%) in NMP onto aluminum foil with a mass loading of the active material about 2.5 mg cm−2. The laminates were then dried at 70 °C under vacuum for at least 12 h prior to use. For the assembly of half cells, the as-prepared laminates were used as the working electrodes, Li metal (99.5%, Sigma-Aldrich) as the counter/reference electrode. A full cell was constructed with a LiFePO4 cathode and a Co-Nb2O5 anode with a capacity ratio of 1.1-1.2. Galvanostatic charge/discharge tests were performed over the potential range from 1 to 3.0 V vs. Li/Li+ using a multichannel battery testing system (LAND CT2001A). GITT curves were also measured using a LAND CT2001A multichannel testing system, which conducted at a pulse current of 20 mA g−1 for 5 min, followed with a relaxation for 30 min. Cyclic voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS) were conducted at room temperature using an electrochemical workstation (CHI600E and Autolab PGSTAT 302N).

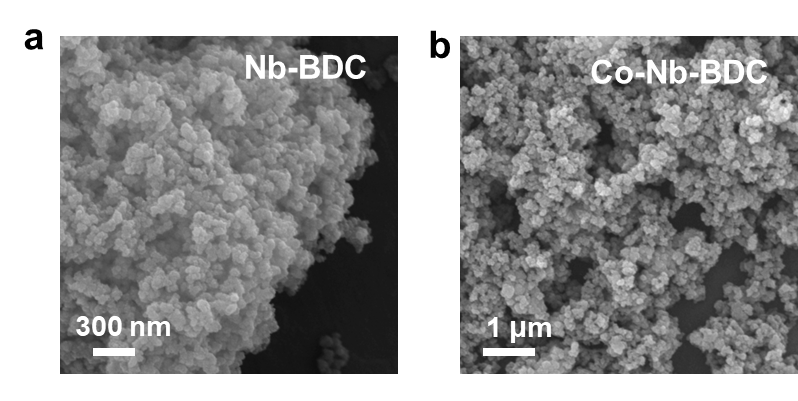
***Lithium storage measurements***

*In situ* XRD experiments during electrochemical testing of batteries were performed on a D8 Discover X-ray diffractometer equipped with a non-monochromated Cu Kα X-ray source scanned at the 2θ range of 20-40°. For *in situ* XRD measurements, the electrode was placed immediately behind an X-ray transparent beryllium window that also served as the current collector. The cathode was cut into 2 mm × 2 mm × 0.1 mm sheet.

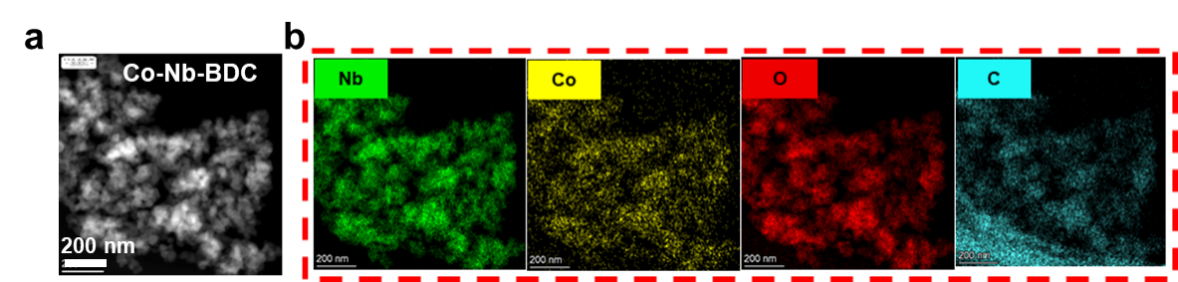
The DFT calculations are carried out by using the projector-augmented wave representations within the spin-polarized DFT as implemented in the Vienna Ab initio Simulation Package.[1] The exchange–correlation interactions of the generalized gradient approximation in the scheme proposed by Perdew-Burke-Ernzerhof functional. The wave functions are expanded by using the plane waves up to a kinetic energy cutoff of 520 eV. Brillouin-zone integrations are approximated by using special k-point sampling of MonkhorstPack scheme with a k-point mesh resolution of 2π × 0.05 Å−1.[2] The Projector Augmented Wave (PAW) method was used to calculate the effect of core electrons on the valence electron density. The convergence tolerance of energy and force on each atom during structure relaxation were less than 1E−05 eV and 0.01 eV Å−1. Activation barrier calculation is performed with the climbing nudged elastic band (NEB) method in unit cell of 16 f.u. (formula unit).[3] During the NEB calculations, the lattice parameters are fixed at the relaxed values of the fully delithiated structures, with all the internal degrees of freedom relaxed. The Bader analysis was performed using the Bader Charge Analysis Code.[4]



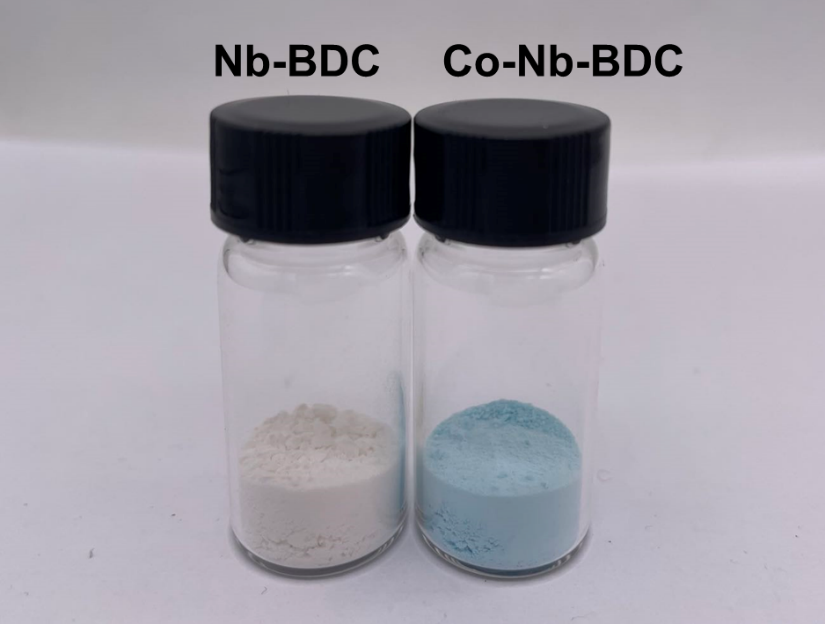
**Fig. S1.** XPS survey spectra for Co-Nb-BDC complex and 1,4-dicarboxybenzene.

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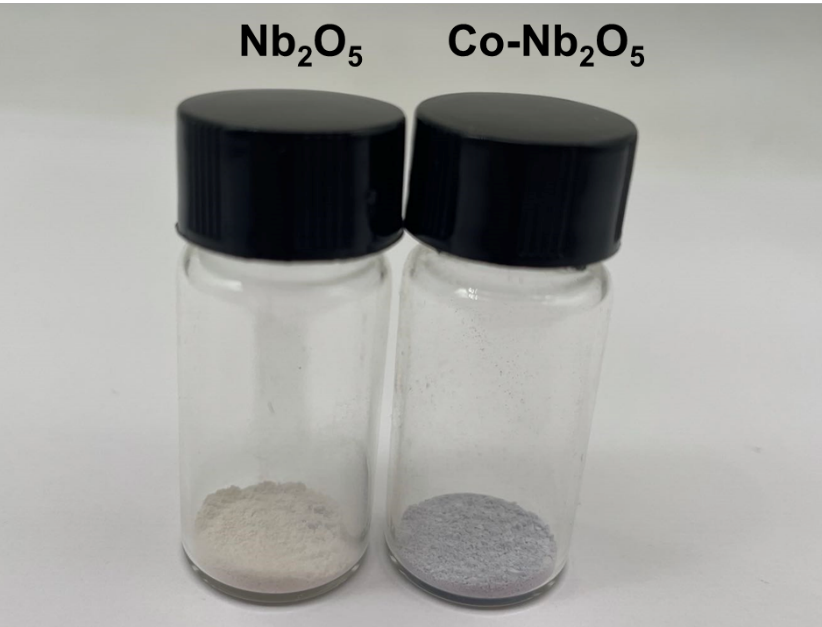
**Fig. S2.** SEM images of Nb-BDC (a) and Co-Nb-BDC (b).

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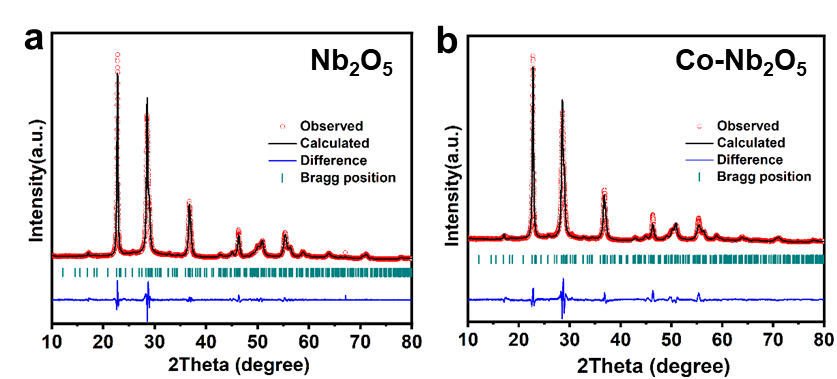
**Fig. S3.** a) HAADF-STEM image and b) EDX mapping image of Co-Nb-BDC, including Nb, Co, O and C elements.

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**Fig. S4.** Powder color comparison of Nb-BDC and Co-Nb-BDC complex precursors.



**Fig. S5.** Powder color comparison of Nb2O5 and Co-Nb2O5.

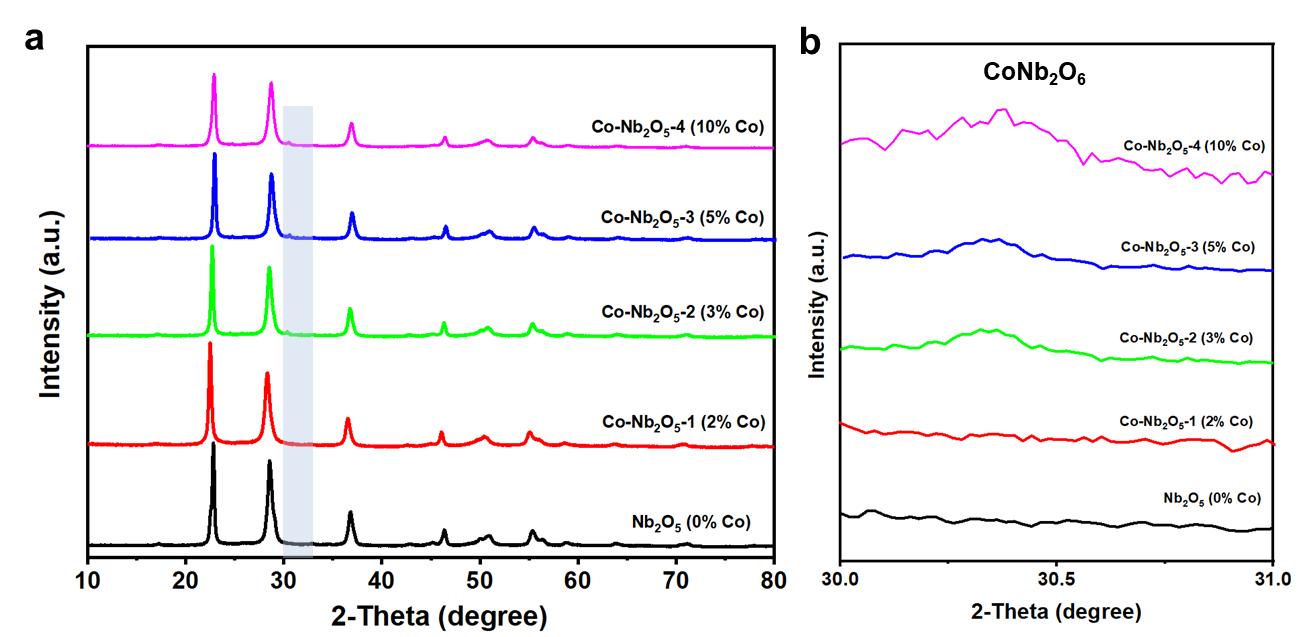


**Fig. S6.** XRD Rietveld refined diffractograms of Nb2O5 (a) and Co-Nb2O5 (b).

图表

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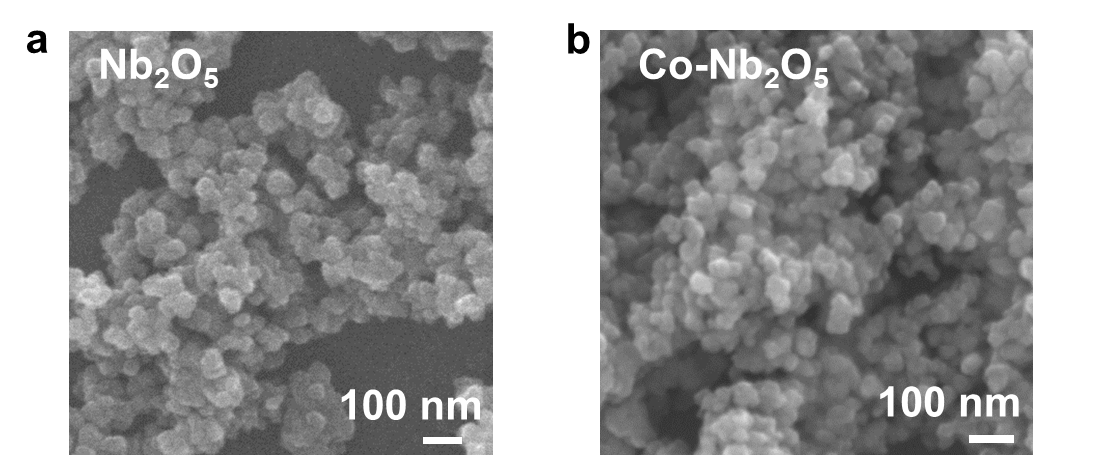
**Fig. S7.** The enlarged view of the XRD pattern of Co-Nb2O5 and Nb2O5 in (001) interlayer peak.



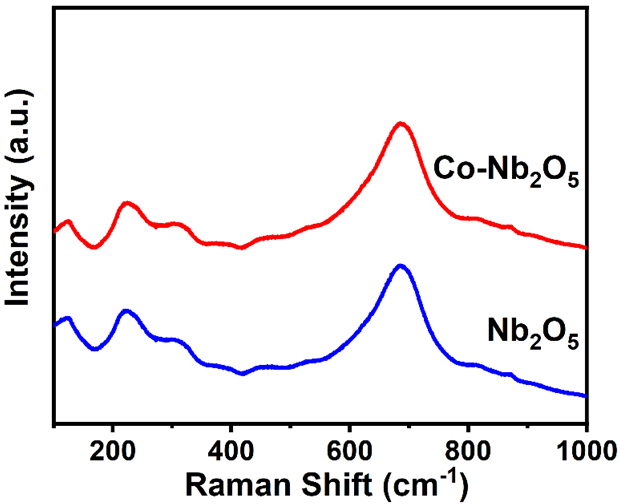
**Fig. S8.** a) The XRD patterns of Nb2O5, Co-Nb2O5-1 (Nb2O5 doped with 2% Co), Co-Nb2O5-2 (Nb2O5 doped with 3% Co), Co-Nb2O5-3 (Nb2O5 doped with 5% Co), and Co-Nb2O5-4 (Nb2O5 doped with 10% Co), and the enlarged view in the 2θ range of 30-31° (b), respectively.



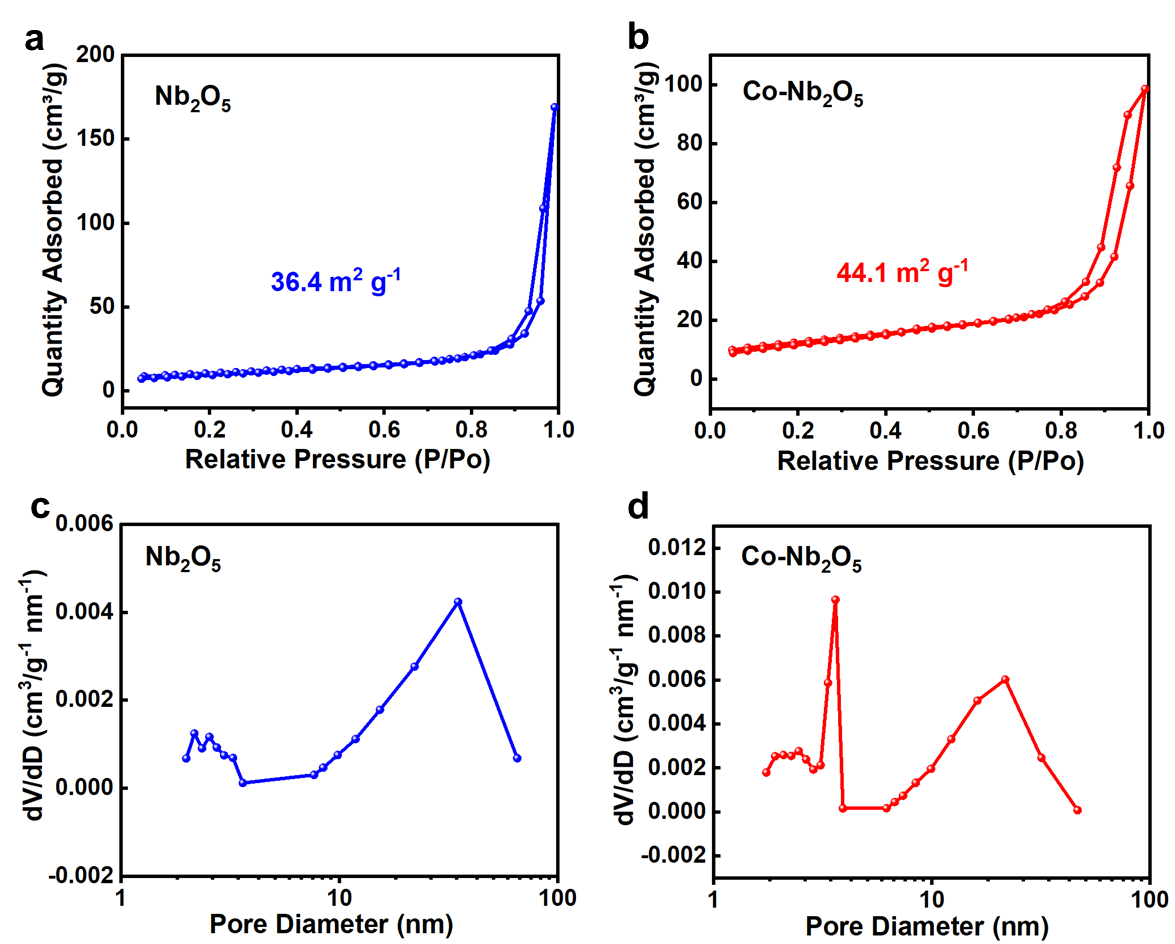
**Fig. S9.** XPS survey spectra for pure Nb2O5 and Co-Nb2O5.



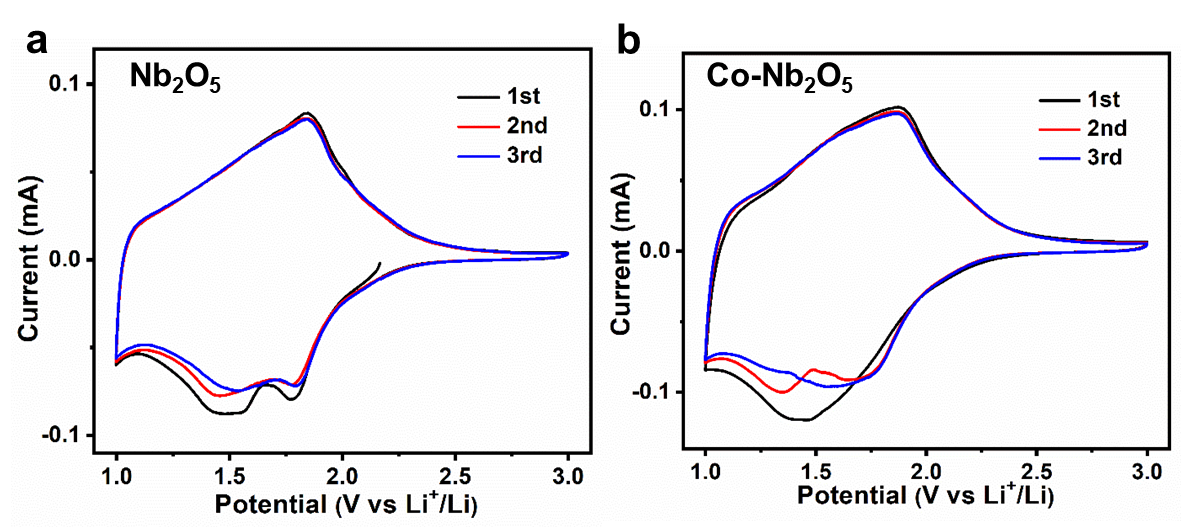
**Fig. S10.** SEM images of Nb2O5 and Co-Nb2O5 nanoparticles.



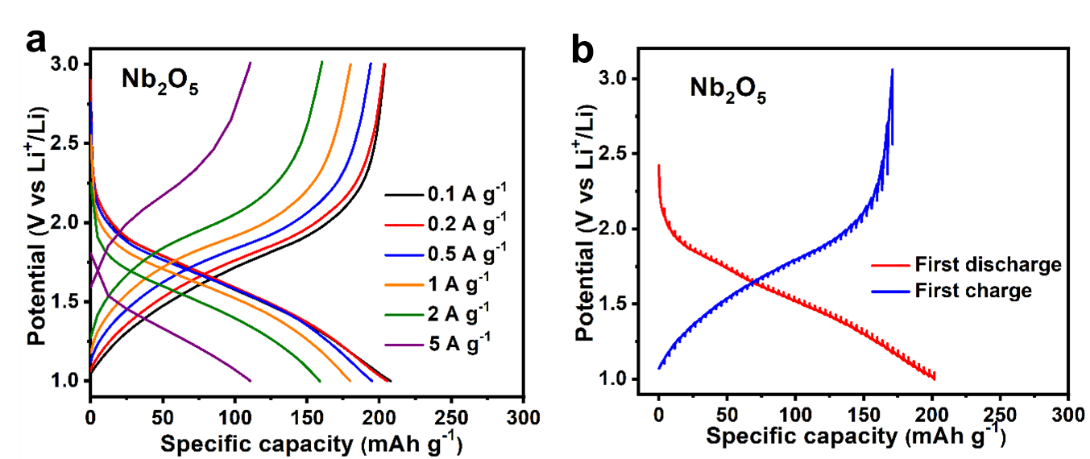
**Fig. S11.** Raman spectra of Nb2O5 and Co-Nb2O5 samples.



**Fig. S12.** a, c) BET and BJH curves of Nb2O5. b, d) BET and BJH curves of Co-Nb2O5 samples.



**Fig. S13.** CV analysis of the first three cycles at 0.1 mV s−1 of Nb2O5 (a) and Co-Nb2O5 (b) electrodes.

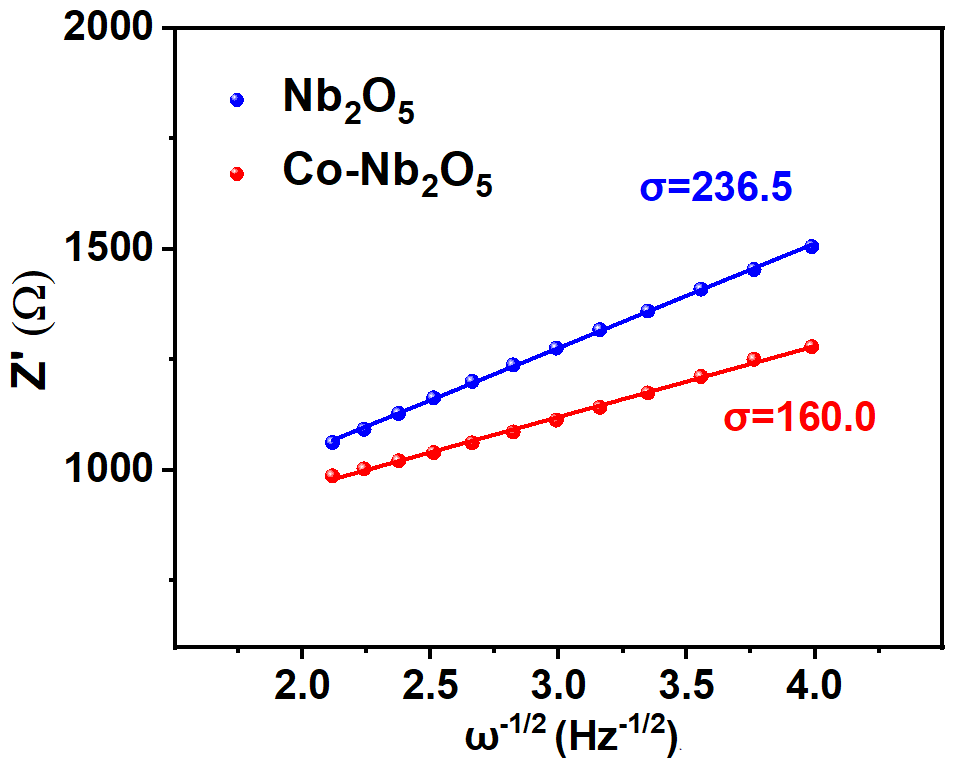


**Fig. S14.** a) The discharge/charge curves of Nb2O5 at various current densities ranging from 0.1, 0.2, 0.5, 1, 2, and 5, back to 0.1 A g−1. b) The GITT curves of charge/discharge process for Nb2O5.

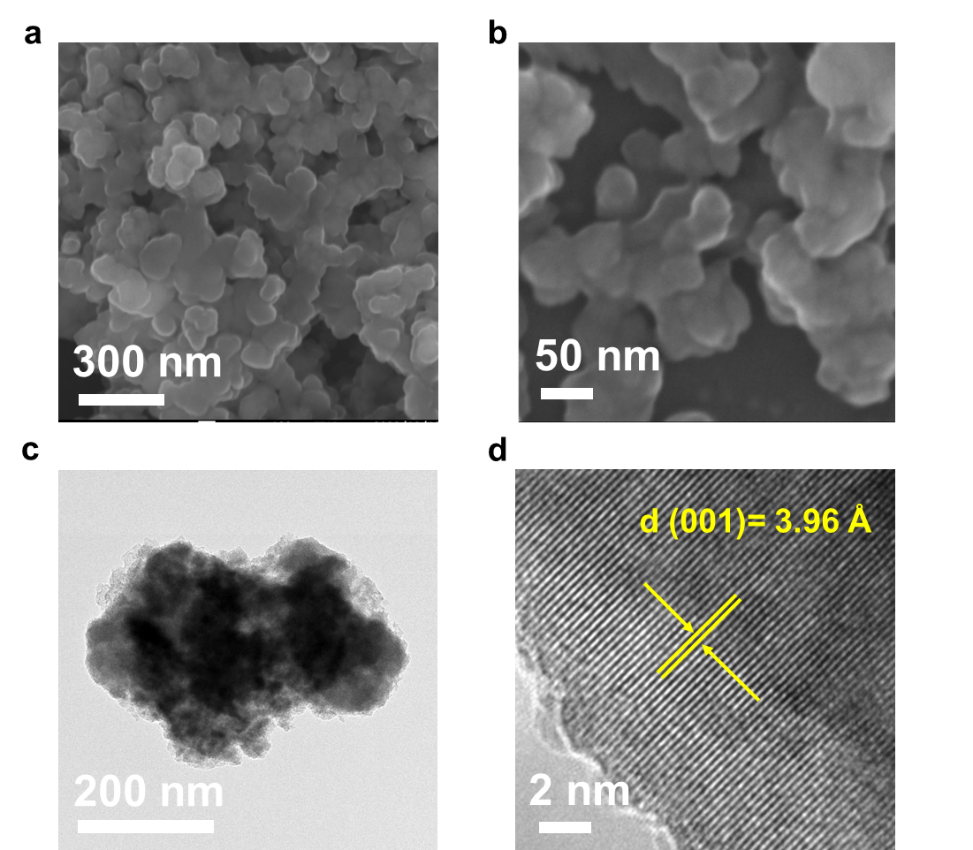
图表, 折线图

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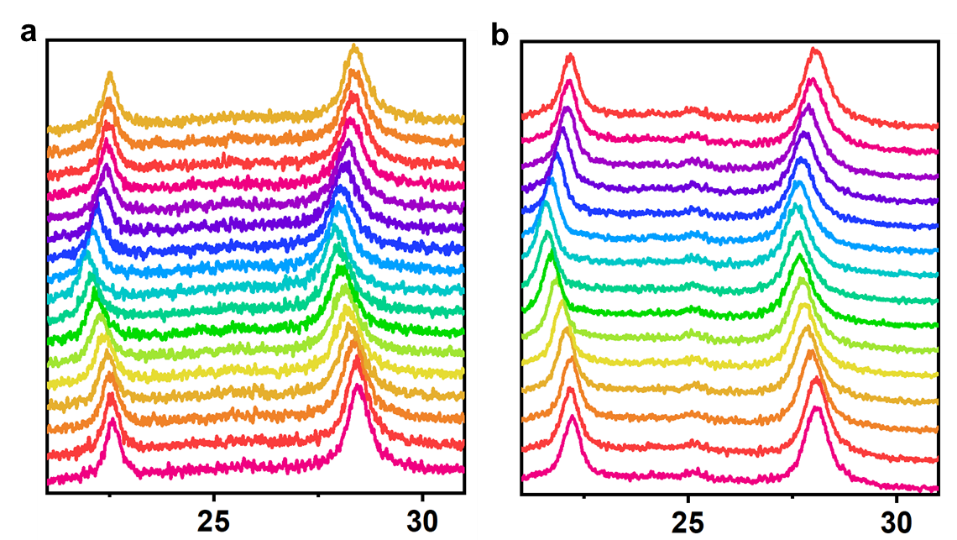
**Fig. S15.** Cycling performance of Nb2O5 with high areal loadings of 2, 3 and 4 mg cm−2 at 0.1 A g−1.



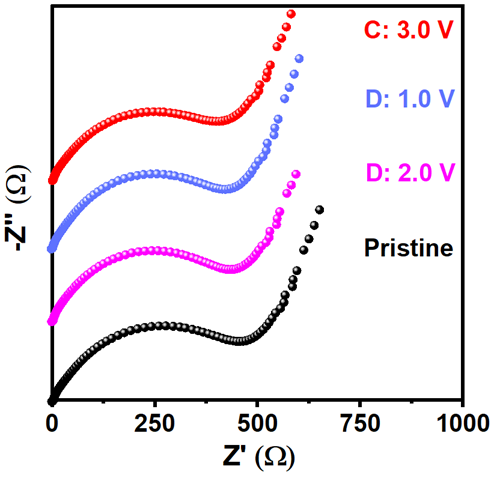
**Fig. S16.** The relationship between Z′ and ω−1/2 (ω = 2πf) of Nb2O5 and Co-Nb2O5 samples.



**Fig. S17.** SEM images (a, b), TEM image (c) and HRTEM image (d) of Co-Nb2O5 after 100 cycles.



**Fig. S18.** *In situ* XRD patterns of a) Nb2O5 and b) Co-Nb2O5 samples during first charge/discharge process at 0.1 A g−1.

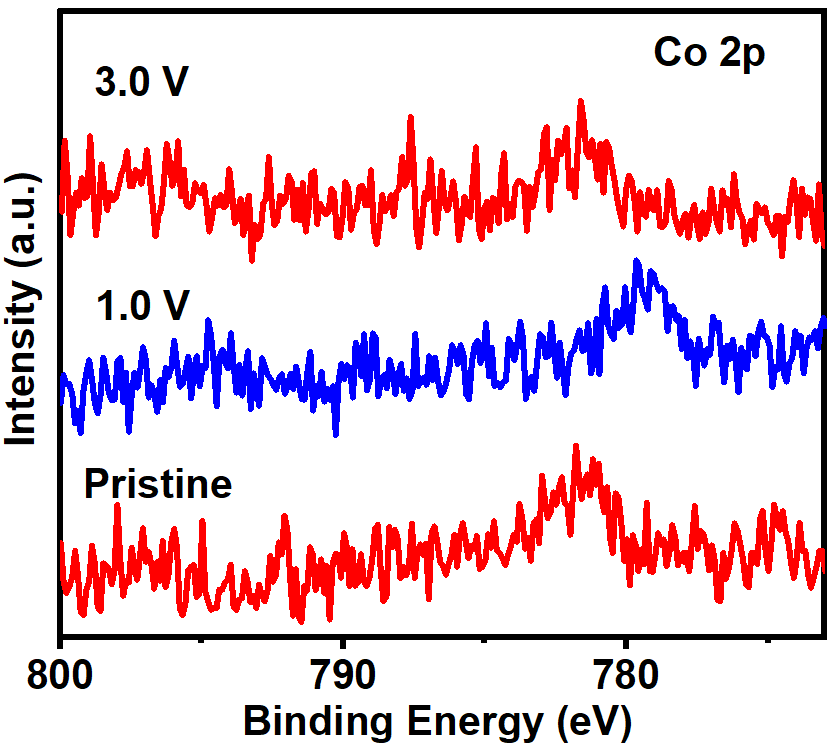


**Fig. S19.** *Ex situ* EIS during the initial cycle of Co-Nb2O5 electrodes.

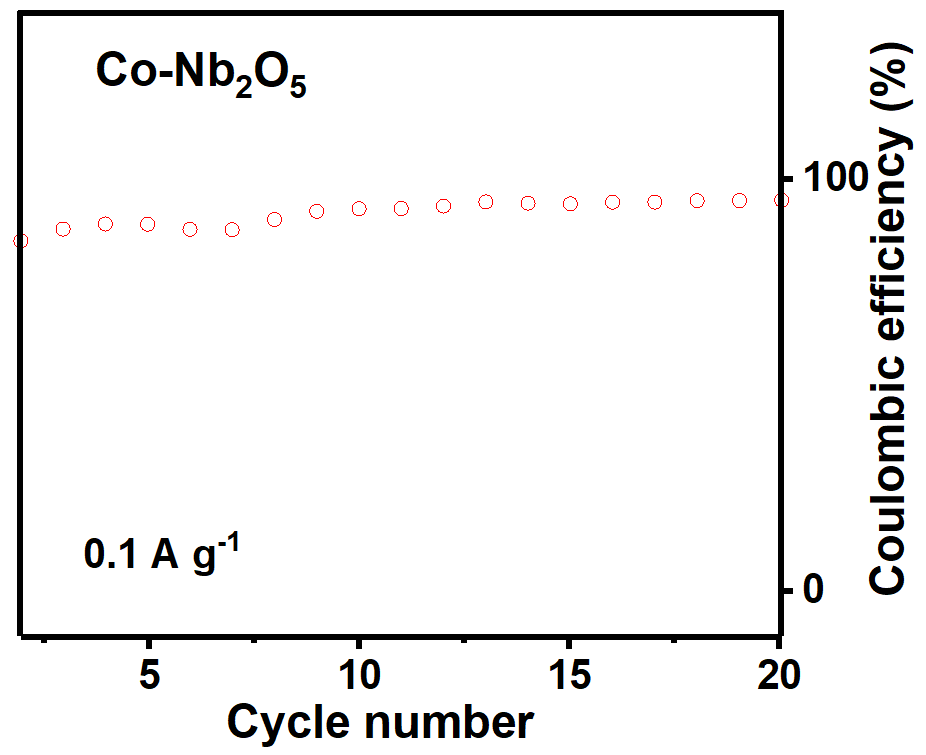
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**Fig. S20.** High-resolution XPS spectra of the T-Nb2O5 electrodes upon lithiation/delithiation processes.

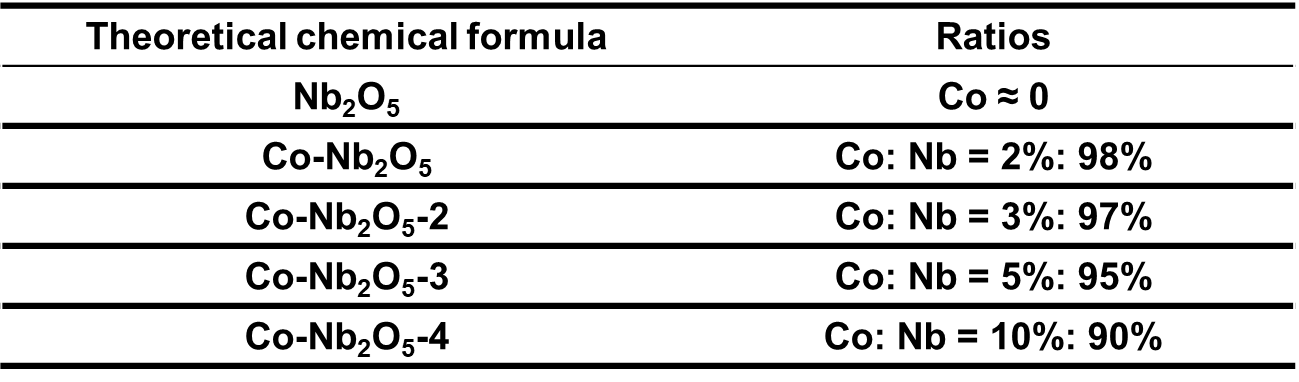


**Fig. S21.** High-resolution XPS spectra of Co 2p for the Co-Nb2O5 electrodes upon lithiation/delithiation processes.

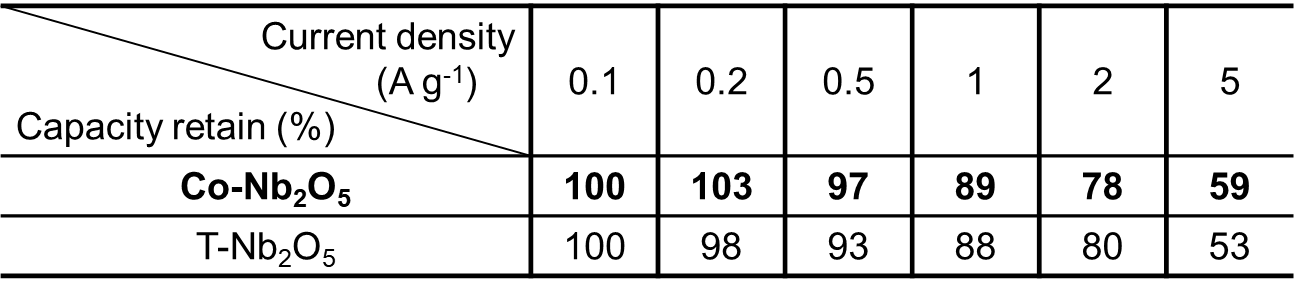


**Fig. S21.** The enlarged Coulombic efficiencies tested at 0.1 A g−1 during first 20 cycles.

**Table S1.** ICP measurement results of Nb2O5, Co-Nb2O5, Co-Nb2O5-2, Co-Nb2O5-3 and Co-Nb2O5-4samples.



**Table S2.** Comparison of the capacity retain of the Co-Nb2O5 and previous T-Nb2O5 with increasing current density.



**Table S3.** Comparison of capacity and cycling life of the Co-Nb2O5 presented herein and selected similar Nb-based oxides reported earlier in literature[5-13].

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **anode** | **Voltage range (V)** | **Capability (mA g-1)** | **Cycling life** | **Capaciy retention** | **Reference** |
| **Co-Nb2O5** | **1.0-3.0** | **256 (0.5C)**  **189 (5C)** | **110**  **500** | **97%**  **90%** | **Our work** |
| (N-C@MSC-Nb2O5) | 1.0-3.0 | 185 (10C) | 1000 | 83% | Adv. Mater. 2020, 32, 2001001. |
| H-Nb2O5 | 1.0-3.0 | 230 (0.5C)  151 (10C) | /  2000 | /  90% | Energy Environ. Sci. 2022, 15, 254-264. |
| T-Nb2O5@C | 1.0-3.0 | 197 (1C) | 200 | 93% | Adv. Energy Mater. 2019, 1802695. |
| Nb2O5@Nb4C3Tx | 1.0-3.0 | 208 (0.25C) | 400 | 94% | Adv. Funct. Mater. 2016, 26, 4143. |
| Nb2O5 | 1.2-3.0 | 182 (0.5C) | 150 | 97% | ACS Nano 2016, 10, 507. |
| T-Nb2O5 | 1.2-3.0 | 175 (0.1C) | 100 | 91% | J. Am. Chem. Soc. 2016, 138, 8888. |
| H-Nb2O5/rGO | 1.0-3.0 | 176 (1C) | 450 | 97% | J. Mater. Chem. A 2019, 7, 693. |
| T‑Nb2O5 NTs200 | 1.0-3.0 | 199 (0.5C)  155 (5C) | 200  500 | 84%  89% | ACS Appl. Mater. Interfaces 2021, 13, 16445. |
| Nb2O5@N-C | 1.0-3.0 | 188 (10C) | 2900 | 41% | J. Alloys Compd. 2021, 876, 160145. |

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