Supplementary Information

In-situ efficient growth of Rubik nanocube WO$_3$·0.33H$_2$O array films for high-performance electrochromic energy storage device

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Proof of the Faraday reaction process

According to the following power law:  

\[ i = av^b \]  

(1)

Where \( i \) is the peak current and \( v \) is the scan rate, and \( a \) and \( b \) refer to the adjustable parameters.

Calculation of areal specific capacitance (Ca)

The \( C_a \) can be calculated at different current densities from the GCD curves according to the following equation:  

\[
C_a = \frac{2I \int V(t)dt}{\frac{t(V_{\text{min}})}{2} - \frac{t(V_{\text{max}})}{2}} \frac{1}{A(V_{\text{max}} - V_{\text{min}})^2}
\]  

(2)

Where \( C_a \) and \( A \) represent the areal capacitance and geometrical area of the electrode involved in the reaction in the electrolyte, \( V_{\text{max}} \) and \( V_{\text{min}} \) are the maximum and minimum potential during galvanostatic discharge measurements, respectively. \( I \) is the current density of charge/discharge.
Fig. S1. XRD patterns of the growth of WO$_3$ film without H$_2$O$_2$ and EG on FTO substrates.
Fig. S2. SEM and EDS mapping images of WO$_3$·0.33H$_2$O film.
**Fig. S3.** Digital photographs of the WO$_3$·0.33H$_2$O films before (a) and after (b) tape adhesion/peeling. Optical microscopes of the WO$_3$·0.33H$_2$O films before (a) and after (b) tape adhesion/peeling.

The process of tape testing is described as follows: First, the cross structure of the WO$_3$·0.33H$_2$O film was marked with a knife (bright section in Figure S2a, b). Afterward, commercial tape (3M, 4910-type) was tightly adhered to the surface of the WO$_3$·0.33H$_2$O film for 5 minutes and then peeled off.
Fig. S4. Comparison of film formation by hydrothermal reaction under different acidic conditions: (a) pH under different acidic conditions. (b) Photo images of film formation in the presence or absence of H$_2$O$_2$, and in the presence of HCl, respectively.
Fig. S5. Image of WO$_3$·0.33H$_2$O films during the coloring and bleaching process.
Fig. S6. (a) CV curves of WO$_3$·0.33H$_2$O film at the potential region of ±1 V at various scan rates ranging from 5 to 60 mV·s$^{-1}$ (b) Calculation of b value from anodic peaks for the electrochromic WO$_3$·0.33H$_2$O film.
Fig. S7. Electrochromic and electrochemical performance of the PB film in 1 M LiClO$_4$/PC electrolyte. (a) CV curves of the PB film at a scan rate of 20 mV s$^{-1}$ in the potential range from −0.5 to 0.5 V (vs Ag$^+$/Ag). (b) Optical transmittance spectra of the PB film in the colored (0.5 V vs. Ag$^+$/Ag, red line) and bleached (-0.5 V vs. Ag$^+$/Ag, black line) states. (c) In situ transmittance responses of PB film in 633 nm obtained under the applied square-wave potential between -0.5 and 0.5 V for 50 s, respectively.
**Fig. S8.** CV curve and in situ transmittance spectrum of the EESD at 633 nm at a scan rate of 20 mV s$^{-1}$. 

[Image of CV curve and in situ transmittance spectrum]
Fig. S9. Solar irradiation spectra of the EESD in bleached and colored states compared to the standard solar radiation curve (AM 1.5G)
Table S1: Electrochromic performance comparisons the thin films obtained with different structural-directing agents.

<table>
<thead>
<tr>
<th>Sample</th>
<th>ΔT (%) / ( \lambda ) (nm)</th>
<th>Hydrothermal conditions</th>
<th>CE (cm(^2) ⋅ C(^{-1}))</th>
<th>( t_b / t_c ) (s)</th>
<th>Cycle stability (retention)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexagonal WO(_3^3)</td>
<td>71.5/700</td>
<td>120 °C, 2 h</td>
<td>72.5</td>
<td>10.7/12.4</td>
<td>5000 (90.8%)</td>
</tr>
<tr>
<td>Hexagonal WO(_3^4)</td>
<td>46/1600</td>
<td>180 °C, 4 h</td>
<td>106.1</td>
<td>3.6/2.4</td>
<td>1000 (96%)</td>
</tr>
<tr>
<td>Hexagonal WO(_3^5)</td>
<td>66/633</td>
<td>180 °C, 12 h</td>
<td>106.8</td>
<td>3.4/6.7</td>
<td>1000 (-)</td>
</tr>
<tr>
<td>Hexagonal WO(_3^6)</td>
<td>72.4/550</td>
<td>180 °C, 3 h</td>
<td>67.6</td>
<td>7/3</td>
<td>500 (67%)</td>
</tr>
<tr>
<td>Hexagonal WO(_3^7)</td>
<td>70.1/680</td>
<td>180 °C, 2.5 h</td>
<td>55.9</td>
<td>3/12</td>
<td>400 (-)</td>
</tr>
<tr>
<td>Monoclinic WO(_5^8)</td>
<td>32.5/700</td>
<td>180 °C, 2 h</td>
<td>42.37</td>
<td>-</td>
<td>100 (95.5%)</td>
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<tr>
<td>Hexagonal WO(_3^9)</td>
<td>64/600</td>
<td>180 °C, 4 h</td>
<td>47</td>
<td>17/10</td>
<td>1000 (96%)</td>
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<tr>
<td>Hexagonal WO(_3^{10})</td>
<td>33.9/633</td>
<td>180 °C, 24 h</td>
<td>37.6</td>
<td>18/25</td>
<td>-</td>
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<tr>
<td>Orthorhombic WO(_3^{11})</td>
<td>43/633</td>
<td>180 °C, 2 h</td>
<td>112.7</td>
<td>1.4/4.3</td>
<td>3000 (-)</td>
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<tr>
<td>Hexagonal WO(_3^{12})</td>
<td>78.1/630</td>
<td>120 °C, 2.5 h</td>
<td>56.5</td>
<td>6/5</td>
<td>15000 (-)</td>
</tr>
<tr>
<td>Orthorhombic WO(_3)·0.33H(_2)O</td>
<td>80.6/633</td>
<td>120 °C, 45 min</td>
<td>65.6</td>
<td>14/15</td>
<td>1000 (80%)</td>
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</tbody>
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