An Excellent Full Sodium-Ion Capacitor Derived From a single Ti-based Metal-Organic Frameworks

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1. Experimental Section

Synthesis and characterization of TiO$_x$N$_y$: TiO$_x$N$_y$ nanowires were obtained by annealing hydrogen titanate nanowires (H$_2$Ti$_3$O$_7$) in ammonia flow at 800 °C. H$_2$Ti$_3$O$_7$ NWs were firstly synthesized by hydrothermal method reported elsewhere. Briefly, TiO$_2$ anatase (2 g) was added into NaOH solution (30 mL, 15 M) under magnetic stirring for 1 h. Then, the suspension was transferred to a Teflon-lined stainless steel autoclave and heated in an electric oven at 180 °C for 72 h. After cooling down at room temperature, the product was stirred in 0.1 M HCl solution for 24 h. The material was filtered, washed with deionized water and alcohol, and dried at 70 °C for 12 h. Finally, H$_2$Ti$_3$O$_7$ were converted to TiO$_x$N$_y$ by annealing in NH$_3$ flow at 800 °C for 4 h with a heating rate of 5 °C min$^{-1}$.

2. Calculations of specific capacity, energy density and power density

The half-cell specific capacity (mAh g$^{-1}$) is calculated by Equation S1;

$$Q = i \times t$$  \hspace{1cm} (1)

Q (mAh g$^{-1}$) is the half-cell specific capacity; $i$ (mA g$^{-1}$) is the current density; $t$ (h) is the charge or discharge time.

The Na-ion capacitors specific capacity (F g$^{-1}$), energy density (E) and power density (P) are calculated based on Equations S2, S3 and S4;

$$C = I \times \Delta t / (\Delta V)$$  \hspace{1cm} (2)

$$E = (C \times \Delta V^2)/2$$  \hspace{1cm} (3)

$$P = E / \Delta t$$  \hspace{1cm} (4)
32 C (F g\(^{-1}\)) is the Na-ion Capacitors specific capacity; I (A g\(^{-1}\)) is the current density; \(\Delta t\) (s) is the discharge time. \(\Delta V\) is the charge-discharge potential window; E (Wh kg\(^{-1}\)) is the energy density and P (W kg\(^{-1}\)) is the power density.

35 **3. Calculate methods and details of capacitive effect contribution and diffusion-controlled contribution**

37 Using the scan-rate-dependent CV curves (Fig. 4A) to quantify the contribution from capacitive effects (both surface pseudocapacitance and doublelayer capacitance) and diffusion-controlled Na\(^{+}\) insertion process to the current response according to the following equation;

\[
I(V) = k_1 v + k_2 v^{1/2}
\]

Where \(I(V)\), \(k_1 v\) and \(k_2 v^{1/2}\) represent the total current response at a given potential \(V\), current due to surface capacitive effects, and current due to diffusion-controlled Na\(^{+}\) insertion process, respectively.

39 The above equation can also be reformulated as;

\[
I(V)/v^{1/2} = k_1 v^{1/2} + k_2
\]

42 By plotting \(I(V)/v^{1/2}\) vs. \(v^{1/2}\) at different potentials, we can calculate the values of \(k_1\) (slope) and \(k_2\) (intercept) from the straight lines. This allows one to quantify the fraction of the current at specific potentials to the capacitive effect (\(k_1 v\)) and diffusion-controlled insertion (\(k_2 v^{1/2}\)) at fixed potential (see Fig. S13 A, B). After integration of the enclosed CV area, the amount of stored charge from different energy storage modes can be distinguished, expressed by the following equation;

\[
Q = Q_s + Q_d
\]

51 Where, \(Q\), \(Q_s\), and \(Q_d\) represent the total stored charge included in the enclosed CV area at set scan rate, surface capacitive effects, and diffusion controlled Na\(^{+}\) insertion process, respectively.
Fig. S1. XRD pattern of as-prepared NH$_2$-MIL-125(Ti).

Fig. S2. (A and B) FESEM images of NH$_2$-MIL-125(Ti) with different resolution.
**Fig. S3.** (A and B) low resolution FESEM images of TiO$_x$N$_y$/C and NHPC, respectively.

**Fig. S4.** bright-field TEM image of TiO$_x$N$_y$/C inside structure.
Fig. S5. (A) FESEM image of nanowires precursor, (B) FESEM image of TiO$_x$N$_y$ nanowires and corresponding FESEM element mapping image.

Fig. S6. XRD pattern of TiO$_x$N$_y$ nanowires.
Fig. S7. Thermogravimetric analysis curves of TiO$_x$N$_y$/C.

The TGA data was obtained by annealing in O$_2$ flow. In the detail, the original specimen is TiO$_x$N$_y$ ($x+y=1$) and carbon. The specimen converted to pure TiO$_2$ phase after TG test. So, according to the final mass of TiO$_2$ and Invariance Principle of Ti elements in this process, the carbon contents in the TiO$_x$N$_y$/C is approximately 22% by calculated.

Fig. S8. (A) The nitrogen adsorption-desorption isotherms of TiO$_x$N$_y$, and (B) the corresponding pore distribution.
Fig. S9. (A and B) XPS spectra of TiO\textsubscript{x}N\textsubscript{y}/C and NHPC, respectively.

Fig. S10. (A, B and C) the contrast of Ti 2p, N 1s and O 1s XPS spectra between TiO\textsubscript{x}N\textsubscript{y}/C and TiO\textsubscript{x}N\textsubscript{y} nanowires, respectively.
Table S1. the structure information of as-prepared samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{BET}$(m$^2$g$^{-1}$)</th>
<th>$V_b$(cm$^3$g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1731</td>
<td>1.12</td>
</tr>
<tr>
<td>TiO$_x$N$_y$/C</td>
<td>248</td>
<td>0.5</td>
</tr>
<tr>
<td>TiO$_x$N$_y$</td>
<td>20.921</td>
<td>0.11</td>
</tr>
</tbody>
</table>

Fig. S11. Charge and discharge curves of TiO$_x$N$_y$/C at different current density.
Fig. S12. CV curves (A), first five galvanostatic discharge–charge profiles at 0.05A g\(^{-1}\) (B), rate performance (C) and the cycling stability of at 1A g\(^{-1}\) of TiO\(_x\)N\(_y\) nanowires.
Fig. S13. (A and B) $I/\nu^{1/2}$ vs. $\nu^{1/2}$ plots of TiO$_x$N$_y$/C used for calculating constants $k_1$ and $k_2$ at different potentials, (C and D) Capacitive charge storage contributions at a scan rate of 0.2 mV s$^{-1}$ and 1 mV s$^{-1}$.

Fig. S14. FESEM images of TiO$_x$N$_y$/C after electrochemical cycles test.
**Fig. S15.** The rapid charging curves in 40s of TiO$_x$N$_y$/C//NHPC SICs (B), and the Photographs of a light emitting diode powered by a rapid charging TiO$_x$N$_y$/C // NHPC SIC in 40 s under time recording by a timer.