Supporting Information

Highly stable supercapacitive performance of the one-dimensional (1D) brookite TiO$_2$ nanoneedles

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Galvanostatic charging-discharging:

The galvanostatic charging-discharging (Fig. S1,) of 1D $\beta$-TiO$_2$ nanoneedles was studied at various current densities of 166.7, 250, 333.3 and 416.7 µA/g. Obviously, the charging curves were relatively symmetric to their discharge counterpart implying that a highly reversible ion transportation is efficiently taking place along the textural boundaries of 1D $\beta$-TiO$_2$ nanoneedles.

The specific capacitance from the galvanostatic charging-discharging was calculated using equation –

$$C_s = \frac{I}{m \cdot (dV/dt)}$$

--- (S1)
where, $C_s$ is specific capacitance (F/g), $I$ is the applied current (A), $m$ is the mass of the active material (g), and $dV/dt$ is the slope of the discharge curve (V/s). The $C_s$ derived from the charge-discharge test (Fig. S1(b)) maintaining good linearity and gradually decreasing with increase in the current density from 166.7 to 416.7 µA/g, since the ion accessibility is limited to the surface of the 1D $\beta$-TiO$_2$ nanoneedles on the relevant timescale. The $C_s$ value of 192.2 mF/g gained at a current density of 166.7 µA/g was decreased up to 27.6 mF/g at 417.7 µA/g. To our knowledge, these $C_s$ values of 1D $\beta$-TiO$_2$ nanoneedles are larger than those achieved by brookite TiO$_2$ thin films and nanostructures. These values are comparable those obtained from anatase, [1] rutile [2] and hexagonal [3] TiO$_2$ structures. Moreover, 1D $\beta$-TiO$_2$ nanoneedles showed a more rapid ion diffusion mechanism in comparison to TiO$_2$ nanoparticles and its multilayer film with graphene, [4] TiO$_2$@C core-shell nanowires, [5] and anatase to rutile transformed TiO$_2$ nanotubes. [6]

The energy density ($E$), power density ($P$), and coulombic efficiency ($\eta$) of the supercapacitor devices was calculated from the equations,

$$E = \frac{1}{2} \times C_s \times (\Delta V) \times \frac{1000}{3600}$$  \hspace{1cm} \text{(S2)}$$

$$P = \frac{1}{2} \times \frac{C_s \times (\Delta V) \times 1000}{\Delta t_d} \times \frac{E}{3600}$$  \hspace{1cm} \text{(S3)}$$

$$\eta(\%) = \frac{\Delta t_d \times 100}{\Delta t_c}$$  \hspace{1cm} \text{(S4)}$$

where, $E$ is the energy density (Wh/Kg), $C_s$ is specific capacitance obtained from Eq. (3), $\Delta V$ is the discharge voltage range (V) on the potential window, $P$ is the power density (W/Kg), $\eta$ is the coulombic efficiency, and $\Delta t_d$ and $\Delta t_c$ are discharge and charging time, respectively. The calculated energy density and power density of the 1D $\beta$-TiO$_2$ nanoneedles are 3.04 Wh/Kg, and 206.09 W/Kg, respectively, at a scan rate of 15 mV/s. To demonstrate the overall performance of 1D $\beta$-TiO$_2$ nanoneedles, a Ragone plot is shown in Fig. S2. A Ragone plot manifests a energy density and power density of 3.04Wh/Kg and 1683W/Kg, respectively, which is better than the previous reported for anatase TiO$_2$ nanotubes, [1] vertically aligned rutile TiO$_2$ nanorods, [2] microwave assisted graphene-TiO$_2$ hybrid nanostructures, [7] and hybrid supercapacitor fabricated with the carbon nanotube (CNT) cathode and TiO$_2$ nanowire anode. [8] The coulombic efficiency of 98 % is obtained from 1D $\beta$-TiO$_2$ nanoneedles and is mainly attributed to the increased contributions of large surface area and textural boundaries. These results clearly demonstrate a new dimension of the 1D $\beta$-TiO$_2$ nanoneedles for the development of high stable supercapacitor of long cycle lifetime.
Fig. S1 Galvanostatic discharge curves of the 1D $\beta$-TiO$_2$ nanoneedles collected at various current densities within the limiting potential of 0 to 0.8 V. (b) The specific capacitance for various current densities calculated from discharging curves.

Fig. S2 Ragone plot derived from CV to determine the performance of the 1D $\beta$-TiO$_2$ nanoneedles.
Fig. S3 Figure shows selected cyclic voltammograms obtained at scan rate of 100 mV/s for number cycles from 1 to 10,000 cycles.

Fig. S4 First 50 glavanostatic charging-discharging cycles extracted out of 5,000 cycles obtained at current density of 250 µA/g. Inset shows first five cycles.

Table 1 – The 1D β-TiO$_2$ nanoneedles shows better stability than the pure and hybrid metal-oxide nanostructures listed in the table below.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Electrode Materials</th>
<th>Capacitance reduction (%)</th>
<th>Number of cycles</th>
<th>Ref. No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>V$_2$O$_5$ nanowires</td>
<td>~ 50.0 %</td>
<td>5000</td>
<td>[9]</td>
</tr>
<tr>
<td>2.</td>
<td>NiO porous microtubes</td>
<td>~ 22.6 %</td>
<td>2000</td>
<td>[10]</td>
</tr>
<tr>
<td>4.</td>
<td>Co$_3$O$_4$ nanowires</td>
<td>~ 15.0 %</td>
<td>1000</td>
<td>[12]</td>
</tr>
<tr>
<td>5.</td>
<td>Co$_3$O$_4$ hollow nanotube</td>
<td>~ 9.0 %</td>
<td>1000</td>
<td>[13]</td>
</tr>
<tr>
<td>6.</td>
<td>α-MnO$_3$ nanobelts</td>
<td>~ 5.0 %</td>
<td>500</td>
<td>[14]</td>
</tr>
<tr>
<td>7.</td>
<td>NiO@MnO$_2$ microtube</td>
<td>~ 18.3 %</td>
<td>2000</td>
<td>[10]</td>
</tr>
<tr>
<td>8.</td>
<td>Graphene@V$_2$O$_5$ nanobelts</td>
<td>~ 12.0 %</td>
<td>5000</td>
<td>[15]</td>
</tr>
<tr>
<td>9.</td>
<td>MnO$_2$ nanowires/ZnO nanorods</td>
<td>~ 6.5 %</td>
<td>1000</td>
<td>[16]</td>
</tr>
<tr>
<td>10.</td>
<td>V$_2$O$_5$ doped α-Fe$_2$O$_3$ nanotubes</td>
<td>~ 24.5 %</td>
<td>200</td>
<td>[17]</td>
</tr>
</tbody>
</table>
11. Carbon coated V$_2$O$_5$ nanorods ~ 24.0 % 1000 [18]
12. V$_2$O$_5$ nanoporous network ~ 24.0 % 600 [19]
13. SnO$_2$ Nanosheets ~ 58.2 % 6000 [20]
14. Co$_3$O$_4$ nanosheets ~ 31.0 % 1000 [21]
15. Co$_3$O$_4$ ultrathin nanosheets ~ 21.5 % 2000 [22]
17. SnO$_2$@Co$_3$O$_4$ core-shell nanosheets ~ 41.7 % 6000 [20]
18. MnO$_2$ nanoparticles ~ 22.8 % 1000 [23]
19. Ni@NiO core-shell nanoparticulate tube ~ 19.0 % 1000 [11]
20. SnO$_2$@MnO$_2$ nanoparticles ~ 18.9 % 1000 [23]
21. Ppy/GO/ZnO nanocomposite on Ni-Fome ~ 97.0 % 1000 [24]
22. Ni(OH)$_2$/Graphene and RuO$_2$/Graphene ~ 8.0 % 5000 [15]
23. MnO$_2$ grafted V$_2$O$_5$ nanostructure ~ 11.0 % 500 [26]
24. NiO-CeO$_2$ nanoparticles composites ~ 15.0 % 1000 [27]

References:


