Supporting Information

A new design of electrochromic energy storage device with high capacity, long cycle lifetime and multicolor display

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1. Materials
Lithium perchlorate (LiClO₄, ACS reagent, ≥95.0 %), aluminum perchlorate (Al(ClO₄)₃, 98 %) and poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonmate)(PEDOT:PSS) were purchased from Sigma-Aldrich. Tungsten hexachloride (WCl₆, 99.5 %), ethanol (CH₃CH₂OH), acetic acid (CH₃COOH) and isopropanol (C₃H₇OH) were purchased from Sinopharm Chemical Reagent Co. Ltd.. Titanium isopropoxide (Ti(OC₃H₇)₄, 99 %), vanadium triisopropoxide oxide (VO(OC₃H₇)₃, 96 %), propylene carbonate (PC, 99.7 %) and aluminum foil (Al, 99.9 %) were purchased from Aladdin Shanghai Aladdin Biochemical Technology Co. Ltd.. All the reagents are of analytical grade and used as-received without further purification. ITO glasses were purchased from Foshan yuanjingmei Glass Co. Ltd..

2. Film synthesis
WO₃ films: In a typical synthesis⁵¹, 0.5 g WCl₆ was dissolved in 5 mL anhydrous ethanol. 200 μL PEDOT: PSS was added into the solution upon sonication for 5 min. As-obtained precursor solution was then spin coated on ITO glass at 2500 rpm (Laurell model WS-650MZ-23NPP-Lite). The resultant films were subjected to UV (PSD Pro Series Digital UV Ozone System; λₘₐₓ at 185 nm and 254 nm) irradiation for 5 min. As-obtained films were annealed in an oven (JMD-FB) in air at 110 °C for 1 hour.

Ti-doped V₂O₅ films: The Ti-doped V₂O₅ films were prepared by controlling the hydrolytic polycondensation of the vanadium triisopropoxide and titanium isopropoxide precursors. In a typical synthesis⁵², VO(OC₃H₇)₃ and Ti(OC₃H₇)₄ were dissolved in isopropanol separately, then 5 mL Ti(OC₃H₇)₄/isopropanol solution (0.14 M) was added into 10 mL VO(OC₃H₇)₃/isopropanol solution (0.14 M) upon continuous stirring. 300 μL acetic acid was added dropwise to tuning the hydrolytic condensation process. Within an hour, a clear and stable yellow solution can be obtained. 200 μL PEDOT: PSS were further added into the solution upon sonication. As-obtained precursor solution was then spin coated on ITO glass at 2500 rpm. As-obtained films were annealed in oven at 280 °C for 50 minutes.
3. Materials characterization

X-ray photoelectron spectroscopy (XPS) analyses were carried out on a Perkin-Elmer PHI-5300 ESCA system spectrometer with Al Ka radiation. The pass energy was 192 eV for the survey scan and 48 eV for the narrow scan. Powder X-ray diffraction (XRD) patterns were collected on a Rigaku D/Max 2200PC diffractometer with a graphite monochromator and Cu Kα radiation (λ= 0.15418 nm). The scanning electron microscopy (SEM, SU8010) images were collected to analyze the morphology and elemental distribution of the samples. Cross-sectional SEM images were performed on films deposited by above method about 400 nm and 600 nm of WO₃ and Ti-doped V₂O₅ films on a glass substrate.

4. Electrochemical and electrochromic measurements

All the electrochemical and electrochromic measurements of the WO₃ and Ti-doped V₂O₅ films were carried out on cary series UV-visible spectrophotometer (Cary 100, Agilent technologies) and electrochemical analyzer (CHI-660E; CH Instruments, Shanghai, China) in a three-electrode spectroelectrochemical cell, using the WO₃ film or Ti-doped V₂O₅ film as the working electrode, an Al foil working as the counter electrode and an Ag/AgCl working as the reference electrode, respectively. The galvanostatic charge/discharge (GCD) measurements were performed in a potential window to obtain the areal capacity of WO₃ and Ti-doped V₂O₅ cathode in a three-electrode cell with a piece of Al foil as the counter electrode and Ag/AgCl as the reference electrode, using the CHI-660E, in different electrolytes (1M LiClO₄/PC, 1M Al(ClO₄)₃/PC and mixed LiClO₄/Al(ClO₄)₃/PC, the proportion of Li⁺ and Al³⁺ in the hybrid electrolyte was adjusted to 80:20). The cycle stability were performed at a current density of 0.5 mA/cm² in the potential window of -1.5~1.0 V (vs Ag⁺/Ag) for WO₃ and -1.2~2.0 V (vs Ag⁺/Ag) for Ti-doped V₂O₅ in 1M LiClO₄/Al(ClO₄)₃/PC electrolyte. In-situ optical transmittance as a function of the applied potential were obtained in a quartz cell recorded by the UV-visible spectrophotometer. The applied potentials were -1 V and 1 V for WO₃, -1.5 V and 2 V for Ti-doped V₂O₅, respectively. And the measurements of the transmittance at specified wavelengths (780 nm for WO₃ and 400 nm for Ti-doped V₂O₅) in real time were performed by the UV-visible spectrophotometer. The transmittance of the ITO glass in the electrolyte was used as the baseline. The cyclic voltammetry (CV) testing of deposited WO₃ and Ti-doped V₂O₅ electrode was performed in a three-electrode cell with a piece of Al foil as counter electrode and Ag/AgCl as reference electrode, using the CHI-660E, in the electrolytes of 1M LiClO₄/PC electrolyte. The electrochemical cyclic voltammetry cycle stability was measured at 50 mV s⁻¹ in 1 M LiClO₄/PC electrolyte. Electrochemical impedance spectroscopy (EIS) was obtained by CHI-660E over a frequency range from 100 KHZ to 0.1 Hz, with an AC amplitude of 10 mV in 1 M LiClO₄/PC.
electrolyte.

The diffusion coefficients $D$ (cm$^2$/s) of Al$^{3+}$ and Li$^+$ in the WO$_3$ and Ti-doped V$_2$O$_5$ were calculated by Randles-Sevcik equation:

$I_p = k n^{3/2} A D^{1/2} C v^{1/2}$ (Equation S1)

where $I_p$ (A) is the peak current, $k$ is the Randles-Sevcik constant, $k= 2.69*10^5$, $n$ is the transferred electron number involved in the redox process, $A$ (cm$^2$) is the area of the electrode, $C$ (mol/cm$^3$) is the concentration of Al$^{3+}$ or Li$^+$ in the bulk solution, and $v$ (V s$^{-1}$) is the scan rate.

**Li-ion diffusion coefficients:**

$$D_{(WO_3)} = \left( \frac{I_p}{v^{1/2} \frac{1}{k n^{3/2} A C}} \right)^2 = \left( \frac{0.29 \times 1.269 \times 10^6 \times 1.32 \times 0.64 \times 1}{2.69 \times 10^5 \times 1.32 \times 1 \times 1} \right)^2 = 2.84 \times 10^{-14}$$

$$D_{(TiV_2O_5)} = \left( \frac{I_p}{v^{1/2} \frac{1}{k n^{3/2} A C}} \right)^2 = \left( \frac{0.24 \times 1.269 \times 10^6 \times 1.32 \times 1 \times 1}{2.69 \times 10^5 \times 1.32 \times 1 \times 1} \right)^2 = 7.96 \times 10^{-13}$$

**Al-ion diffusion coefficients:**

$$D_{(WO_3)} = \left( \frac{I_p}{v^{1/2} \frac{1}{k n^{3/2} A C}} \right)^2 = \left( \frac{0.11 \times 1.269 \times 10^6 \times 3.32 \times 0.49 \times 1}{2.69 \times 10^5 \times 3.32 \times 0.49 \times 1} \right)^2 = 2.72 \times 10^{-14}$$

$$D_{(TiV_2O_5)} = \left( \frac{I_p}{v^{1/2} \frac{1}{k n^{3/2} A C}} \right)^2 = \left( \frac{0.12 \times 1.269 \times 10^6 \times 3.32 \times 0.96 \times 1}{2.69 \times 10^5 \times 3.32 \times 0.96 \times 1} \right)^2 = 7.99 \times 10^{-15}$$

5. **Electrochromic energy storage device assembly**

Electrochromic energy storage device was assembled using two pieces of ITO glass (5*5 cm$^2$) with WO$_3$ and Ti-V$_2$O$_5$ deposited on them, respectively. The Al metal frame was used as the anode, and propylene carbonate (PC) containing LiClO$_4$(0.8 M)/Al(ClO$_4$)$_3$(0.2 M) were used as the electrolyte. First, the two ITO electrodes and the Al metal frame (in the middle of the two ITO electrodes) were assembled as a cell. Epoxy glue was used to seal three sides of the cell. The electrolyte was injected into the cell by a syringe through the unsealed side of the cell. Before injection, the empty cell and the electrolyte in a vial were purged with dry N$_2$ for 15 min to drive away ambient air. The assembled device had an active area of 20.25 cm$^2$. 
Figure S1. XRD patterns of as-prepared WO$_3$ and Ti-V$_2$O$_5$ films.

Figure S2. (a-c) SEM, cross-section SEM and the EDS elemental mappings results for the WO$_3$ film. (d-f) SEM, cross-section SEM and the EDS elemental mappings results for the Ti-V$_2$O$_5$ film.

Figure S3. Real-time transmittance spectra for the Ti-V$_2$O$_5$ film in pure Li-ion and Al-ion electrolyte monitored at 400 nm.

Figure S4. The ex-situ X-ray photoemission spectroscopy (XPS) spectra of the WO$_3$ film and the Ti-V$_2$O$_5$ film under different applied potentials. (a) The W 4f signals in the WO$_3$ film. (b) The V 2p signals in the Ti-V$_2$O$_5$ film. (c) The Ti 2p signals in the Ti-V$_2$O$_5$ film.
Figure S5. The first GCD profiles of the WO$_3$ and the Ti-V$_2$O$_5$ films in (a, b) single Li-ion electrolyte, (c, d) the mixed Li/Al-ion electrolyte and (e, f) Al-ion electrolyte at 0.5 mA/cm$^2$.

Figure S6. The cycle stability by monitoring the transmittance changes (a) at 780 nm for the WO$_3$ film and (b) 400 nm for the Ti-V$_2$O$_5$ film in the single Al-ion electrolyte.
Figure S7. Cyclic voltammograms of the Ti-V$_2$O$_5$ film in (a) Li/Al-ion electrolyte, (b) Li-ion electrolyte and (c) Al-ion electrolyte at various scan rates. Cyclic voltammograms of the WO$_3$ film in (e) Li/Al-ion electrolyte, (f) Li-ion electrolyte and (g) Al-ion electrolyte at various scan rates. (d, h) Anodic peak current of the Ti-V$_2$O$_5$ film and the WO$_3$ film obtained from the cyclic voltammograms in the Li/Al-ion electrolyte, Li-ion electrolyte and Al-ion electrolyte versus the square roots of the scan rates.

Figure S8. (a, b) Cross-section SEM images showing the thickness of the prepared thin WO$_3$ and Ti-V$_2$O$_5$ films. (c, d) Optical transmittance spectra of as-prepared WO$_3$ film and the Ti-V$_2$O$_5$ film. (e, f) The first GCD profiles of the WO$_3$ and the Ti-V$_2$O$_5$ films.
Figure S9. The electrochemical cyclic voltammetry curves of (a) Ti-V$_2$O$_5$ films with PEDOT:PSS, (b) Ti-V$_2$O$_5$ films without PEDOT:PSS, (c) WO$_3$ films with PEDOT:PSS, (d) WO$_3$ films without PEDOT:PSS, measured at 50 mV s$^{-1}$ in 1 M LiClO$_4$/PC electrolyte.

Figure S10. The SEM images of (a) WO$_3$ films with PEDOT:PSS, (b) WO$_3$ films without PEDOT:PSS, (c) Ti-V$_2$O$_5$ films with PEDOT:PSS, (d) Ti-V$_2$O$_5$ films without PEDOT:PSS, after 200 continuous cyclic voltammetry cycles.

Figure S11. The electrochemical impedance spectroscopy of (a) WO$_3$ films with PEDOT:PSS and WO$_3$ films without PEDOT:PSS, (b) Ti-V$_2$O$_5$ films with PEDOT:PSS and Ti-V$_2$O$_5$ films without PEDOT:PSS, measured in 1 M LiClO$_4$/PC electrolyte.
Figure S12. Color changes in photos at different times. (a) WO$_3$: transparent to blue, wait 20 seconds for the next photo, (b) Ti-V$_2$O$_5$: yellow to red, wait 15 seconds for the next photo.

Figure S13. The cycle stability by monitoring the transmittance changes (a, c) at 400 nm and (b, d) at 780 nm for as-assembled EES device. (a, b) With PEDOT:PSS for 500 cycles. (c, d) Without PEDOT:PSS for 200 cycles.
Figure S14. The yellow Ti-V$_2$O$_5$ film of the device can light an LED bulb (1.8 V, 0.04W) for 8.5 min.

Figure S15. The EES device can be used in the storage of green energy, such as energy harvested from solar and wind, and the energy stored can be reused in urban life to reduce the energy demands.

Table S1. Comparison of Current State-of-the-Art Electrochromic Films and Devices

<table>
<thead>
<tr>
<th>Electrode materials</th>
<th>Electrolyte</th>
<th>Capacity</th>
<th>OCP(V)</th>
<th>Stability of charge capacity</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al/WO$_3$/Ti-V$_2$O$_5$</td>
<td>LiClO$_4$:Al(ClO$_4$)$_3$:PC</td>
<td>933 mAh/m$^2$ in all-</td>
<td>Al-N: 3.492</td>
<td>WO$_3$ film: 1000 cycles (72% capacity retention)</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Al-W: 302 mAh/m$^2$</td>
<td>Al-W: 2.588</td>
<td>Ti-V$_2$O$_5$ film: 1000 cycles (78% capacity retention)</td>
<td></td>
</tr>
<tr>
<td>PLAP-WO$_3$, nanowire</td>
<td>LiClO$_4$/PC</td>
<td>91 mAh/m$^2$ (0.132 Wh m$^2$)</td>
<td>2.59</td>
<td>1000 cycles (75% capacity retention)</td>
<td>S3</td>
</tr>
<tr>
<td>Zn-amorphous WO$_3$, (~450 nm)</td>
<td>Zn$^{2+}$:AlCl$_3$ aqueous</td>
<td>126.3 mAh/m$^2$</td>
<td>1.15</td>
<td>2500 cycles (70% capacity retention)</td>
<td>S4</td>
</tr>
<tr>
<td>Zn-MTWO nanowire</td>
<td>ZnSO$_4$ aqueous</td>
<td>150 mAh/m$^2$</td>
<td>1.2</td>
<td>100 cycles (53% capacity retention)</td>
<td>S5</td>
</tr>
<tr>
<td>Zn-crystalline V$_2$O$_5$, (~220 nm)</td>
<td>Zn$^{2+}$:AlCl$_3$ aqueous</td>
<td>15.2 mWh/g</td>
<td>1.38</td>
<td>100 cycles (40% capacity retention)</td>
<td>S6</td>
</tr>
<tr>
<td>Al-W$<em>{18}$O$</em>{49}$, nanowire</td>
<td>AlCl$_3$ aqueous</td>
<td>429 mAh/g</td>
<td>1.2</td>
<td>3 cycles (capacity loss of 18%)</td>
<td>S7</td>
</tr>
<tr>
<td>Al-Pristine blue (~450 nm)</td>
<td>KCl aqueous</td>
<td>75 mAh/g</td>
<td>1.26</td>
<td>50 cycles (81% capacity retention)</td>
<td>S8</td>
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</table>

a: Al-W: The Al anode is connected to the WO$_3$; Al-V: The Al anode is connected to the Ti-V$_2$O$_5$; W-V: The WO$_3$ is connected to the Ti-V$_2$O$_5$

References


S5. Li, H., McRae, L., Firby, C. J., & Elezzabi, A. Y., Rechargeable aqueous electrochromic batteries utilizing Ti-substituted tungsten molybdenum oxide based Zn$^{2+}$ ion intercalation cathodes. *Advanced Materials* 2019, 31(15), 1807065.

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