Supporting Information

All Solid State Electrochromic Devices Based on LiF Electrolyte

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Content:

Experimental Section

Preparation of films and ECD

The indium tin oxide glass(ITO glass, 3 cm * 4 cm, 10 Ω/square) and quartz glass substrates were obtained from Ningbo Nanotech Advanced Materials Co., Ltd. The substrates were ultrasonically cleaned in deionized water and alcohol for 10 min, respectively. All evaporation particles (WO_3, LiF, NiO and ITO) were 1~3 mm in diameter and obtained from ZhongNuo Advanced Material (Beijing) Technology Co., Ltd. The basic pressure of the deposition chamber was 5.0×10^{-4} Pa. The distance between substrate and the evaporation source was 25 cm.

The WO_3, NiO and top ITO films were deposited by electron beam evaporation and LiF thin film was deposited by resistance evaporation method. The deposition conditions of the thin films are listed in Table S1. All single layer films were fabricated on the quartz glasses to study the morphology, structural, and optical properties. The ECDs with the structure of Glass/ITO /WO_3/LiF/NiO/ITO were fabricated on the ITO glasses using the same evaporation parameters listed in Table S1. The effective EC area of ECDs is about 2 cm * 3 cm. After evaporation, in order to enhance the optical and electrical properties of the top ITO thin film, the ECD was annealed at 300 ℃ for 60 min in a muffle furnace. All single layer films were also annealed at the same conditions to match their properties in the device.

Table S1 Deposition conditions for the thin films

Film	Thickness(nm)	Working vacuum(Pa)	Deposition rate(Å/s)
WO_3	450	1.8×10^{-3}	1.5
LiF	90	6.8×10^{-4}	1.0

NiO	250	2.5×10^{-3}	1.5
ITO	150	1.1×10^{-3}	1.5

Characterizations

The morphologies of the samples were characterized by scanning electron microscopy (SEM) using a Zeiss supra 55 at an accelerating voltage of 20 kV. The crystalline structures of the films were characterized by Japan Rigaku DMax-rb rotation anode X-ray diffractometer equipped with graphite monochromatized Cu K_α radiation (0.15418 nm) in the range from 10° to 80°. The transmittance spectra of the samples were characterized by Vis-NIR fiber optic spectrometer (MAYA 2000-Pro, Ocean Optics).

The EC performances of the devices were investigated with the combination of CHI 660E electrochemical station and Vis-NIR fiber optic spectrometer. The cyclic voltammetry (CV) measurement of the devices were performed at a scan rate of 50 mV/s over the voltage range of -2.5~2.5 V. The chronoamperometry (CA) measurement of the devices were performed by applying -2.5 V and 2.5 V with 15 s duration. In order to obtain the maximum reversible spectra modulations, the devices were colored at -2.5 V for 100 s and bleached at 2.5 V for 40 s.

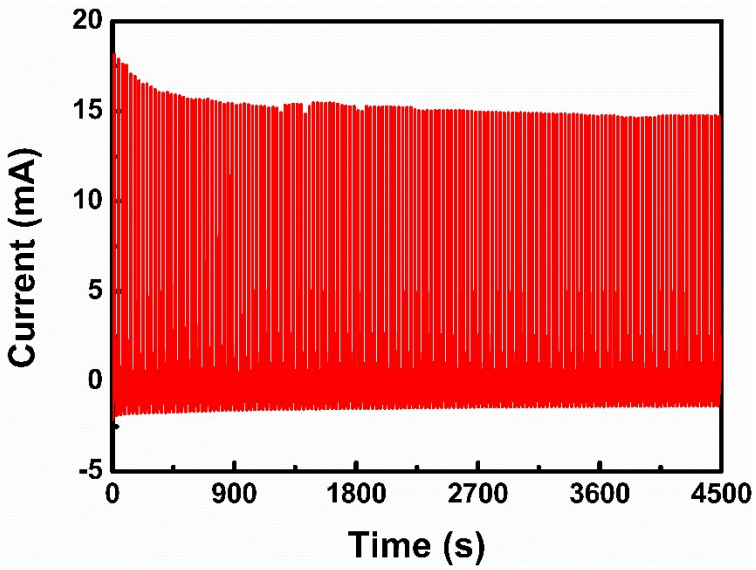

Figure S1 The corresponding chronoamperometry (CA). The corresponding CA measurements of the device are performed by applying −2.5 V and +2.5 V with 15 s duration.

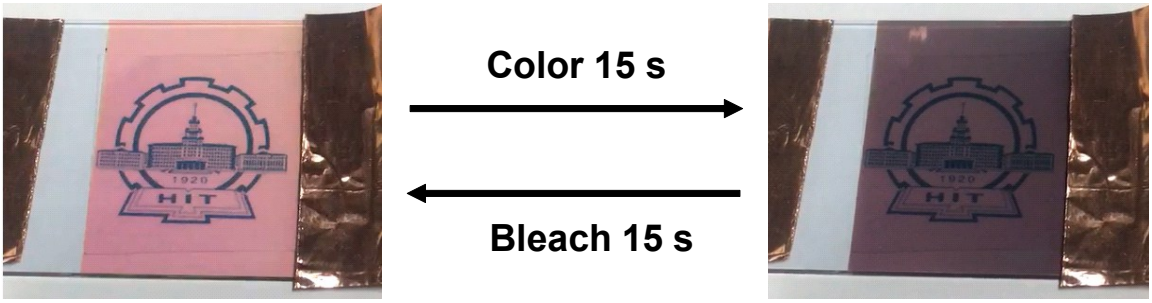

Figure S2 Digital photos of ECD at different stages.

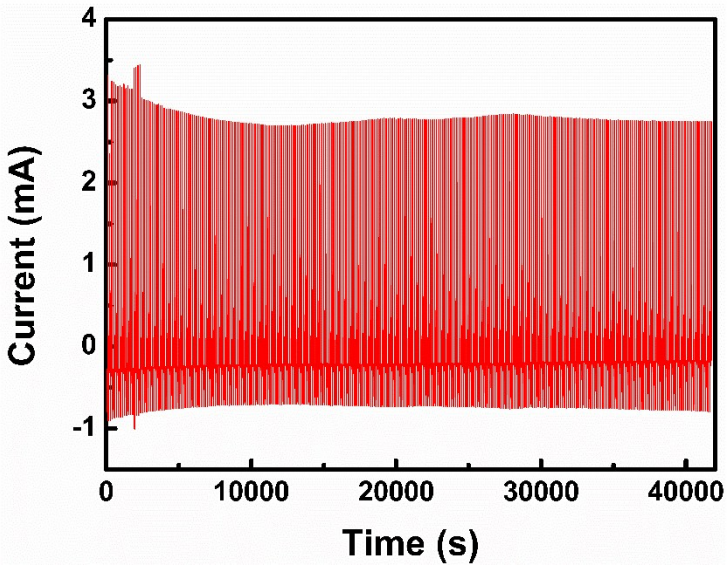

Figure S3 The corresponding current density curve. The corresponding current density curve extend the coloring time to 100 s and the bleaching time to 40 s

Table S2 Reported performance of all solid state electrochromic devices.

Device structure	t_c / t_b (s)	ΔT_{max} (%)	CE (cm^2/C)	Ref.
Glass/ITO/NiO_x/LiBSO/WO_3/ITO	20 / 8	52.2*	NG	S1
Glass/ITO/MoO_3/$LiAlO_2$/NiO_x/ITO	NG	43.2*	NG	S2
Glass/ITO/MoO_3/LiBSO/NiO_x/ITO	NG	46.5	NG	S3
PET/ITO/NiO_x/$LiTaO_3$/WO_3/ITO	7 / 55	63	68.5	S4
Glass/ITO/NiO_x/Ta_2O_5/$LiNbO_3$/Ta_2O_5/ WO_3/ITO	21 / 21	52.5	98.1	S5
Glass/ITO/NiO/Si_3N_4/$LiNbO_3$/Si_3N_4/WO_3/ ITO	within 30	43	NG	S6
Glass/ITO/NiO_x/Ta_2O_5:H/WO_3/ITO	within 40	60	NG	S7
Glass/ITO/NiOx:H/ZrO_2/WO_3/ITO	70 / 42	68	NG	S8
Glass/ITO/NiO/Si_3N_4/Li_xMg_yN/WO_3/ITO	NG	40*	77	S9
Glass/ITO/NiO:(Li,Mg)/Ta_2O_5/WO_3/ITO	NG	58	NG	S10
Glass/ITO/NiOx/ZrO_2:H/WO_3/ITO	25 / 15	65.2	NG	S11
Glass/ITO/WO_3/$LiNbO_3$/NiO_x/ITO	45 / 25	65	NG	S12
Glass/ITO/NiOx/$LiTaO_3$/WO_3/ITO	85 / 42	67	NG	S13
Glass/ITO/WO_3/LiPON/NiO/ITO	within 30	40	NG	S14
Glass/ITO/NiO/LTO/WO_3/ITO	within 30	40	NG	S15
Glass/ITO/WO_3/$LiNbO_3$/Ta_2O_5/NiO/ITO	NG	31.4	NG	S16
Glass/ITO/ dry lithiated WO_3/wet lithiated Ta_2O_5/NiO/ITO	10 / 7	71.7	NG	S17
Glass/TCO/V_2O_5/LiPON/Li_xWO_3/TCO	within 30	40	NG	S18
Glass/ITO/WO_3/LiF/NiO/ITO	9.6 / 4.0	58.9	88.5	this work

* represent the average visible light transmittances modulation; NG refers to not available data.

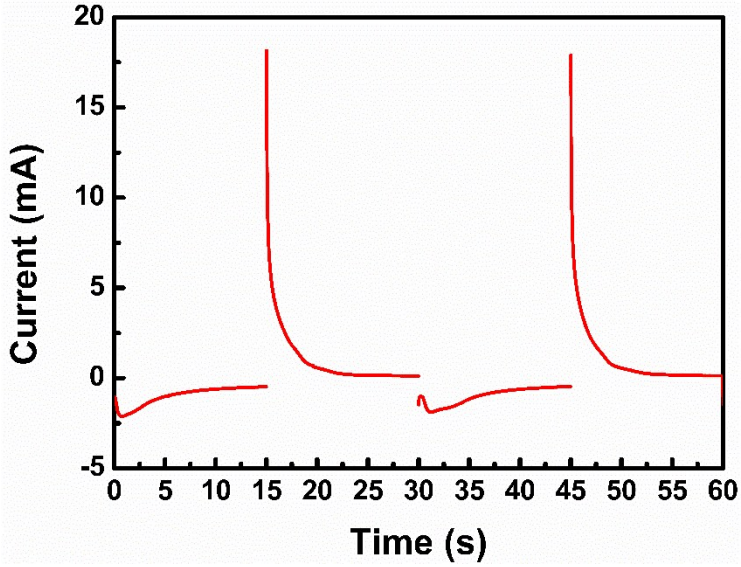

Figure S4 The first two cycles full coloring /bleaching CA curves.

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