Supporting Information

High-performance all-solid-state electrochromic asymmetric Zn-ion supercapacitors for visualizing energy storage

Chengfu Deng, Kai Zhang, Lei Liu, Zhibing He, Jinglin Huang, Tao Wang, Yansong Liu, Xiaoshan He, Kai Du*, Yong Yi*

Content of Supporting Information

1. The annealing parameters of the films
2. Morphology and microstructure of the films
3. The BET, SEM and XRD characterization of the WO₃ electrode
4. The thicknesses of the WO₃ and MnO₂ films
5. Ex-situ XPS patterns of the MnO₂ electrode
6. Electrochemical properties of the WO₃ electrode
7. CA curves and in-situ transmittance spectra of the WO₃ electrode
8. Long-term cycling stability of the WO₃ electrode
9. Typical charging/discharging process of the WO₃ electrode
10. Overview of the charge storage/release contribution and electrochromic behavior
11. Typical charging process of the half-cell Zn-ion supercapacitor
12. Electrochemical impedance spectroscopy behaviors of the WO₃ electrode
14. Volumetric capacitance and in-situ spectrum evolution of the WO₃ electrode
15. The three types of adsorption sites of ZnₓWO₃ system
16. Top-view of the (2 0 0) plane after adsorb Zn atom at the hollow site
17. Charge density difference of the (2 0 0) plane on the hollow site

18. Charge density difference of the (2 0 0) plane on the bridge site

19. Partial density of states (PDOS) of Zn$_x$WO$_3$ with $x = 0.292$

20. Surface migration behaviors of Zn atoms

21. Migration behaviors of Zn atoms from surface to bulk

22. Bulk migration behaviors of Zn atoms

23. Summary of focusing strategies and associated parameters of the EAZS

24. Volumetric capacitance and cycling durability of the EAZS as a function of various temperatures

25. Detailed information of deposition parameters of the WO$_3$ electrode

26. The adsorption energy of Zn adsorbed on WO$_3$ planes

27. The Bader charge of from the WO$_3$ (2 0 0) plane to Zn atom

28. The performances comparison of recent among electrochromic energy storage electrodes/devices

29. Comparison of current various electrochromic energy storage electrodes/devices

30. More details on the color changes of the WO$_3$ electrode

31. The red LED was powered by the ZEAS

32. The green LED was powered by the ZEAS

33. The green LED was powered by the ZEAS

34. References
1. The annealing parameters of the films

The MnO$_2$ film was prepared by electrodeposition on the surface of transparent fluorine-doped tin oxide (FTO) glass substrates at a current of 2.5 mA for 10 min in a three-electrode system. The WO$_3$ film was deposited on indium tin oxide (ITO) glass substrates by the DCMS method. Then, as-fabricated films were heated at 180 °C (MnO$_2$) and 350 °C (WO$_3$) for 2 h in Ar atmosphere and then followed by slow cool down to room temperature. Here, annealing process was divided into three steps of the heating up, thermal retardation and cooling.

**Figure S1.** The annealing parameters of the films. (a) MnO$_2$. (b) WO$_3$. 
2. Morphology and microstructure of the films

Morphology and microstructure of films were shown in Figure S2. Clearly, the unannealed pristine WO$_3$ films has a uniformly dispersed nanoparticles and amorphous structure (Figure S2a-b). Zn lines were observed, which confirmed Zn$^{2+}$ was successfully intercalated into electrodes (Figure S2c). The MnO$_2$ films show a uniform, continuous and longitudinally grown nanosheets structure (Figure S2d). There were two vividly peaks (Figure S2e), which it can be matched with α-MnO$_2$ structure (JCPDS 42-0141). Based on the low polarizabilities and overlapping of vibration modes, fitting the Raman spectra with Lorentz curves (Figure S2f), and the results are consistent with those previously reported α-MnO$_2$. The mode of $\sim$653 cm$^{-1}$ is attributed to the Mn-O symmetric stretching vibrations of the MnO$_6$ octahedra.

Figure S2. Morphology and microstructure of the films. (a-d) SEM images, the scale bar is 200 nm. (b-e) XRD patterns. (c) Zn2p HR-XPS spectra. (f) The Lorentz fitted and original Raman spectra.
3. The BET, SEM and XRD characterization of the WO3 electrode

**Figure S3.** (a) N$_2$ adsorption isotherms and pore size distribution of the WO$_3$ electrode. (b-c) XRD and SEM results of the WO$_3$ electrode after cycling tests.
4. The thicknesses of the WO3 and MnO2 films

**Figure S4.** The thicknesses of the WO3 and MnO2 films.
5. Ex-situ XPS patterns of the MnO\textsubscript{2} electrode

XPS survey spectrum was investigated to demonstrate the existence of MnO\textsubscript{2} and show the chemical composition, which all peaks of Mn, C, O elements are clearly observed after calibrating the peak of C1s (Figure S5a). XPS spectrum of electrode was clearly fitted into multiple peaks, and the detailed results were shown in Figure S4b. After charging, the amount of Mn\textsuperscript{4+}, Mn\textsuperscript{3+} and Mn\textsuperscript{2+} are about 59.6%, 32.1% and 8.3%, respectively (Figure S5b, bottom). After discharging, the amount of Mn\textsuperscript{4+}, Mn\textsuperscript{3+} and Mn\textsuperscript{2+} are about 33.8%, 40.5% and 25.7%, respectively (Figure S5b, top). Hence, there is the reversible transition of Mn valence states during the charging/discharging process in Zn\textsuperscript{2+} electrolyte.

![Figure S5. Ex-situ XPS patterns of the MnO\textsubscript{2} electrode. (a) XPS pattern. (b) HR-XPS Mn2p patterns.](image-url)
6. Electrochemical properties of the WO$_3$ electrode

Switching time of the coloring/bleaching process are 11.0/10.1 s, respectively (Fig. S6a). The coloring efficiency was calculated to be 75.6 cm$^2$ C$^{-1}$ by using the slope of the optical density versus charge density curves (Fig. S6b). Fig. S6c shows the GCD curve and in-situ spectrum. Evidently, the electrode emerged a reversible color transition from transparent to dark blue during the charge storage, and transmittance changes from 62.0% to 3.8%.

**Figure S6.** Electrochemical properties of the WO$_3$ electrode .(a) Chronoamperometry profile and in-situ spectrum. (b) The optical density versus charge density curves. (c) GCD curve and in-situ spectrum.
7. CA curves and *in-situ* transmittance spectra of the WO$_3$ electrode

Figure S7 shows the CA curves and *in-situ* transmittance spectra at 550 nm of the WO$_3$ electrode. As the square-wave potential pulse width gradually increasing from 25 to 60 s, the corresponding ΔT increasing from 54.13% to 60.13%.

**Figure S7.** CA curves and *in-situ* transmittance spectra of the WO$_3$ electrode. (a) Applied potential between -0.8 and 0.8 V vs Ag/AgCl. (b-e) CA curves and the corresponding *in-situ* transmittance spectra. (f) The ΔT versus potential pulse widths.
8. Long-term cycling stability of the WO$_3$ electrode

Figure S8a delivers a high volumetric capacitance of 419.2 F cm$^{-3}$. An increase tendency in the early electrochemical testing, indicating that electrode will undergo an activation process (Figure S8b-c). There is hardly capacity decay and shape change after 15520 cycles, suggesting that excellent cycling performance and structural reversibility. As gradually increasing from 1 to 16 A cm$^{-3}$, the electrode acquired an average volumetric capacitance from 437.5 to 39.1 F cm$^{-3}$ (Figure S8d). When reset back to 1 A cm$^{-3}$, the volumetric capacitance can nearly the original level, which indicating excellent rate-performance.

Figure S8. Long-term cycling stability of the WO$_3$ electrode. (a) Volumetric capacitance at various scan rates. (b) CV curves. (c) Volumetric capacitance versus cycle number. (d) Volumetric capacitance at various current densities.
9. Typical charging/discharging process of the WO$_3$ electrode

Typical charging/discharging process of the WO$_3$ electrode in Zn$^{2+}$ electrolyte was shown in Figure S9. Specifically, according to the reaction kinetics, three nonlinear charging/discharging regions was observed, which attributed to surface capacitive storage of the absorption/desorption, redox reaction and bulk storage/release of the diffusion controlled.

**Figure S9.** Typical charging/discharging process of the WO$_3$ electrode.
10. Overview of the charge storage/release contribution and electrochromic behavior

**Figure S10.** Overview of the charge storage/release contribution and electrochromic behavior.
11. Typical charging process of the half-cell Zn-ion supercapacitor

**Figure S11.** Typical charging process of the half-cell Zn-ion supercapacitor.
12. Electrochemical impedance spectroscopy behaviors of the WO$_3$ electrode

The electrochemical behavior of the WO$_3$ electrode was further estimated by using electrochemical impedance spectroscopy (EIS) at the fixed potential of -0.2 V (the colored state) with a perturbation of 10 mV from $10^{-2}$ to $10^5$ Hz (Figure S12). After 1000 and 15520 CV cycles, exhibiting a low equivalent series resistance about 25.7 Ω, computed according to the intersection on the real axis of the Nyquist plots, suggesting that the fast Zn$^{2+}$ kinetic response during electrochemical process.

![Figure S12.](image)

Figure S12. The EIS curves of the WO$_3$ electrode range from $10^{-2}$ to $10^5$ Hz. (a-b) After 1000 and 15520 cycles at 50mV s$^{-1}$. 


Electrochemical behaviors and electrochromic performance of the WO$_3$ electrode were shown (Figure S13). To make electrode work stably, the potential working window was studied (Figure S13a). The peak position shows a significant blue-shift in the coloring process, while unchanged in the bleaching process (Figure S13b). The \textit{in-situ} transmittance spectra were measured in various potential operating windows and different sweep rates (Figure S13). Evidently, as the potential operating window increasing from 0.5 to 0.8 V, the corresponding \textit{in-situ} $\Delta T$ increases from 42.2% to 63.7%, which attributed to two respects of the colored area deepens downward and bleached area extends upward. Meanwhile, Figure S13d shows transmittance almost completely reversible in the electrochemical process.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure_s13.png}
\caption{Electro-chemical-chromic performance of the WO$_3$ electrode. (a) CV curves. (b) The transmittance spectra at the bleached and colored states. (c-d) \textit{In-situ} transmittance spectra. (e-h) CV curves and transmittance spectra at various scan rates.}
\end{figure}
14. Volumetric capacitance and \textit{in-situ} spectrum evolution of the WO$_3$ electrode

Volumetric capacitance and \textit{in-situ} transmittance spectrum evolution of the WO$_3$ electrode was obtained at various current densities (Figure S14). The optical modulation amplitude ($\Delta T$) was transformed from 18 to 63\%, and the corresponding volumetric capacitance converted from 39.1 to 437.5 F cm$^{-3}$.

\textbf{Figure S14.} Volumetric capacitance and \textit{in-situ} spectrum evolution of the WO$_3$ electrode. (a) GCD curve and corresponding transmittance spectrum. (b) Volumetric capacitance and optical modulation at various current densities.
15. The three types of adsorption sites of $\text{Zn}_x\text{WO}_3$ system

Figure S15. The three types of adsorption sites of $\text{Zn}_x\text{WO}_3$ system. (a-c) Hollow, bridge and top sites, respectively. The green, yellow, and red balls indicate W, O, and Zn atoms, respectively.
16. Top-view of the (2 0 0) plane after adsorb Zn atom at the hollow site

Figure S16. Top-view of the (2 0 0) plane after adsorb Zn atom at the hollow site.

The isosurface value is 0.0025.
17. Charge density difference of the (2 0 0) plane on the hollow site

**Figure S17.** Charge density difference of the (2 0 0) plane on the hollow site. The isosurface value is 0.0025.
18. Charge density difference of the (2 0 0) plane on the bridge site

Figure S18. Charge density difference of the (2 0 0) plane on the bridge site. The isosurface value is 0.0025.
Figure S19. Partial density of states (PDOS) of Zn\textsubscript{x}WO\textsubscript{3}.
20. Surface migration behaviors of Zn atoms

Figure S20. Surface migration behaviors of Zn atoms.
21. Migration behaviors of Zn atoms from surface to bulk

**Figure S21.** Migration behaviors of Zn atoms from surface to bulk.
22. Bulk migration behaviors of Zn atoms

Figure S22. Bulk migration behaviors of Zn atoms.
23. Summary of focusing strategies and associated parameters of the EAZS

Figure 23. Summary of focusing strategies and associated parameters of the EAZS.
24. Volumetric capacitance and cycling durability of the EAZS as a function of various temperatures

**Figure S24.** (a) Volumetric capacitance of the EAZS as a function of various temperatures under 1 A cm$^{-3}$. (b) Cycling durability at room temperature and high-temperatures.
25. Detailed information of deposition parameters of the WO$_3$ electrode

**Table S1.** Detailed information of deposition parameters of the WO$_3$ electrode

<table>
<thead>
<tr>
<th>Power/W</th>
<th>Time/s</th>
<th>Target</th>
<th>Method</th>
<th>Pressure/Pa</th>
<th>Ar/sccm</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>1500</td>
<td>WO$_3$</td>
<td>DCMS</td>
<td>2.6</td>
<td>$3 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

DCMS: Direct current magnetron sputtering. Ar: argon. sccm: standard cubic centimeter per minute.
26. The adsorption energy of Zn adsorbed on WO₃ surfaces

As shown in Table S2, the adsorption energy (E_{ads}) of the (2 0 0) plane is larger than the (0 2 0) and (0 0 2) planes. The E_{ads} of the hollow site (-5.823 eV) is obviously higher than other sites (-4.698 and -4.934 eV for the top and bridge site, respectively), indicating that Zn is more inclined to adsorb on the hollow site on the (2 0 0) plane.

**Table S2.** The E_{ads} of Zn adsorbed on WO₃ (2 0 0), (0 2 0) and (0 0 2) planes

<table>
<thead>
<tr>
<th>Adsorption planes</th>
<th>Adsorption energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Top site</td>
</tr>
<tr>
<td>(2 0 0)</td>
<td>-4.698</td>
</tr>
<tr>
<td>(0 2 0)</td>
<td>-4.747</td>
</tr>
<tr>
<td>(0 0 2)</td>
<td>-3.789</td>
</tr>
</tbody>
</table>
**27. The Bader charge from WO$_3$ (2 0 0) plane to Zn atom**

**Table S3.** Bader charges of the WO$_3$ (2 0 0) plane in the hollow and bridge sites

<table>
<thead>
<tr>
<th>Species</th>
<th>Zn</th>
<th>O</th>
<th>W</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hollow</td>
<td>-1.3537</td>
<td>+ 0.9389</td>
<td>-2.9388</td>
</tr>
<tr>
<td>Bridge</td>
<td>-1.2287</td>
<td>+ 0.9933</td>
<td>-2.9855</td>
</tr>
</tbody>
</table>
28. The performances comparison of recent among electrochromic energy storage electrodes/devices

Table S4. The performances comparison of recent among electrochromic energy storage electrodes/devices

<table>
<thead>
<tr>
<th>Electrodes or devices</th>
<th>Electrolytes</th>
<th>$A_{C}$ (mF cm$^{-2}$)</th>
<th>Retention/% (cycle life)</th>
<th>Voltage /V</th>
<th>ΔT/% (550nm)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiO</td>
<td>KOH</td>
<td>74.8</td>
<td>100 (5000)</td>
<td>-0.2-0.6</td>
<td>40.0</td>
<td>13</td>
</tr>
<tr>
<td>AgNWs/NiO</td>
<td>PVA/KOH</td>
<td>3.5</td>
<td>80.7 (10000)</td>
<td>0-1.0</td>
<td>--</td>
<td>7</td>
</tr>
<tr>
<td>WO$_3$/NiO</td>
<td>LiClO$_4$/PC</td>
<td>--</td>
<td>96.4 (5000)</td>
<td>-1.5-2.0</td>
<td>56.2</td>
<td>14</td>
</tr>
<tr>
<td>WO$_3$</td>
<td>H$_2$SO$_4$</td>
<td>23.4</td>
<td>92.0 (3000)</td>
<td>-0.5-0.0</td>
<td>--</td>
<td>19</td>
</tr>
<tr>
<td>V$_2$O$_5$/MnO$_2$</td>
<td>LiClO$_4$/PC</td>
<td>13.7</td>
<td>93.6 (3000)</td>
<td>-1.0-1.5</td>
<td>26.0</td>
<td>8</td>
</tr>
<tr>
<td>WO$_3$/PB</td>
<td>LiClO$_4$/PC</td>
<td>2.6</td>
<td>82.5 (2500)</td>
<td>0-1.2</td>
<td>30.5</td>
<td>5</td>
</tr>
<tr>
<td>AgNWs/WO$_3$</td>
<td>H$_2$SO$_4$</td>
<td>13.6</td>
<td>72.6 (5000)</td>
<td>-0.5-0.2</td>
<td>38.5</td>
<td>9</td>
</tr>
<tr>
<td>Mo$_2$WO$_3$/MnO$_2$</td>
<td>LiClO$_4$/PC</td>
<td>19.1</td>
<td>93.8 (2000)</td>
<td>0-2.0</td>
<td>70.0</td>
<td>11</td>
</tr>
<tr>
<td>WO$_3$</td>
<td>LiClO$_4$/PC</td>
<td>14.9</td>
<td>84.5 (1000)</td>
<td>-1.0-1.0</td>
<td>50.9</td>
<td>16</td>
</tr>
<tr>
<td>WO$_3$</td>
<td>LiClO$_4$/PC</td>
<td>2.5</td>
<td>87.0 (1000)</td>
<td>-0.8-0.1</td>
<td>50.5</td>
<td>18</td>
</tr>
<tr>
<td>WO$_3$</td>
<td>Li/PC</td>
<td>21</td>
<td>65.0 (1000)</td>
<td>-1.5-1.5</td>
<td>50.6</td>
<td>17</td>
</tr>
<tr>
<td>PANI/GO</td>
<td>H$_2$SO$_4$</td>
<td>25.7</td>
<td>53.1 (1000)</td>
<td>-0.5-0.8</td>
<td>26.5</td>
<td>20</td>
</tr>
<tr>
<td>PICA/TiO$_2$</td>
<td>LiClO$_4$/PMMA</td>
<td>23.3</td>
<td>91.0 (5000)</td>
<td>-0.5-2.0</td>
<td>--</td>
<td>6</td>
</tr>
<tr>
<td>P5FIW/VO$_3$</td>
<td>H$_2$SO$_4$</td>
<td>34.1</td>
<td>93.0 (5000)</td>
<td>-0.5-1.3</td>
<td>--</td>
<td>10</td>
</tr>
<tr>
<td>PANI-NiO</td>
<td>pTSA</td>
<td>1.1</td>
<td>90.0 (7000)</td>
<td>-0.3-0.9</td>
<td>30.2</td>
<td>12</td>
</tr>
<tr>
<td>WO$_3$/MnO$_2$</td>
<td>Zn(ClO$_4$)$_2$/PC</td>
<td>19.5</td>
<td>95.9 (12000)</td>
<td>-0.8-0.8</td>
<td>72.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.5A cm$^{-3}$</td>
<td>at 1.5A cm$^{-3}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>10.7</td>
<td>111 (15520)</td>
<td>-0.8-0.8</td>
<td>72.5</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.4 at 50mV s$^{-1}$</td>
<td>at 50mV s$^{-1}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.4 at 8 A cm$^{-3}$</td>
<td>at 8A cm$^{-3}$</td>
<td>0-2.0</td>
<td>51.7</td>
<td></td>
</tr>
</tbody>
</table>

29. Comparison of current various electrochromic energy storage electrodes/devices

**Table S5.** Comparison of current various electrochromic energy storage electrodes/devices

<table>
<thead>
<tr>
<th>Materials</th>
<th>Electrolytes</th>
<th>Electrodes or devices</th>
<th>Retention/% (cycle life)</th>
<th>Voltage/ V</th>
<th>ΔT/% (550nm)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>W:TiO₂</td>
<td>ZnSO₄</td>
<td>W:TiO₂</td>
<td>91.1 (1000)</td>
<td>0-1.3</td>
<td>-</td>
<td>21</td>
</tr>
<tr>
<td>Zn foil</td>
<td></td>
<td>Device</td>
<td></td>
<td>0-1.3</td>
<td>66.0</td>
<td></td>
</tr>
<tr>
<td>Mo/Ti:WO₃</td>
<td>ZnSO₄</td>
<td>Mo/Ti:WO₃</td>
<td>-</td>
<td>0-1.2</td>
<td>-</td>
<td>22</td>
</tr>
<tr>
<td>Zn foil</td>
<td>WO₃</td>
<td>Device</td>
<td>69 (100)</td>
<td>0-1.2</td>
<td>59.0</td>
<td></td>
</tr>
<tr>
<td>Zn foil</td>
<td>ZnSO₄/AlCl₃</td>
<td>WO₃</td>
<td>-</td>
<td>0.1-1.2</td>
<td>-</td>
<td>23</td>
</tr>
<tr>
<td>Mo/Ti:WO₃</td>
<td>ZnSO₄/KCl</td>
<td></td>
<td>-</td>
<td>-1.6</td>
<td>51.1</td>
<td>24</td>
</tr>
<tr>
<td>W₁₇O₄₇</td>
<td>Zn(ClO₄)₂/PC</td>
<td>W₁₇O₄₇</td>
<td>74.3 (4000)</td>
<td>-0.8-0.7</td>
<td>-</td>
<td>25</td>
</tr>
<tr>
<td>ZnHCF</td>
<td></td>
<td>Device</td>
<td>68.1 (300)</td>
<td>-</td>
<td>62.5</td>
<td></td>
</tr>
<tr>
<td>TiO₂₄</td>
<td>LiClO₄/PC</td>
<td>TiO₂₄</td>
<td>95.6 (2000)</td>
<td>1.5-3.5</td>
<td>-</td>
<td>26</td>
</tr>
<tr>
<td>NiO</td>
<td></td>
<td>Device</td>
<td>-</td>
<td>-3.2-1.0</td>
<td>68.5</td>
<td></td>
</tr>
<tr>
<td>LMO@LNO</td>
<td>LiClO₄/PC</td>
<td>LMO@LNO</td>
<td>89.8 (1000)</td>
<td>0.2-1.5</td>
<td>30.0</td>
<td>27</td>
</tr>
<tr>
<td>WO₃</td>
<td></td>
<td>Device</td>
<td>83.5 (3000)</td>
<td>0.2-3</td>
<td>42.1</td>
<td></td>
</tr>
<tr>
<td>Mo:WO₃</td>
<td>LiClO₄/PC</td>
<td>Mo:WO₃</td>
<td>-</td>
<td>-1.0-0.0</td>
<td>63.7</td>
<td>11</td>
</tr>
<tr>
<td>MnO₂</td>
<td></td>
<td>Device</td>
<td>93.8 (2000)</td>
<td>0-2.0</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>WO₃</td>
<td>LiClO₄/PC</td>
<td>WO₃</td>
<td>98.5 (5000)</td>
<td>-1.0-0.7</td>
<td>-</td>
<td>28</td>
</tr>
<tr>
<td>NiO</td>
<td></td>
<td>Device</td>
<td>96.4 (5000)</td>
<td>-1.5-2.0</td>
<td>57.6</td>
<td></td>
</tr>
<tr>
<td>W₁₁O₃₉</td>
<td>AlCl₃</td>
<td>W₁₁O₃₉</td>
<td>-</td>
<td>-0.7-0.6</td>
<td>-</td>
<td>29</td>
</tr>
<tr>
<td>PANI</td>
<td></td>
<td>Device</td>
<td>95.9 (6000)</td>
<td>0-1.8</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>WO₃₅</td>
<td>Al(ClO₄)₃/PC</td>
<td>WO₃₅</td>
<td>94.5 (2000)</td>
<td>-1.0-0.7</td>
<td>-</td>
<td>30</td>
</tr>
<tr>
<td>ITO</td>
<td></td>
<td>Device</td>
<td>-</td>
<td>-4.0-1.0</td>
<td>63.2</td>
<td></td>
</tr>
<tr>
<td>WO₃</td>
<td>Zn(ClO₄)₂/PC</td>
<td>WO₃</td>
<td>95.9 (12000) at 1.5A cm⁻³</td>
<td>-0.8-0.8</td>
<td>72.5</td>
<td>This work</td>
</tr>
<tr>
<td>MnO₂</td>
<td></td>
<td>Device</td>
<td>111 (15520) at 50mV s⁻¹</td>
<td>72.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Device</td>
<td>93 (20000) at 8A cm⁻³</td>
<td>0-2.0</td>
<td>51.7</td>
<td></td>
</tr>
</tbody>
</table>

PC: Propylene carbonate. LMO@LNO: LiMn₂O₄@LiNbO₃. PB: Prussian blue.

30. **More details on the color changes of the WO$_3$ electrode.**

Detailed information about the color changes of the WO$_3$ electrode was shown separately in Video S1. The testing was implemented in the potential window of -0.8-0.8 V at scan rate of 50 mV s$^{-1}$.

31. **The red LED was powered by the ZEAS.**

Significantly, on the level of practical application, the ZEAS was employed to power a 1.5 V red light-emitting-diode (LED) and successfully lightened it for over 90s (Video S2).

32. **The green LED was powered by the ZEAS.**

Additionally, the ZEAS was employed to power a 2.5 V green-LED and successfully lightened it for over 45s (Video S3).

33. **More details on the color changes of the ZEAS.**

Detailed reversible coloring/bleaching process of the ZEAS was provided in Video S4. The testing was performed in the voltage window of -0.2-2.0 V at 50 mV s$^{-1}$. 
34. References