Supplementary Information

High-Power and High-Energy Asymmetric Supercapacitors Based on Li⁺-intercalation into T-Nb₂O₅/Graphene Pseduocapative Electrodes

Lingping Kong, a Chuanfang Zhang, a Songmin Zhang, a Jitong Wang, a Rong Cai, b Chunxiang Lv, *b Wenming Qiao, a Licheng Ling a and Donghui Long* a

a State Key Laboratory of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, China.
b National Engineering Laboratory for Carbon Fiber Technology, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, China

*To whom correspondence should be addressed.

Donghui Long, Tel: +86 21 64252924, Fax: +86 21 64252914,

E-mail: longdh@mail.ecust.edu.cn
**Content:**

**Fig. S1** TG analysis of $T$-Nb$_2$O$_5$/graphene nanocomposite and $T$-Nb$_2$O$_5$ in air flow.

**Fig. S2** TG analysis (a), XRD pattern (b), SEM image (c) and HR-TEM image (d) of $T$-Nb$_2$O$_5$/graphene nanocomposite with 25 wt.% graphene.

**Fig. S3** XRD pattern of the $T$-Nb$_2$O$_5$.

**Fig. S4** $N_2$ adsorption-desorption isotherms (a) and BJH pore size distributions (b) of $T$-Nb$_2$O$_5$ and $T$-Nb$_2$O$_5$/graphene nanocomposite.

**Fig. S5** SEM images of $T$-Nb$_2$O$_5$/graphene electrode film after 3000 charge-discharge process at current density 1 A g$^{-1}$.

**Fig. S6** CV curves (a) and rate performance (b) of $T$-Nb$_2$O$_5$/graphene nanocomposite in TEABF$_4$ in propylene carbonate (PC).

**Fig. S7** Electrochemical performances of the $T$-Nb$_2$O$_5$/graphene electrodes with and without conductive agents.

**Fig. S8** Electrochemical performances of the $T$-Nb$_2$O$_5$/graphene electrodes with 10 wt.% and 25 wt.% graphene.

**Fig. S9** Nyquist plot ranging from 100 kHz to 0.01 Hz for $T$-Nb$_2$O$_5$/graphene nanocomposites (initial-black line and after CV test-red line).

**Fig. S10** Galvanostatic charge-discharge curves at different current densities and CV curves at different scan rates of the MC and AC based symmetric supercapacitors.

**Fig. S11** Coulombic efficiency during 3000 cycling at current density of cell

**Table S1** The porosity parameter of the samples
Table S2  The porosity parameters of MC and AC.

**Fig. S1** TG analysis of $T$-$\text{Nb}_2\text{O}_5$/graphene nanocomposite and $T$-$\text{Nb}_2\text{O}_5$ in air flow.

The pure $T$-$\text{Nb}_2\text{O}_5$ sample has only a slight weight loss during heat treatment, while the $T$-$\text{Nb}_2\text{O}_5$/graphene nanocomposites have a 10 wt% weight loss corresponding to the weight ratio of graphene in the nanocomposites.
Fig. S2 TG analysis (a), XRD pattern (b), SEM image (c) and HR-TEM image (d) of T-Nb$_2$O$_5$/graphene nanocomposite with 25 wt.% graphene.

The weight ratio of graphene in the nanocomposites can be easily adjusted by changing the amount of GO solution. The increased percent of graphene did not dramatically change the structure and morphology of the nanocomposite. However, higher percent of graphene in the electrode would lead to the decrease of the total capacitance and energy density in the compacted system, due to the decrease of the active materials.
Fig. S3 XRD pattern of $T$-$\text{Nb}_2\text{O}_5$.

The pure $T$-$\text{Nb}_2\text{O}_5$ prepared using the same conditions but without adding GO solution has also a standard XRD profiles of orthorhombic structure.
Fig. S4 $N_2$ adsorption-desorption isotherms (a) and BJH pore size distributions (b) of $T$-Nb$_2$O$_5$ and $T$-Nb$_2$O$_5$/graphene nanocomposite.

The BET specific surface area of $T$-Nb$_2$O$_5$/graphene nanocomposite is 104 m$^2$ g$^{-1}$, higher than that of $T$-Nb$_2$O$_5$ (39 m$^2$ g$^{-1}$). The $T$-Nb$_2$O$_5$/graphene nanocomposite possesses a certain amount of macropores and mesopores with pore volume of 0.33 cm$^3$ g$^{-1}$ that issues form a sheet-like porous system which agree well with the SEM images.
Fig. S5 SEM images of $T$-$\text{Nb}_2\text{O}_5$/graphene electrode film after 3000 charge-discharge process at current density $1 \text{ A g}^{-1}$.

The layer-by-layer assembled film of $T$-$\text{Nb}_2\text{O}_5$/graphene could maintain very well after long-term cycling, confirming the structural advantages of the $T$-$\text{Nb}_2\text{O}_5$/graphene nanocomposite in keeping the structural stability and electrode integrity.
Fig. S6 CV curves (a) and rate performance (b) of \( T\)-\( \text{Nb}_2\text{O}_5 \)/graphene nanocomposite in TEABF\(_4\) in propylene carbonate (PC).

In order to estimate the contribution of double-layer capacitance of \( T\)-\( \text{Nb}_2\text{O}_5 \)/graphene, CVs were conducted in TEABF\(_4\) in propylene carbonate with the sweep rate from 1 to 50 mV s\(^{-1}\). Compared with the total capacitance in LiPF\(_6\) system, the contribution of double-layer capacitance is negligible.
Fig. S7 Electrochemical performances of the T-Nb$_2$O$_5$/graphene electrodes with and without conductive agents: CV curves of T-Nb$_2$O$_5$/graphene conductive agent-free electrode (a) and with conductive agent electrode (b); charge storage as a function of sweep rate (c), b-value characterization (d), rate performance (e), and impedance analysis (f, g, h).
(e) and Nyquist plot (f) for $T$-Nb$_2$O$_5$/graphene with or without conductive agent electrode; schematic diagram of the $T$-Nb$_2$O$_5$/graphene electrode without conductive agents (g) and with conductive agents (h). Specific capacitance is based on the total material (including PVDF, Super C65 and $T$-Nb$_2$O$_5$/graphene nanocomposites) on the electrode film).

From the above electrochemical comparisons, it can be concluded that the conductive $T$-Nb$_2$O$_5$/graphene nanocomposite could form an effective electronic conducting network even without the addition of the conductive agents. These results further emphasize the incorporation of graphene sheets in the composite could provide enough electronic conductivity to achieve sound electrochemical performance.
**Fig. S8** Electrochemical performances of the T-Nb2O5/graphene electrodes with 10 wt.% and 25 wt.% graphene: CV curves of T-Nb2O5/graphene electrode with 10 wt.% graphene (a) and with 25 wt.% graphene (b); charge storage as a function of sweep rate (c) and rate performance (d). Specific capacitance is based on the total active material (including T-Nb2O5 and graphene).

The T-Nb2O5/graphene electrode with 25% graphene demonstrated very similar capacitive and high-rate behavior with the T-Nb2O5/graphene electrode with 10 % graphene. However, higher percent of graphene in the electrode would lead to the decrease of the total capacitance, due to the decrease of the active materials.
Fig. S9 Nyquist plot Comparison of $T$-$Nb_2O_5$/graphene nanocomposite before (black line) and after (read line) CV cycling.

Nyquist plot features a high phase-angle impedance plot and a low faradic charge transfer resistance, indicating low charge transfer resistance and facile Li$^+$ ion intercalation into the $T$-$Nb_2O_5$/graphene nanocomposite. to proceed redox reaction.
Fig. S10 Galvanostatic charge-discharge curves at different current densities and CV curves at different scan rates of the MC and AC based symmetric supercapacitors. The AC deliver higher specific capacitance at a low current density, while MC perform superior rate performance, making them more suitable to pair with high-rate T-Nb2O5/graphene electrode.
Fig. S11 Coulombic efficiency during 3000 cycling at 0.2 A g⁻¹ (cell current density)
**Table S1** Porosity parameters of $T$-Nb$_2$O$_5$ and $T$-Nb$_2$O$_5$/graphene nanocomposite.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$^{a}S_{BET}$ / m$^2$ g$^{-1}$</th>
<th>$^{b}V_T$ / cm$^3$ g$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>T-Nb$_2$O$_5$</td>
<td>39</td>
<td>0.21</td>
</tr>
<tr>
<td>T-Nb$_2$O$_5$/graphene</td>
<td>104</td>
<td>0.33</td>
</tr>
</tbody>
</table>

$^a$ BET specific surface area; $^b$ total pore volume

**Table S2** Porosity parameters of MC and AC.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$^{a}S_{BET}$ / m$^2$ g$^{-1}$</th>
<th>$^{b}V_T$ / cm$^3$ g$^{-1}$</th>
<th>$^{c}D_{ave}$ / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>MC</td>
<td>1266</td>
<td>2.07</td>
<td>6.5</td>
</tr>
<tr>
<td>AC</td>
<td>1973</td>
<td>0.99</td>
<td>2.0</td>
</tr>
</tbody>
</table>

$^a$ BET specific surface area; $^b$ total pore volume; $^c$ BJH average pore diameter derived from desorption branch