Eectronic Supplementary Material (ESI) for Chemical Communications.

Interlayer spacing expansion for V_2O_5 towards ultra-stable zinc anode-based flexible electrochromic displays in

Zn^{2+}/Li^+-PC organic electrolyte

Experimental section

Materials

All chemicals were of analytical grade and were used without further purification. Zinc foil (Zn, 99.9%), zinc perchlorate hexahydrate (Zn(ClO$_4$)$_2$·6H$_2$O, reagent grade), propylene carbonate (PC), vanadate oxide (V$_2$O$_5$, 99%) and polymethyl methacrylate (PMMA, Mw~35,000) were purchased from Macklin Biochemical Technology Co. Ltd. Lithium perchlorate (LiClO$_4$, ≥99.0%) were purchased from Sinopharm Chemical Reagent Co. Ltd. ITO glasses were purchased from Zhuhai Kaivo Glass Co. Ltd. Flexible PET-ITO conductive films were purchased from South China Science & Technology Co. Ltd. 3 M transparent double-sided tapes (VHB, 3 m ×10 mm × 1.0 mm) were purchased from 3 M China Co. Ltd.

Synthesis of PEDOT@V$_2$O$_5$ nanofibers

First, add 7 g of commercial V$_2$O$_5$ to 200 mL of deionized water and stir for 30 minutes. Next, add x mL of EDOT to the liquid and stir for 5 days to turn it from yellow to dark green. Then, centrifuge the dark green solution twice with deionized water and ethanol, respectively, and dry overnight at 70 °C to obtain PEDOT@V$_2$O$_5$ powders. Repeat the above steps for commercial V$_2$O$_5$ without adding EDOT to obtain bare V$_2$O$_5$ as control samples. The amount of EDOT were varied as 1 mL, 3 mL and 5 mL, respectively, and the resulted samples were marked as 1-PEDOT@V$_2$O$_5$, 3-PEDOT@V$_2$O$_5$ and 5-PEDOT@V$_2$O$_5$.

Fabrication of PEDOT@V$_2$O$_5$ electrodes

Add 15 mg of dried powder into 40 ml of deionized water and sonicate for at least 1 hour to disperse evenly. Treat the ITO glass with a plasma cleaning machine for 60 seconds, spray all the suspension onto the ITO glass with an effective area of 4 cm × 5 cm on a 150 °C heating plate, and then continue annealing at this temperature for 20 hours.

Assembly of Zn-PEDOT@V$_2$O$_5$ flexible electrochromic displays

The PMMA-based gel electrolyte was prepared by gradually adding 10 g of PMMA powder into 40 mL of the hybrid PC solution comprising 0.1 M Zn(ClO$_4$)$_2$ and 0.8 M LiClO$_4$. Spray a pineapple-shaped PEDOT@V$_2$O$_5$ film on a 5 cm x 8 cm PET-ITO conductive film to obtain the cathode, paste the zinc foil frame onto another PET-ITO conductive film to obtain the anode, and the PMMA-based gel electrolyte is used as an electrolyte to assemble a flexible electrochromic display as shown in **Fig. 5a** (Electrolyte not marked).

Characterization

The crystal structures, morphology and chemical structures of the samples were examined by X-ray diffraction (XRD, Rigaku D/Max 2200/PC 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 microscope (FESEM, FEI Quanta 250 FEG) and high-resolution transmission electron microscope (HRTEM, JEM-F200(HRP)). The interlayer spacing was calculated according to equation S1.

$$2d \sin\theta = n\lambda \qquad \qquad \textbf{(S1)}$$

where d is the crystal plane spacing, θ is the angle between the incident X-rays and the corresponding crystal plane, λ is the wavelength of the X-rays, and n is the number of diffraction stages.

Electrochemical and optical measurements

All electrochemical measurements were carried out using an electrochemical workstation (CHI-760E, CH Instruments, Shanghai, China) in a two-electrode configuration, using the electrochromic electrode as the working electrode, a zinc foil as the counter electrode and reference electrode. All optical measurements were performed using a UV–visible–NIR Spectrophotometer (UH5700). In situ optical transmittance as a function of the applied potential was obtained in a quartz cuvette recorded by the UV–visible–NIR Spectrophotometer. Add electrolyte to a quartz cuvette and immerse an ITO glass in it as a baseline to measure the performance of the electrode. However, in the dissolution experiment shown in **Fig. 3**, the transmittance was measured using air as the baseline. In this work, two types of solutions were used as electrolytes: the hybrid organic solution comprised of 0.1 M $Zn(ClO_4)_2$ and 0.8 M $LiClO_4$ (marked as Zn^{2+}/Li^+-PC), and hybrid aqueous solution comprised of 0.1 M $Zn(ClO_4)_2$ and 0.8 M $LiClO_4$ (marked as Zn^{2+}/Li^+-H_2O).
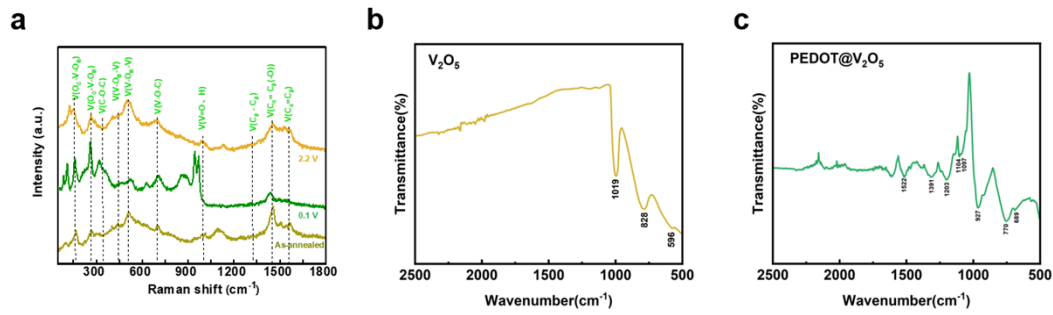
Fig. S1 a Raman spectra of PEDOT@V$_2$O$_5$ at different states. As-prepared, discharged to 0.1 V and charged to 2.2 V. **b** FTIR spectra of commercial V$_2$O$_5$. **c** FTIR spectra of PEDOT@V$_2$O$_5$.

The chemical structure of PEDOT@V$_2$O$_5$ was evaluated by Raman spectroscopy (Fig. S1a). The peak at 101 cm^{-1} is attributed to the external Ty mode. The peak at 165 cm^{-1} arises from the bending vibrations of the skeleton. Peaks at 178 and 264 cm^{-1} correspond to bending vibrations of the OC-V-OB bond. Peaks at 305, 406, 531, and 704 cm^{-1} are related to C-O-C bond bending, V-OB-V bond bending, V-OB-V bond stretching, and V-O-C bond stretching vibrations, respectively. The V=O bond at 986 cm^{-1} is crucial for understanding the layered structure of the V$_2$O$_5$ electrode[1], which connects with oxygen atoms and contributes to electrode stability.
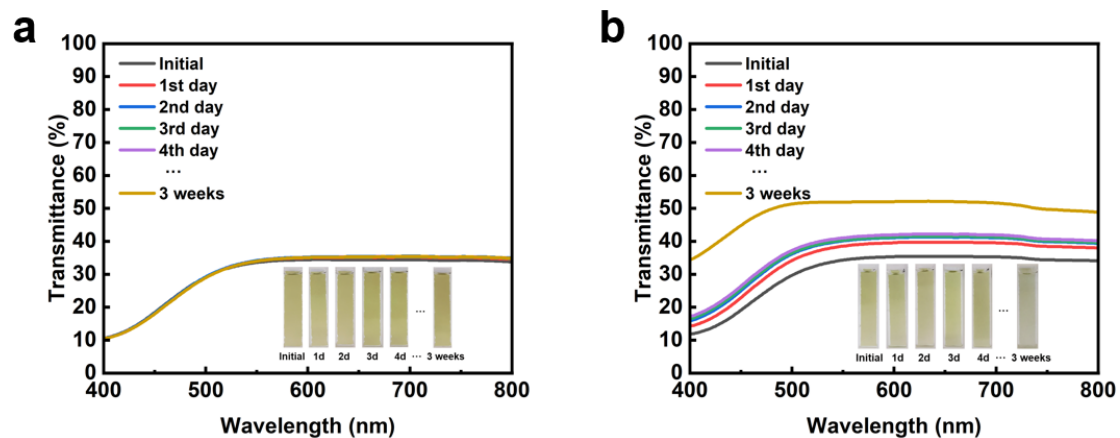
Fig S2. a, b T% transmittance spectra and corresponding digital photos of PEDOT@V_2O_5 electrode soaked in **a** Zn^{2+}/Li^+-PC and **b** Zn^{2+}/Li^+-H_2O for 3 weeks, respectively.

The PEDOT@V_2O_5 film shows negligible dissolution and transmittance variation after soaking in Zn^{2+}/Li^+-PC for 3 weeks. However, the same electrode is obviously dissolved into Zn^{2+}/Li^+-H_2O with gradually increased transmittance, forming soluble vanadium ion species (V^{3+}, VO^+, VO^{2+}, $H_2VO_4^-$ and $HV_2O_5^-$) in aqueous electrolytes[2].
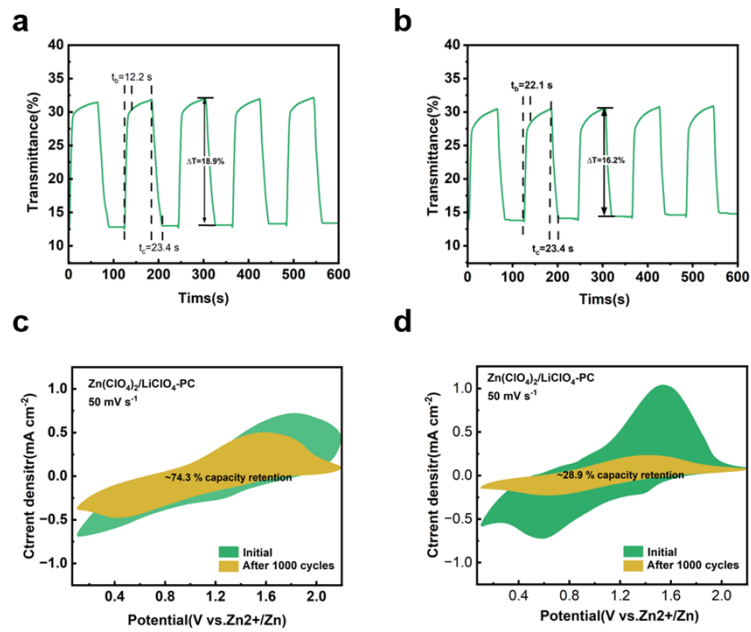
Fig. S3 Electrochemical performance of PEDOT@V_2O_5 electrode in Zn^{2+}/Li^+- PC. **a** Dynamic T% test of the 1-PEDOT@V_2O_5 electrode at 400 nm in the 0.1-2.2 V window. **b** Dynamic T% test of the 5-PEDOT@V_2O_5 electrode at 400 nm in the 0.1-2.2 V window **c** CV cycling stability of 1-PEDOT@V_2O_5. **d** CV cycling stability of 5-PEDOT@V_2O_5.
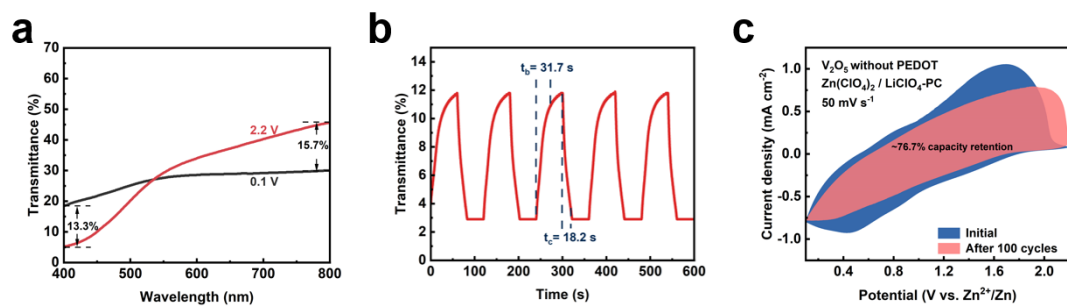
Fig. S4 Electrochemical performance of V_2O_5 stirred without EDOT electrode in Zn^{2+}/Li^+- PC. **a** T% spectra at 0.1 and 2.2 V. **b** Dynamic T% test of the V_2O_5 electrode at 400 nm in the 0.1-2.2 V window. **c** CV cycling stability.
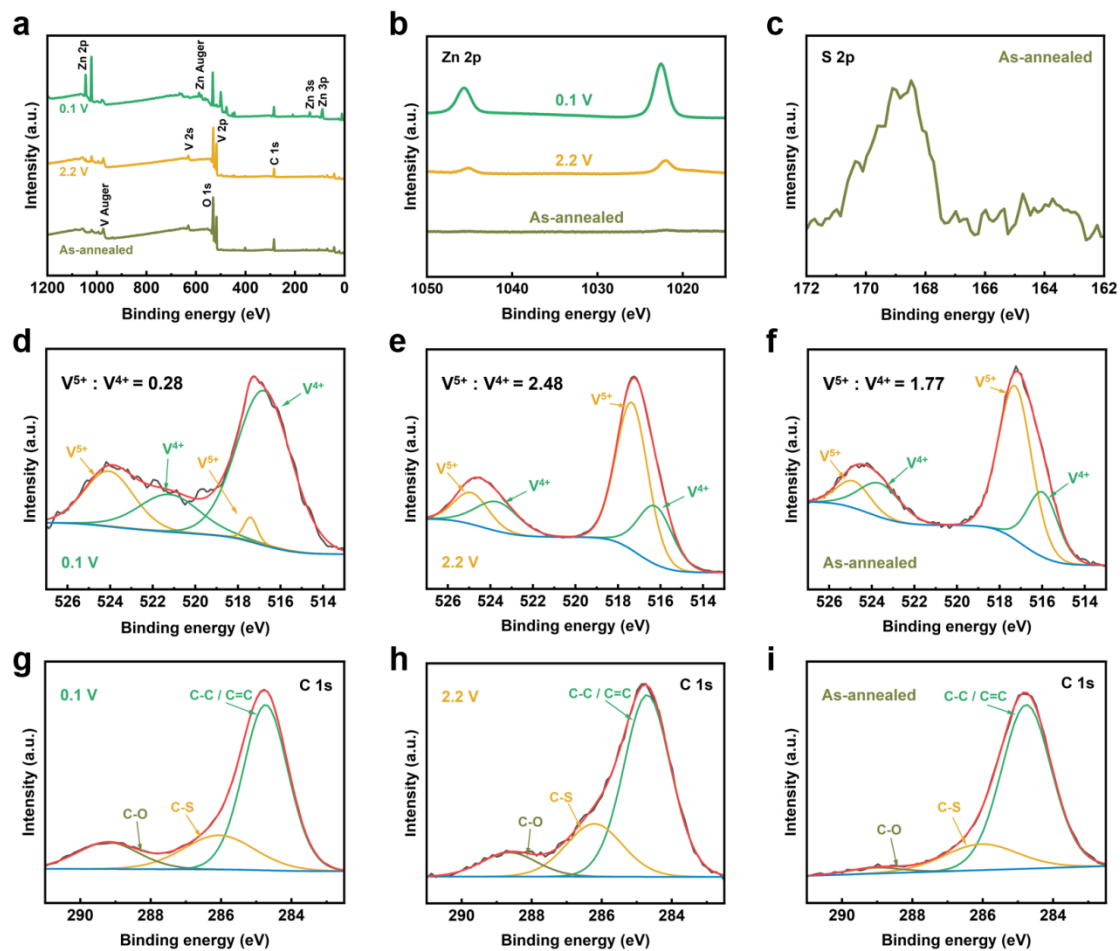
Fig. S5 The XPS survey spectra of PEDOT@V_2O_5 electrode at different states. **a** full survey. **b** Zn 2p. **c** S 2p. **d-f** V 2p. **g-i** C 1s.

Table S1. The atomic ratio of V^{4+} and V^{5+} in reduced (0.1 V), oxidized (2.2 V), and as-annealed PEDOT@V_2O_5 films.

Sample conditions	The atomic percentage of V in different valence states		V^{5+}/V^{4+}
	V^{4+}	V^{5+}	
0.1 V	0.781	0.219	0.28
2.2 V	0.287	0.713	2.48
As-annealed	0.361	0.639	1.77

Table S1 shows that the molar ratio of V^{5+}/V^{4+} in the reduced (0.1V-discharged) PEDOT@V_2O_5 electrode is 0.28, and 2.48 in the oxidized (2.2V-charged) PEDOT@V_2O_5. These results indicate that the color switching of Zn-PEDOT@V_2O_5 electrochromic systems is attributed to the reversible V valence change between V^{5+}/V^{4+}.
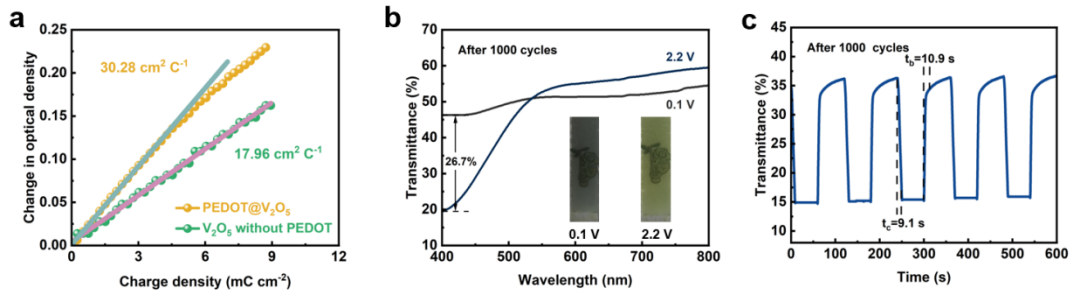
Fig. S6. The performance of PEDOT@V_2O_5 electrode. **a** Coloration efficiency compared to the V_2O_5 electrode. **b** T% spectra after 1000 CV cycles. **c** The bleaching/coloration times after 1000 CV cycles.

Table S2. Comparison of V_2O_5 performance in different organic electrolytes.

| electrolytes	Electrode material	Bleaching/Coloration time(s)	Transmittance modulation	CV cycles	Refs
1M Zn^{2+}/Li^+-PC	PEDOT@V_2O_5	10.9 s/9.1 s	27.1%@400 nm	85.6%/1000 cycles	This work
1M Li^+-PC	a-V_2O_5	21.2 s/17.1 s	38%@750 nm	70%/1000 cycles	[3]
0.3M LiTFSI-BMITFSI	V_2O_5	120 s/120 s	20%@630 nm	98%/50 cycles	[4]
1M Li^+-PC	$TaVO_x$	30s/30s	12%@550 nm	99%/100 cycles	[5]
1M Li^+-PC	Ti-V_2O_5	20 s/56 s	28%@500 nm	45%/100 cycles	[6]
1M Li^+-PC	VMC	3.6 s/5.6 s	18.95%@664 nm	53%/500 cycles	[7]
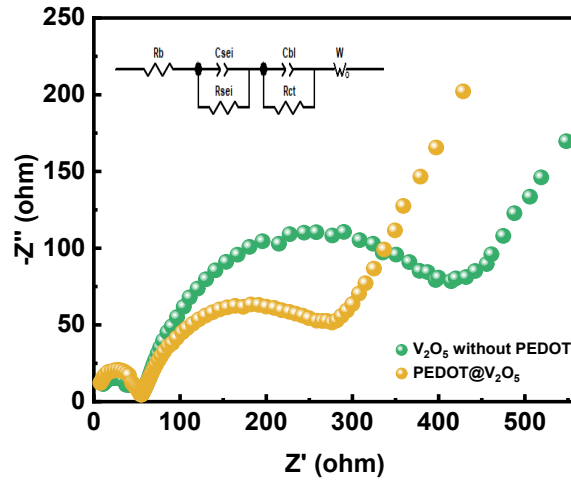
Fig. S7 Nyquist plots of V_2O_5 and PEDOT@V_2O_5.

The semicircle in the high-frequency region corresponds to the resistance of the Solid Electrolyte Interphase (SEI) film (R_{SEI}), the semicircle in the middle-frequency region indicates the charge transfer resistance (R_{CT}), and the oblique line in the low-frequency region represents the Warburg impedance.

Notes and references

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