Supporting Information

Rapid response and wide-band regulation of electrochromic device achieved by ultra-small V_2O_5 nanodots and Zn^{2+}/Li^+ electrolyte

Ling Wang,[a#] *Bin Wang,*[b.c#] *Haizeng Li*[b,c*] *Lixin Qiao*[d*]

[a] *College of Chemistry and Chemical Engineering, Dezhou University, Dezhou 253023, China.*

Email: WanglingZ90@126.com

[b-] *Optics and Thermal Radiation Research Center, Institute of Frontier & Interdisciplinary Science, Shandong University, Qingdao 266237, China*

Email: haizeng@sdu.edu.cn

[c] State Key Laboratory of Vanadium and Titanium Resources Comprehensive Utilization Pangang Group Research Institute Panzhihua 617000, China

[d] *Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao, 266101, China*

qiaolx@qibebt.ac.cn

Experimental Section

Materials: All the chemicals were of analytical grade and were used without further purification. Hydrogen peroxide solution (H_2O_2, 30%), zinc foil (Zn, 99.9%), vanadium oxide (V_2O_5, 99%), lithium perchlorate ($LiClO_4$, 98%), zinc perchlorate ($Zn(ClO_4)_2$, 98%), aluminum perchlorate ($Al(ClO_4)_3$, 98%), propylene carbonate (PC), ethanol were purchased from Macklin Biochemical Technology Co. Ltd. Poly(ethylene oxide) (PEO) was purchased from Aladdin Chemical Co. Ltd., and ITO glass was purchased from Zhuhai Kaivo Glass Co. Ltd. All experimental water used was deionized (DI) water (18.25 MΩ).

Synthesis of V_2O_5 nanodots: Firstly, 3.6 g of commercial V_2O_5 powder was added to 190 ml of DI water at room temperature, and the mixture was stirred for 2 hours to form a yellow suspension. Next, 10 ml of H_2O_2 was slowly added to the solution and continued stirring for 5 days until a homogeneous dark red colloid was obtained. A small amount of the colloid was taken for determination of solid content.

Fabrication of the electrodes via a spraying method: Before spraying, the precursor solution was diluted to 1 mg/mL with ethanol. Using a spray gun to spray the precursor solution onto the ITO conductive substrate, with the distance between the nozzle and the substrate being 10 cm, the nozzle diameter is 0.5 mm, and the spraying pressure is 0.1 MPa. During the spraying process, the conductive substrate was set on a heating plate at 120 °C. After spraying, the sample was further heated at 180°C for 8 hours to remove moisture.

Preparation of electrolytes with different cationic ions: Adding 0.1 M of $Zn(ClO_4)_2$ and 0.4 M of $LiClO_4$ in PC and stir until completely dissolved to obtain a Zn^{2+}/Li^+ electrolyte; Dissolve 0.5 M $Zn(ClO_4)_2$ in PC to obtain Zn^{2+} electrolyte. Dissolve 0.1 M $Zn(ClO_4)_2$ and 0.4 M $Al(ClO_4)_3$ in PC to obtain Zn^{2+}/Al^{3+} mixed electrolyte. The Zn^{2+}/TBA^+ electrolyte contains 0.1 M $Zn(ClO_4)_2$ and 0.4 M TBAB.

Assembly of electrochromic display: Firstly, 6 g of PEO was added to 60 mL of Zn^{2+}/Li^+ electrolyte to form a gel electrolyte. The V_2O_5-Zn-V_2O_5 electrochromic displays were constructed by sandwiching a thin Zn disconnected frame between two pieces of V_2O_5 electrodes. The PEO- Zn^{2+}/Li^+ gel was used as the electrolyte.

Characterization: The crystal structures and morphology of the samples were examined by X-ray diffraction (XRD, Rigaku D/Max 2500PC diffractometer with a graphite monochromator and Cu Kα radiation (λ= 0.15418 nm)), X-ray photoelectron spectroscopy (XPS) (PHI 5000 VersaProbe III), Field emission scanning electron microscopy (SEM) (Quanta 250 FEG), Transmission electron microscopy (TEM) (FEI Tecnai G2 F20), UV-Visible-Near IR Spectrophotometry (UH5700), and high-resolution transmission electron microscopy (HRTEM) (FEI Talos F200X G2). All electrochemical measurements were carried out using an electrochemical workstation (CHI-760E; CH Instruments, Shanghai, China) in a two-electrode configuration, using the V_2O_5 electrode as the working electrode and Zn foil as both the counter electrode and reference electrode. In-situ optical transmittance, as a function of the applied potential, was obtained in a quartz cuvette recorded by the UV-Visible-Near IR Spectrophotometer. The active thermal insulation of the device in two states was characterized by an infrared thermometer (TiX501, Fluke). ITO glass in the electrolyte was used as the baseline for measuring the transmittance curve of the electrodes, which means that all the optical transmittance spectra were measured by subtracting the transmission loss due to the substrate.

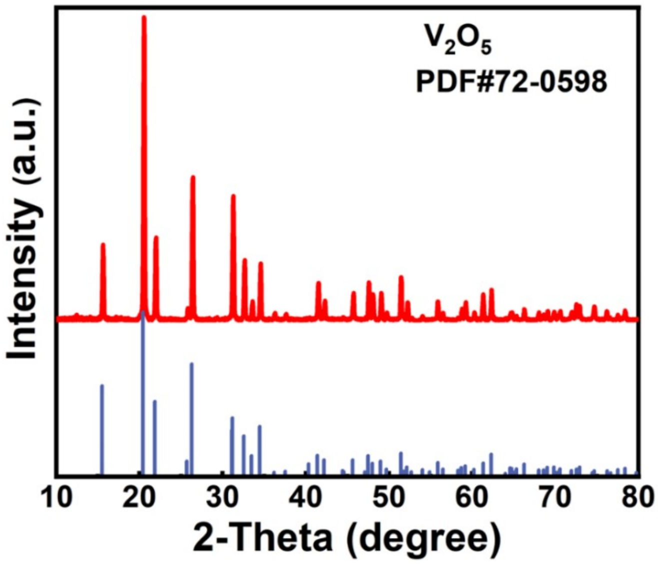

Figure S1. XRD pattern of the commercial V_2O_5 powder.

As shown in Figure S1, the commercial V_2O_5 powder diffraction peaks are perfectly indexed to the orthorhombic V_2O_5 phase (Joint Committee on Powder Diffraction Standards No. 72-0598). Compared to V_2O_5 nanodots, the XRD patterns of commercial V_2O_5 powder show sharper and clearer diffraction peaks.

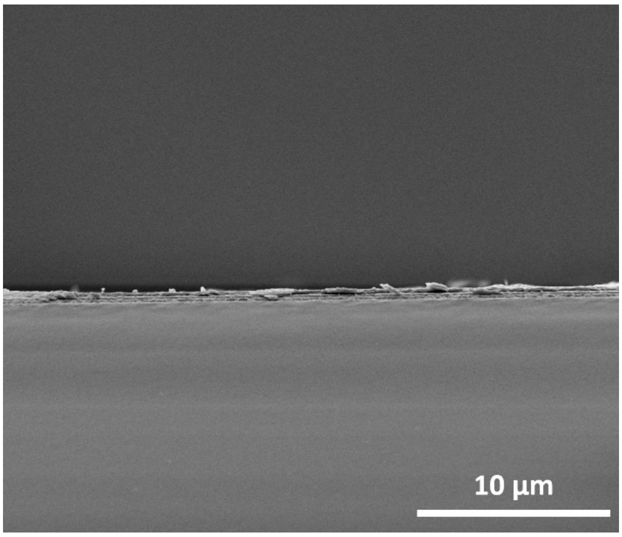

Figure S2. Cross-section SEM image of the V_2O_5 electrode.

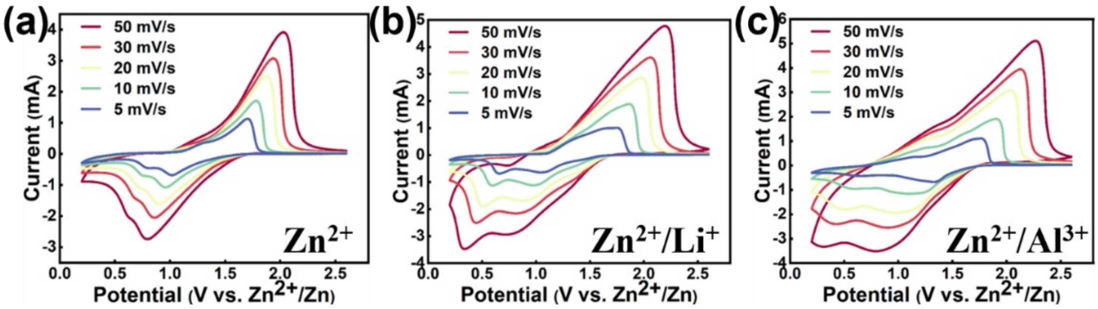

Figure S3. The cyclic voltammetry curve measured by the V_2O_5 electrodes in (a) Zn^{2+}, (b) Zn^{2+}/Li$^{+,}$ and (c) Zn^{2+}/Al^{3+} electrolyte ranging from 0.2 to 2.6 V at a scan rate of 5 mV/s to 50 mV/s.

Based on the function relationship between the scan rate and peak current density (Figure S3), the scan rate of active ions in the electrolyte can be calculated independently, and the mechanism of charge storage in the V_2O_5 electrode can be identified.

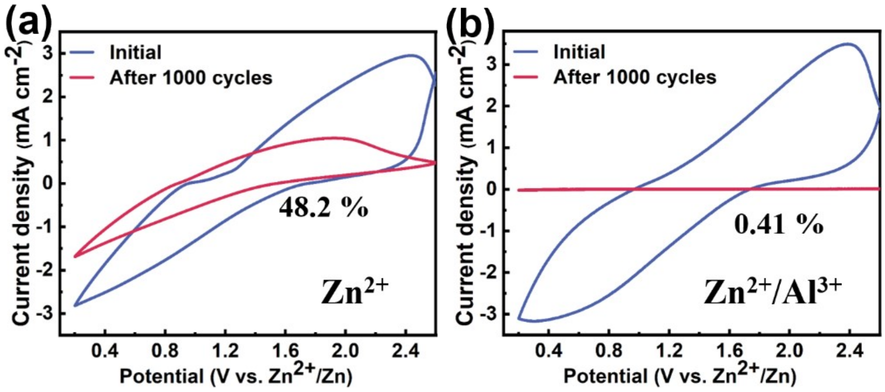

Figure S4. Cyclic voltammetry (CV) measurement of the V_2O_5 electrodes over 1000 cycles between 0.2 and 2.6 V in (a) Zn^{2+}, (b) Zn^{2+}/Al^{3+} electrolyte.

The electrochemical cyclic voltammetry cycle stability is measured at 100 mV s^{-1} between 0.2 and 2.6 V. As shown in Figure S4a, the V_2O_5 electrode in Zn^{2+} electrolyte retains 48.2 % capacity after 1000 cycles. In contrast, the V_2O_5 electrode in the Zn^{2+}/Al^{3+} electrolyte containing 0.41 % of the initial capacity after 1000 cycles.

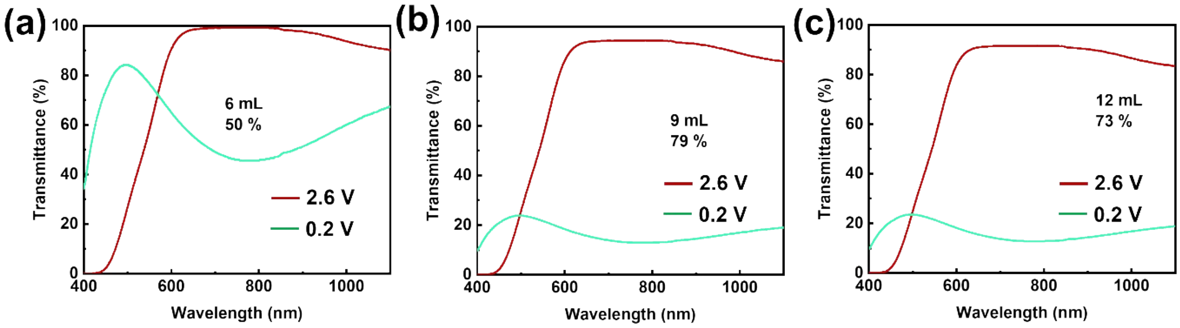

Figure S5. Optical transmittance spectra of the V_2O_5 electrode with different thicknesses (different spraying amounts) (a) 6 mL, (b) 9 mL, (c) 12 mL at different applied voltages.

Other than using the Zn^{2+}/Li^+ electrolyte, the thickness of the films was also tuned (to control the film thickness by spraying different amounts of precursor solution) to obtain better optical contrast. As shown in Figure S5, when the spraying amount is 6 mL, the optical contrast is 50%, and when the spraying amount is 9 mL, the optical contrast is 79%. However, when the spraying amount is 12 mL, the optical contrast is 73%, which slightly decreases because excessive thickness will reduce the transmittance of the faded state. Hence, the final spraying amount is determined to be 9 mL.

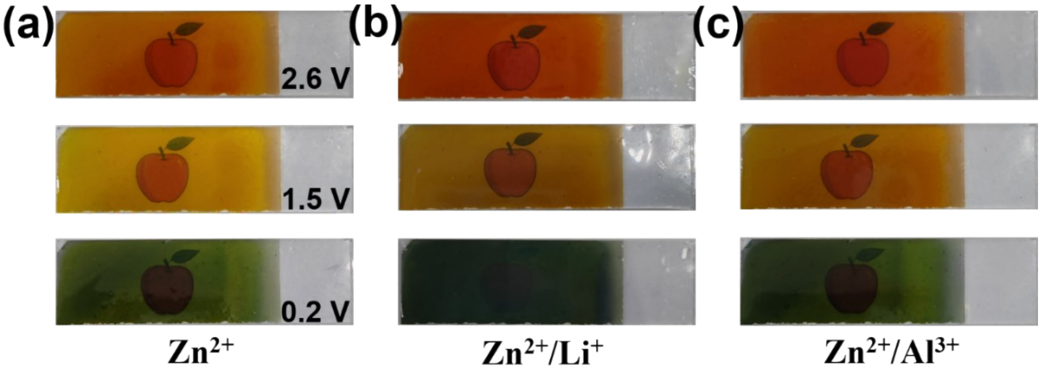

Figure S6. Digital photographs of V_2O_5 electrode in (a) Zn^{2+}, (b) Zn^{2+}/Li^+ and c) Zn^{2+}/Al^{3+} electrolytes at different applied voltages.

As shown in Figure S6, the V_2O_5 electrode expresses orange, yellow, and green at the voltage of 2.6 V, 1.5 V, and 0.1 V, respectively. Furthermore, the V_2O_5 electrolyte in Zn^{2+}/Li^+ electrolyte exhibits a more intense color, particularly in the colored state of the V_2O_5 electrode, which is opaque to the underlying cartoon pattern.

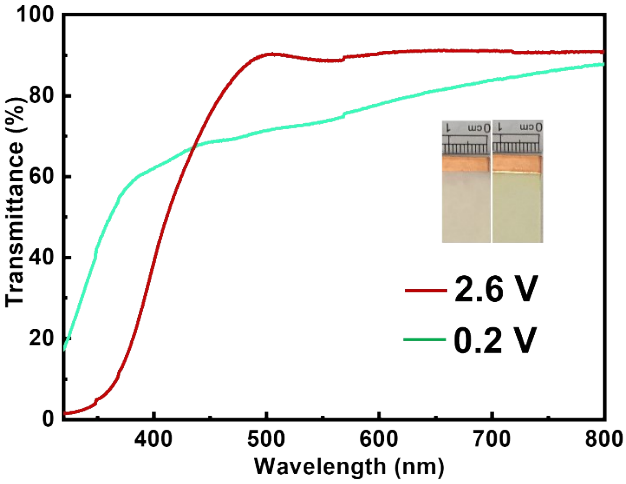

Figure S7. Optical transmittance spectra (inset: digital photographs) of the commercial V_2O_5 electrode at different applied voltages.

As shown in Figure S7, the commercial V_2O_5 electrode expresses light yellow and light brown at the voltage of 2.6 V and 0.2 V, respectively. Furthermore, it only achieves an optical contrast of 25 % at 500 nm.

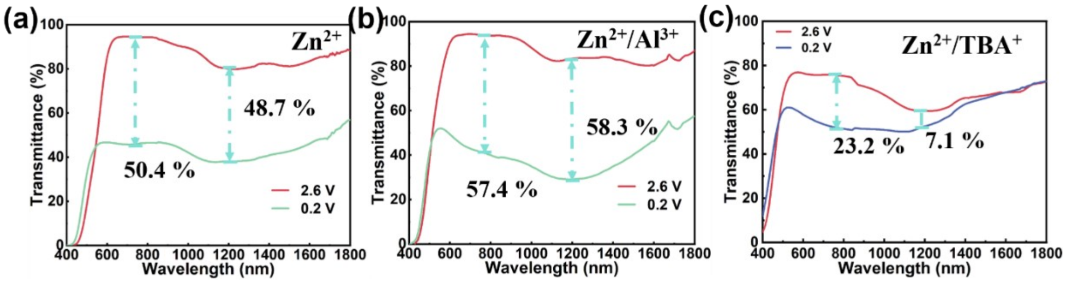

Figure S8. Optical transmittance spectra of the V_2O_5 electrode in (a) Zn^{2+} electrolyte, (b) Zn^{2+}/Al^{3+} and (c) Zn^{2+}/TBA^{+} at different applied voltages.

The small size of Al^{3+} enables the electrode to exhibit significant optical contrast (57.4 % at 728 nm, 58.3 % at 1200 nm) in the Zn^{2+}/Al^{3+}electrolyte compared with Zn^{2+} electrolyte (50.4 % at 728 nm, 48.7 % at 1200 nm) (Figure S8). However, electrostatic interactions also restrict the incorporation of Al^{3+} into the V_2O_5 electrode. Hence, the tuning range of the V_2O_5 electrode in the Zn^{2+}/Al^{3+} electrolyte is narrower compared to that in the Zn^{2+}/Li^{+} electrolyte. Meanwhile, the poor electrochromic performance of the V_2O_5 electrode in the Zn^{2+}/TBA^{+} electrolyte indicates that the discoloration of the electrode is caused by the insertion of active ions.

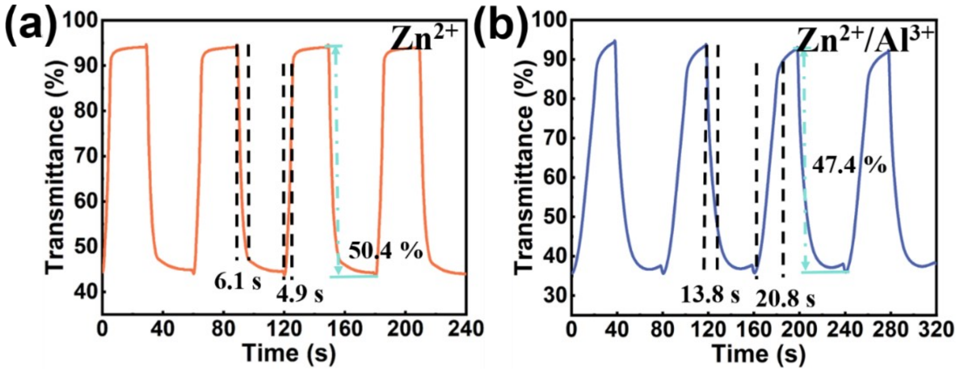

Figure S9. The real-time transmittance spectra of the V_2O_5 electrode at 728 nm in the (a) Zn^{2+} electrolyte and (b) Zn^{2+}/Al^{3+} electrolyte.

Although the switching times of the V_2O_5 electrode in pure Zn^{2+} electrolyte (Figure S9a) are the fastest among the three electrolytes, the V_2O_5 electrode in the Zn^{2+}/Li^+ electrolyte shows higher optical contrast (~79 % at 728 nm) in comparison to the V_2O_5 electrode in the pure Zn^{2+} electrolyte (~50.4 % at 728 nm). This indicates that the Zn^{2+}/Li^+ electrolyte endows rapid switching speed. The aforementioned results affirm that Zn^{2+}/Li^+ electrolyte is a promising candidate for building high-performance Zn-V_2O_5 electrochromic displays.

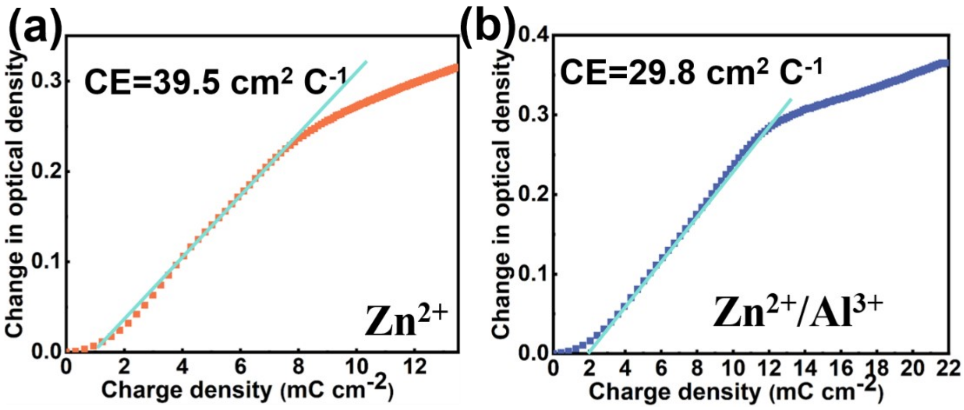

Figure S10. Coloration efficiency (CE) of the V_2O_5 electrode in the (a) pure Zn^{2+} electrolyte and the (b) Zn^{2+}/Al^{3+} electrolyte.

The coloration efficiency (CE) is closely related to ΔT and current density, with CE defined as the change in optical density (ΔOD) relative to the unit charge density (ΔQ) as observed during the coloring process[1]. As displayed in Figure S10, the CEs of the V_2O_5 electrode in the pure Zn^{2+} electrolyte and the Zn^{2+}/Al^{3+} electrolyte are 39.5 cm^2 C^{-1} and 29.8 cm^2 C^{-1}, respectively.

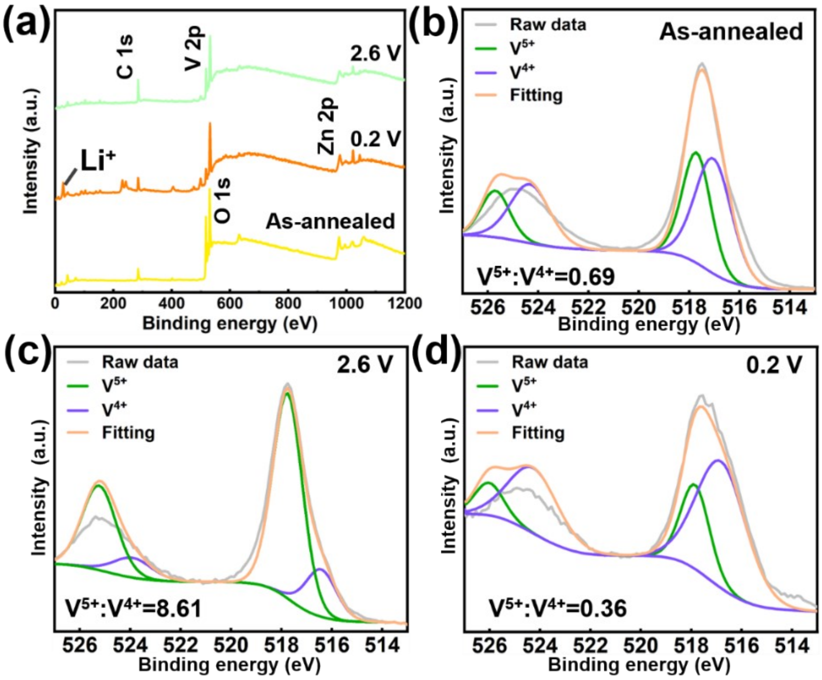

Figure S11. The *ex-situ* XPS survey spectra of the V_2O_5 electrode in Zn^{2+}/Li^+ electrolyte after being discharged/charged: (a) Full survey and (b) V 2p.

As shown in Figure S11a, the as-prepared V_2O_5 electrode contains V, and O elements (excluding C). Figure S11b-d depicts the high-resolution V 2p core-level XPS spectra of the V_2O_5 electrode under different color states, indicating that the electrochromic properties of the V_2O_5 electrode are achieved by the chemical valence change of V at different voltages. The most intense doublet peaks, observed at 517.7 and 525.4 eV, are assigned to the V^{5+}[2], whereas the two peaks centered at 516.7 and 524.21 eV correspond to the V^{4+}. As shown in the XPS V 2p spectra of the as-annealed V_2O_5 electrode, the ratio of V^{5+}/V^{4+} is 0.69 (Figure S11b), indicating that this electrode is not fully oxidized. After being charged at 2.6 V, the ratio of V^{5+}/V^{4+} is 8.61 (Figure S11c), meaning that an electrochemical process is further oxidizing the V_2O_5 electrode. When the V_2O_5 electrode is changed from a charged state (2.6 V charged) to a discharged state (0.2 V discharged), the V^{5+}/V^{4+} ratio increases from 8.61 to 0.36, which confirms that Zn^{2+}/Li^+ intercalation results in a reduction of the V_2O_5 electrode.

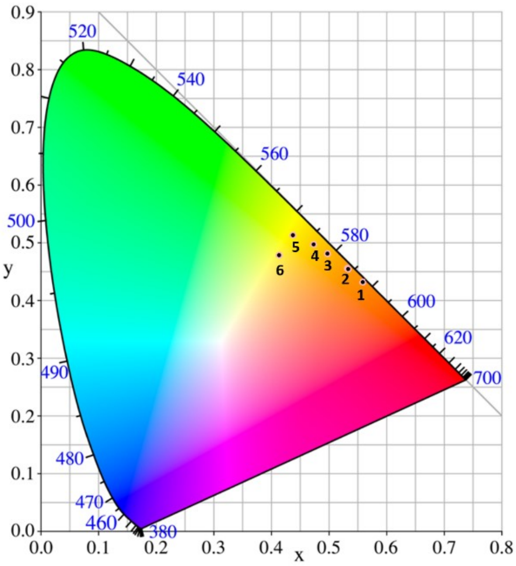

Figure S12. 2D CIE color coordinates of the V_2O_5-Zn-V_2O_5 electrochromic display prototype.

The 2D CIE color space tunability of the zinc-anode-based electrochromic displays are demonstrated in transmissive modes (Figure S12). Since the two electrochromic electrodes can be operated independently, while the V_2O_5 electrode induces reversible color switching of the display as numbered: 1 ⇄ 2 ⇄ 3 ⇄ 4⇄ 5 ⇄ 6 ⇄ 1.

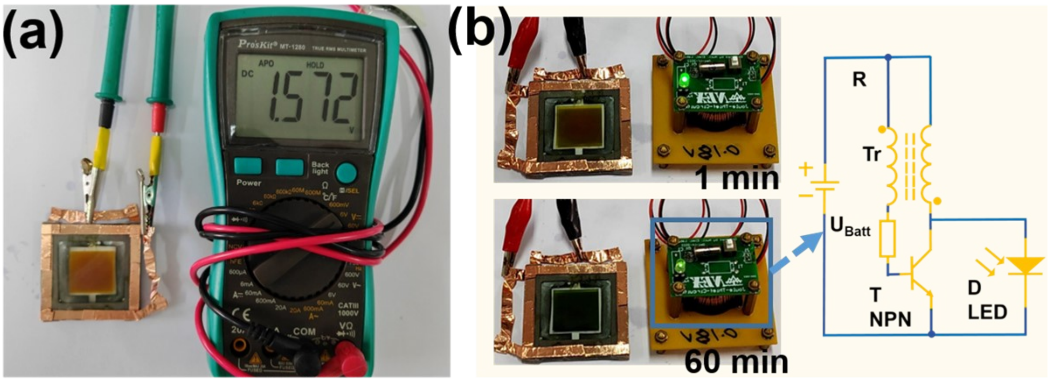

Figure S13. (a) A digital photograph depicting the display with an OCP of 1.57 V. (b) Digital photograph of a 0.18 V regulated LED powered by the V_2O_5-Zn-V_2O_5 electrochromic display at 1 and 60 min, connected via the “Joule thief circuit”.

As shown in Figure S13a, the V_2O_5-Zn-V_2O_5 electrochromic display delivers an open-circuit potential (OCP) of 1.57 V. This OCP can light up an LED through the “Joule thief circuit”, alongside a spontaneous coloration process of the device (Figure S13b).

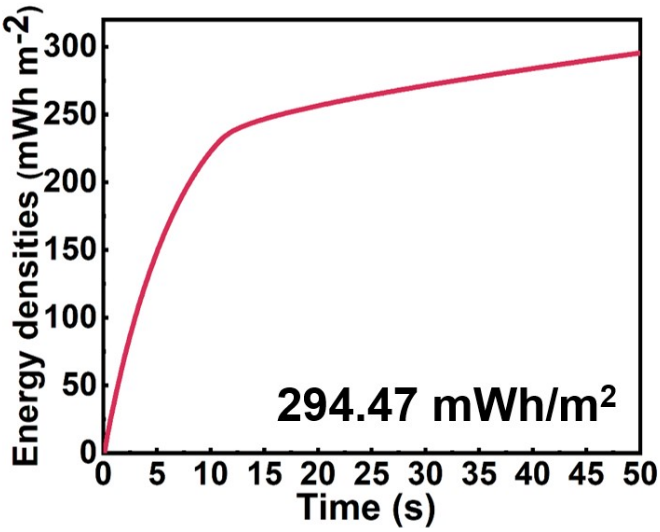

Figure S14. Energy density characteristics of the V_2O_5-Zn-V_2O_5 electrochromic display as determined by applying a voltage of 2.6 V for 50s.

To permit the calculation of the input energy density of the V_2O_5-Zn-V_2O_5 electrochromic display, a voltage of 2.6 V is applied for 50s. As shown in Figure S14, the energy density profile indicates that the bleaching process of the V_2O_5-Zn-V_2O_5 electrochromic display requires 294.47 mWh/m^2.

Table S1. Comparison of properties with previously reported V_2O_5-based electrochromic materials.

Electrode materials	Electrolyte	Optical contrast (%)	Switching times ^{a}（s）	Coloration efficiency（cm^2 C^{-1}）	Cycling stability ^{b}	Ref.
V_2O_5 nanodots	Zn^{2+}/Li^+	79 (728nm) 61 (1200)	t_c=12.0, t_b=14.6	35.6	1000 cycles-96.7%	This work
KVO ^{c}	Zn^{2+}	25.3(521 nm)	t_c=12.9, t_b=16.9	62.08	1000 cycles-89%	[3]
SVO	Zn^{2+}	/	t_c=23.4, t_b=28.9	44.58	1000 cycles-2.06%	[3]
V_2O_5 film	Li^+	48 (460 nm) 40 (890 nm) 48 (1100nm)	t_c=12, t_b=18	29.6	/	[10]
V_2O_5 nanobelts	Li^+	41.6 (490 nm)	t_c=1.4, t_b=4.2	83.3	1000 cycles- 94%	[14a]
V_2O_5	Li^+	38.7 (550 nm)	t_c=5, t_b=4	14.05	/	[14b]
V_3O_7 nanoparticles	Zn^{2+}	21 (632.8 nm)	t_c=10.4, t_b=28.6	20.6	/	[21]
Ti-V_2O_5^{d}	Li^+/Al^{3+}	35.3 (400 nm)	t_c=2.4, t_b=3.8	/	1000 cycles-69.5%	[23]
V_2O_5@C microrods	Li^+	54.6 (680 nm)	t_c=1.1, t_b=1.0	109	2000 cycles-96%	[28]
V_2O_5 nanobelts	Li^+	45 (422 nm) 35.2 (1000 nm)	t_c=1.1, t_b=3.5	97.1	3000 cycles -86%	[30]
LaSVO ^{e}	Zn^{2+}/Na^+	/	t_c=4.5, t_b=8.8	70.74	1000 cycles-68.1%	[35]
VR/GO^f	Li^+	40.92 (415 nm)	t_c=1.4, t_b=2.5	/	500 cycles-94.9%	[36b]

a: Switching time: t_c and t_b are the coloration time and bleaching time, respectively.

b: Cycling stability: Initial optical contrast retention rate.

c: KVO: $K_2V_6O_{16}$·1.5H_2O.

d: Ti-V_2O_5: Ti doped V_2O_5.

e: LaSVO: La^{3+}/Na^+ bimetallically doped vanadate.

f: VR/GO: V_2O_5 nanorod /graphene oxide nanocomposite films.

References

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[2] W. Zhang, H. Li, M. Al-Hussein, A. Y. Elezzabi, *Adv. Opt. Mater.* 8 (2019) 1901224.