Inorganic All-solid-state Electrochromic Devices with Reversible Color Change between Yellow and Green

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1. Experimental Section

1.1 Materials

The targets used in this study were WO_3 particles (99.99%), V_2O_5 particles (99.99%), Ta_2O_5 particles (99.99%) and low density ITO particles (99.99%) with diameter of 1-3 mm purchased from Zhongnuo Advanced Materials Technology Co., Ltd. The substrates are ITO coated glass(1×4 cm^2, 8 Ω/ square) from Zhuhai Kaivo Optoelectronic Technology Co., Ltd.

1.2 Preparation of the WO_3, V_2O_5, Ta_2O_5 and ITO films

The WO_3, V_2O_5, and Ta_2O_5 films were deposited by e-beam evaporation on ITO glass. The chamber was evacuated below 6×10^{-4} Pa before the deposition. The substrates holder was rotated at a certain speed during deposition process to ensure the uniformity of the films. All thin films were prepared without heating during deposition, and after preparation they are annealed at 300 ℃ in air in a muffle furnace.

1.3 Preparation of the all-solid-state ECD

The all-solid-state ECD is consisted of top transparent conductor ITO, electrochromic layer WO_3, electrolyte ion Li, ion conductor layer Ta_2O_5, complementary V_2O_5 and bottom transparent conductor ITO glass and prepared by e-beam and resistive evaporation. The ECDs was deposited continuously in a multi-target e-beam and resistive evaporation system at room temperature without breaking the vacuum. Covers

are equipped for the e-beam and resistive evaporation source to avoid cross contamination. The base pressure of the chamber was pumped down to 6×10^{-4} Pa and the distance between the targets and substrates was 30 cm. The substrate was kept rotating to obtain homogeneous films. The thickness of each layer was measured by quartz crystal thickness monitor. The ECD was annealed at 300 ℃ in air in a muffle furnace after fabrication. The detailed parameters of ECD were showed in Table 1.

Table 1 Detailed parameters of all-solid-state ECD

Layer	Power source	Pressure (Pa)	Deposition rate （$nm\cdot min^{-1}$）	Thickness (nm)
WO_3	e-beam	2×10^{-3}	9	475
Ta_2O_5	e-beam	5×10^{-3}	3	195
Li	resistance	4×10^{-4}	3	40
V_2O_5	e-beam	3×10^{-4}	1	140
ITO	e-beam	1×10^{-3}	3	150

1.4 Characterization

The structure of the films were Characterized by X-ray diffraction (XRD, PANalytical B. V. Model X′pert Pro) with a Cu-Kα radiation with grazing angle of 1.0°. Scanning electron microscopy (SEM, Zeiss supra 55) was used to obtain the cross-sectional image of the ECD. The electrochemical properties ECDs were investigated on CHI 660E electrochemical workstation. The electrochemical tests of ECDs were performed

in a two electrode system, where the bottom ITO layer near WO_3 was used as the working electrode and the top ITO layer close to V_2O_5 acted as the counter and reference electrodes. Cyclic voltammetry (CV) measurements were carried out from +2.5 V to −2.5 V at a scan rate of 0.1 V/s. Chronoamperometry (CA) measurements were performed at −2.5 V for coloring and +2.5V for bleaching and the duration for each step was 30 s. The optical transmittance spectra in the spectral range 350-1050 nm were recorded in situ by Vis–NIR fiber optic spectrometer (MAYA 2000-Pro, Ocean Optics, America).

2. Supplementary Figures

Referring to some previous experimental results, the device structure and preparation method of Li electrolyte are optimized [2]. The stability of WO_3 is improved by heat treatment [3]. Thus, the electrochromic performance of V_2O_5 is mainly considered while proposing the innovative device structure It is found that the as-prepared V_2O_5 film is amorphous, which is not conducive to its electrochromic stability. After annealed at 300 ℃, V_2O_5 presents a typical crystalline structure which can ensure the stability of ECD during cycling. The XRD patterns of the V_2O_5 films are shown in Fig. S1.

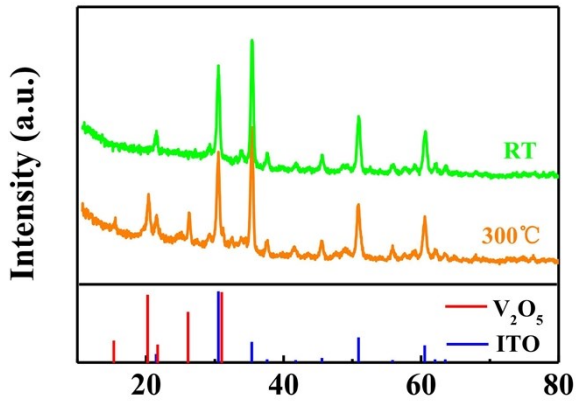

Fig. S1 XRD patterns of V_2O_5/ITO films annealed at 300℃ and without annealing.

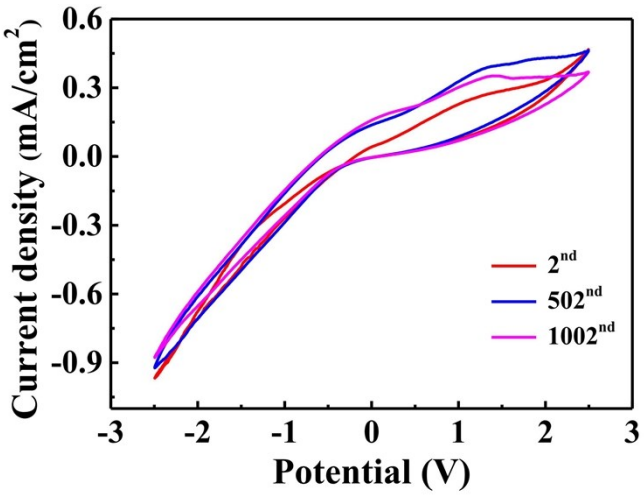

Fig. S2 CV curves of the ECD in the 2nd, 502nd and 1002nd cycles.

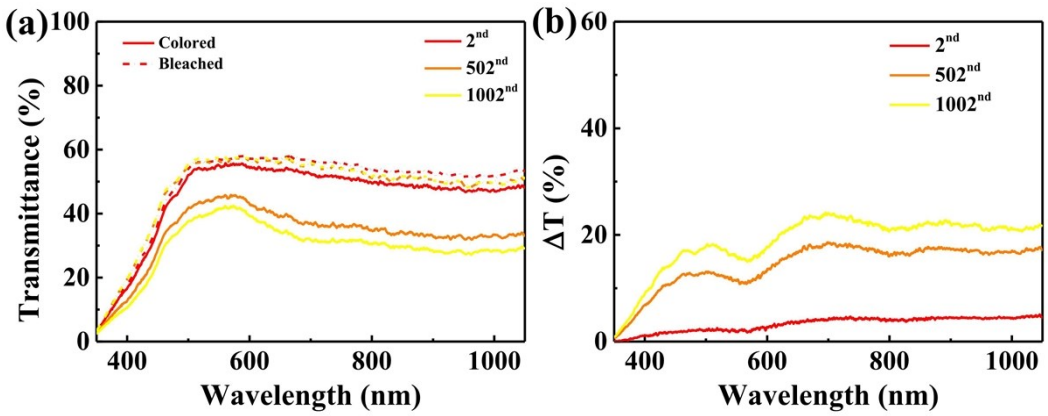

Fig. S3 (a) Transmittance spectra and (b) Transmittance modulation of the ECD in the 2nd, 502nd and 1002nd cycles.

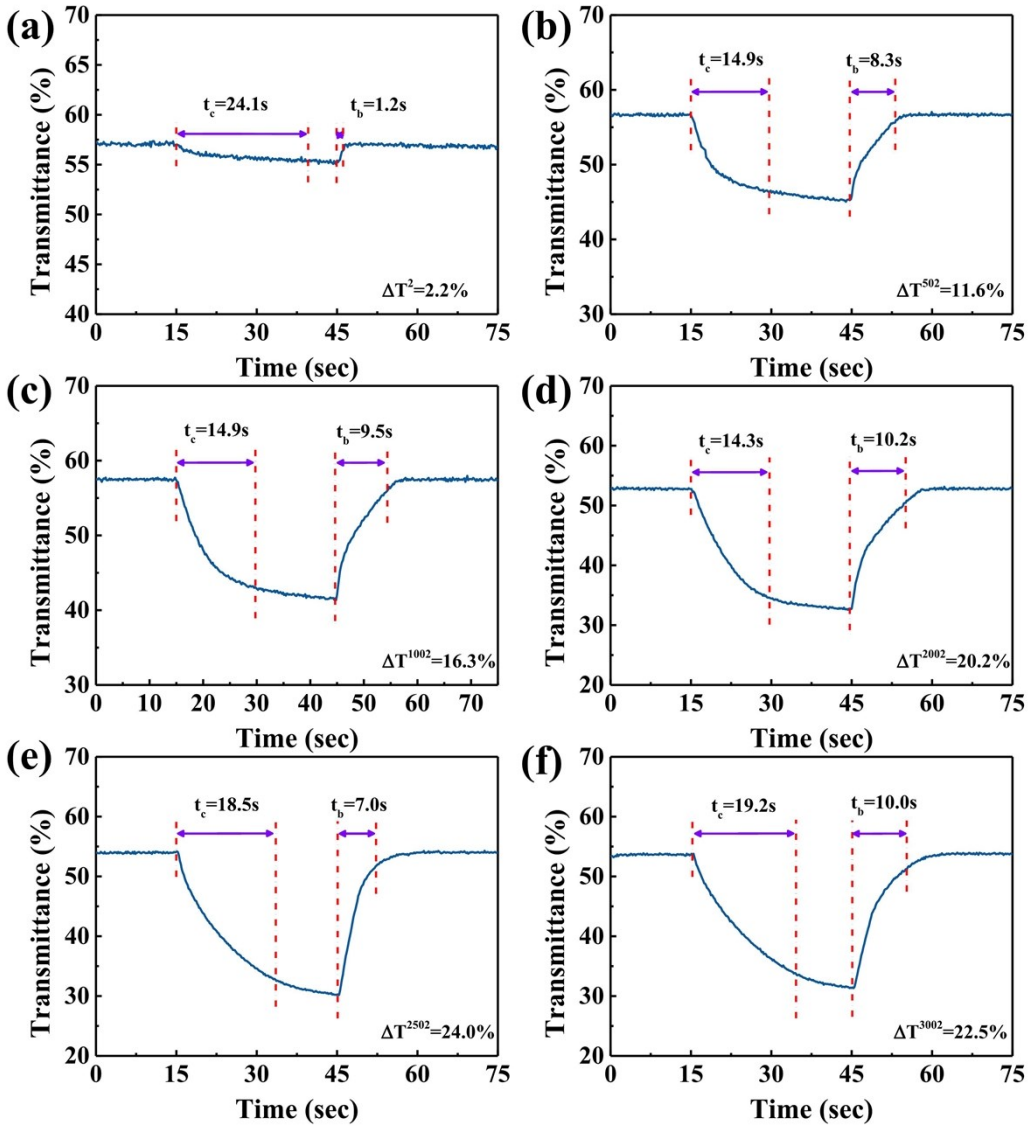

Fig. S4 Time dependent transmittance curves of the ECD in the 2nd (a), 502nd (b), 1002nd (c), 2002nd (d), 2502nd (e) and 3003nd (f) cycles.

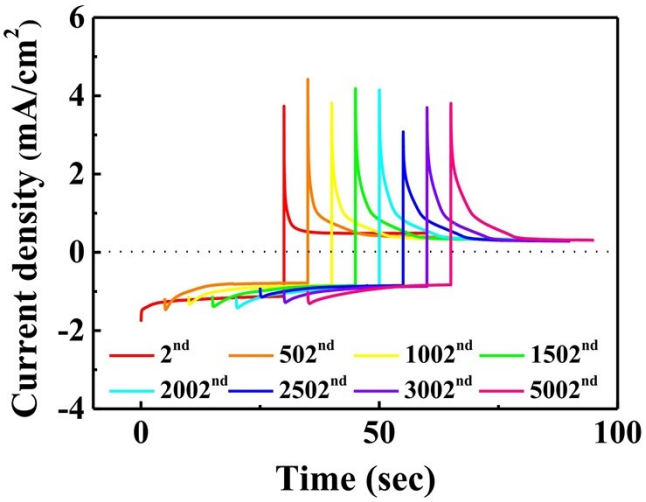

Fig. S5 CA curves of the ECD.

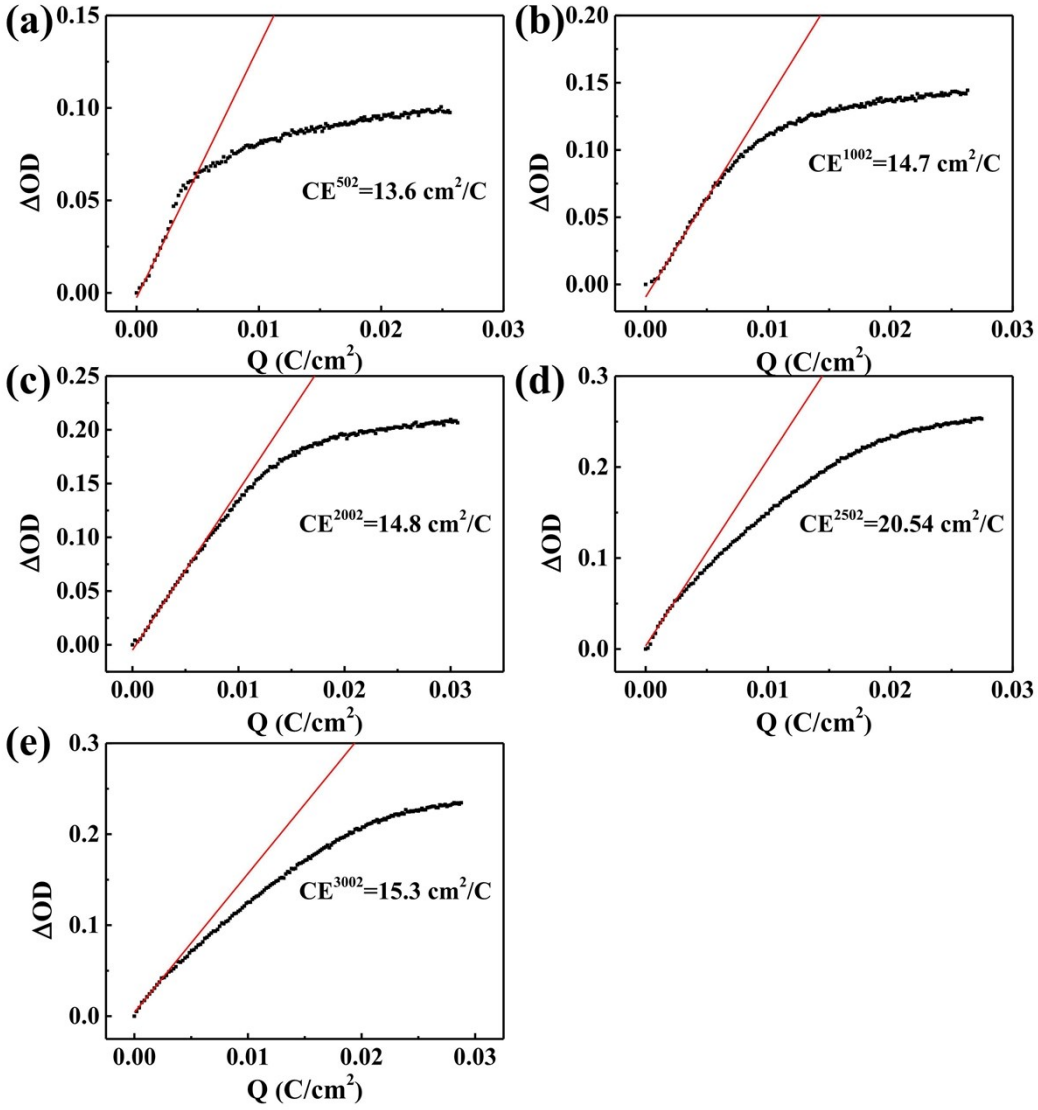

Fig. S6 CE curves of the ECD in the 502nd (a), 1002nd (b), 2002nd (c), 2502nd (d) and 3003nd (e) cycles.

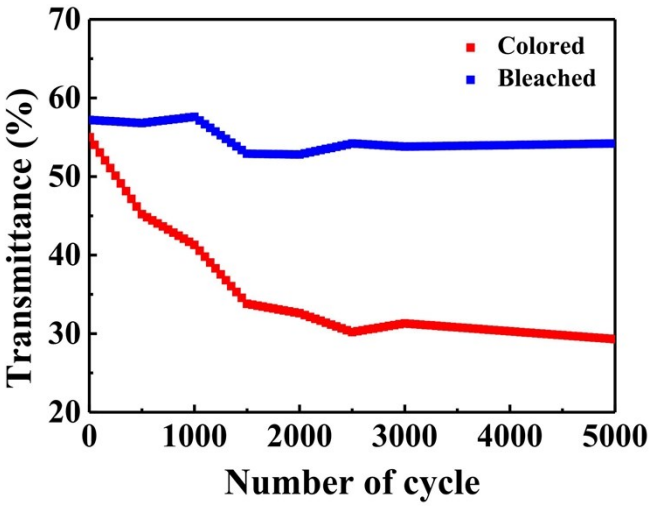

Fig. S7 Cyclic performance of the ECD. The applied voltages are + 2.5 V and - 2.5 V with duration of 30 s.