**Supplementary materials**

**Facile formation of tetragonal-Nb2O5 microspheres for high-rate and stable lithium storage with high areal capacity**

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**Fig. S1** Schematic illustrations of the crystal structures of (a) TT-Nb2O5, (b) T-Nb2O5, (c) M-Nb2O5 and (d) H-Nb2O5. Oxygen and niobium sites are represented by red and dark cyan spheres, respectively.

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**Fig. S2** TG-DSC curves of the Nb powder from 25 to 1000 ℃ at a heating rate of 10 ℃ min-1 in flowing air atmosphere.

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**Fig. S3** XRD patterns of evolutive phases observed upon heating the Nb powder precursor at different temperatures ranging from 500 to 1000 ℃

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**Fig. S4** SEM images of the Nb powder.

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**Fig. S5** Characterizations of the TT-Nb2O5, T-Nb2O5, M-Nb2O5 and H-Nb2O5 samples. (a) XPS spectra of wide survey. (b) High-resolution Nb 3d XPS spectra. (c) High-resolution O 1s XPS spectra. (d) Raman spectra.



**Fig. S6** Electrochemical analysis of the obtained TT-Nb2O5, T-Nb2O5, M-Nb2O5 and H-Nb2O5 samples. (a-d) CV curves tested at various current densities from 0.1 to 1 mV s-1. (e) Determination of the *b* values using the relationship between peak current and scan rate (the *b*1 values are according to the anodic peaks and the *b*2 values are for the cathodic peaks).

Generally, the CV curves follows the power law:

***i = avb*  (1)**

Where *a* and *b* are adjustable parameters, *i* is the current, and *v* is the sweep rate. Equation (1) can be equally converted to Equation (2)

**log(*i*) = log(*a*) + *b*log(*v*)(2)**

The value of *b* can be calculated from log(*i*) versus log (*v*) plots. The *b*-value is close to 0.5 and 1, which corresponds to the diffusion-controlled process and surface-controlled pseudocapacitive reaction, respectively[1-4].



**Fig. S7** (a) The Nyquist plots of the TT-Nb2O5, T-Nb2O5, M-Nb2O5 and H-Nb2O5 fresh electrodes. (b) The corresponding kinetics calculations based on the frequency (ω-1/2) and Z′ values at low frequency region.

As shown in the Fig. S7a, the Nyquist plots of the TT-Nb2O5, T-Nb2O5, M-Nb2O5 and H-Nb2O5 pristine electrodes all display a single semicircle in the high frequency region and a straight line in the low-frequency range. The diameter of the semicircle reflects the interfacial charge-transfer impedance (Rct) in the assembled cells. The low-frequency Warburg contribution of the impedance response is directly related to the lithium-ion diffusion process in an electrode material[5].

**Calculation of the Lithium-ion Diffusion Kinetics for EIS[6]:**

**(3)**

**(4)**

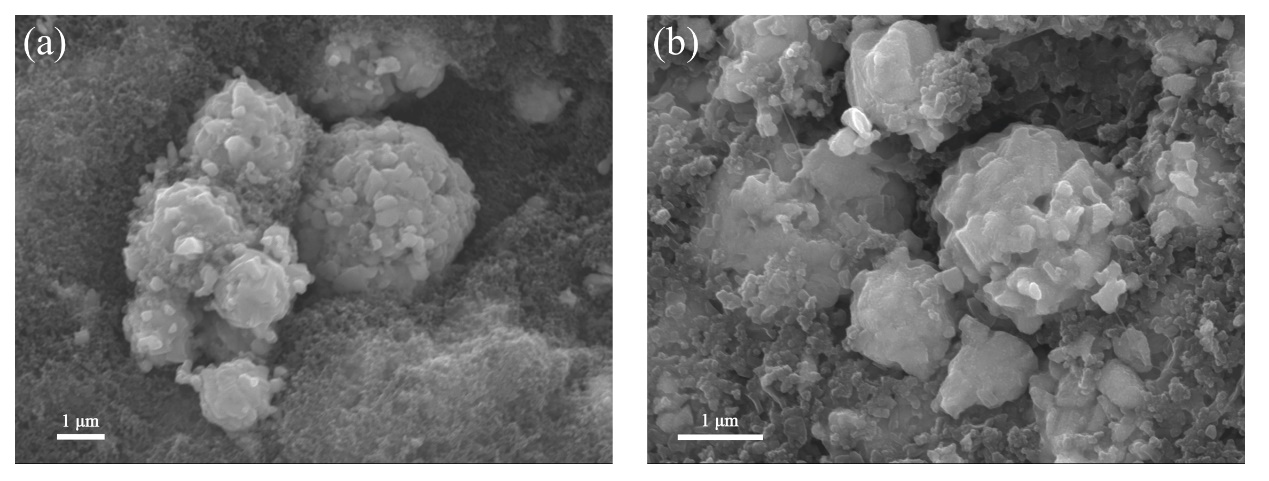
Where DLi is the lithium-ion diffusion coefficient, R is the gas constant, T is the absolute temperature, A is the surface area of cathode, n is the number of electrons per molecule during oxidization, F is Faraday's constant, CLi is the concentration of lithium ion, ω is the angular frequency, and σ is the Warburg factor which could be obtained by equation 4. By linear fitting of Z' and ω-1/2, the slope is described as σ value. Combining with equation 3, the square of σ value has an inverse relationship with DLi.



**Fig. S8** High symmetric point path in the brillouin zones of (a) TT-N2O5 (Γ-Y-F-L-I-Z-Γ-X-Q-M-N-X|Z-N), (b) T-N2O5 (Γ-M-X-Γ-Z-A-R-Z|A-M|R-X), (c) M-N2O5 (Γ-M-X-Γ-Z-A-R-Z|M-A|X-R) and (d) H-N2O5 ((Γ-Y-F-L-I|S-Z-Γ-X|T-Y|M-Γ-N|Z-R).



**Fig. S9** *In-situ* XRD pattern of M-Nb2O5 samples during galvanostatic charge and discharge at 0.2 A g−1.



**Fig. S10** SEM images of M-Nb2O5 electrodes at high mass loading of 12.58 mg cm−2. (a) Before cycling; (b) After 100 cycles for lithium storage.

**References**

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