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Supplementary Information

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5 Sample Preparation

Modification of LPEI and PDDA on ITO

Linear polyethylenimine (LPEI, M_w 25000, PolySciences, Inc.) and poly(diallyldimethylammonium chloride) (PDDA, M_w 100000-200000, Sigma-Aldrich) were used for ITO modification (sheet resistance of 8-12 Ω , Delta Technologies). ITO was cleaned by sonication in acetone, isopropyl alcohol, ethanol and water for 5 min, respectively, and was immersed in 30% H_2O_2 solution at 70-80 °C for 20 min. After cleaning, the samples were rinsed with water and dried with nitrogen flow. The cleaned ITO samples were immersed in aqueous solution of 1 $mg\ mL^{-1}$ LPEI (pH 2.5 adjusted by 1 M HCl) or 1 $mg\ mL^{-1}$ PDDA for 20 min.

Electrodeposition of electrochromic films

The vanadium oxide solution was prepared according to Fontenot et al.¹ V_2O_5 powder (99.9% metals basis, Alfa Aesar) was dissolved (vanadium concentration of 0.11 M) in H_2O_2 (30 wt %, Merck KGaA). The resultant gel was then redispersed in deionized water before use. Peroxo-polytitanic acid (PPT acid) was prepared according to the literature.² Titanium powder (<20 μm , 93%, Alfa Aesar) was added into 30 wt % H_2O_2 solution and stirred for 3 days at room temperature. A yellowish solution of PPT acid was obtained, which was filtered to remove non-reacted Ti powder. The two solutions were mixed with Ti:V molar ratio of 1:25. The mixture was aged for at least one week. A small amount of ethanol solvent was added to the mixture before electrodeposition.

Peroxytungstic acid (PTA) was used as a precursor for electrodepositing amorphous tungsten oxide (WO_3) films. The solution was prepared by oxidative dissolution of tungsten powder in H_2O_2 , and was stabilized with the addition of an optimum amount of ethanol.³ Electrodeposition was carried out in a conventional three-electrode system. Bare, LPEI- or PDDA-modified ITO was used as working electrodes, Ag/AgCl was used as the reference electrode and a platinum foil (10 mm \times 20 mm \times 0.2 mm) was used as counter electrode. After deposition, the oxide films were dried in air at room temperature without any thermal treatment.

Preparation of the samples for ATR-FTIR measurements

The samples of pure LPEI and pure vanadium oxide were prepared by drop-casting on silicon wafers. The sample of LPEI/vanadium oxide film was prepared by layer-by-layer (LbL) deposition.^{4,5} The layers were prepared by alternating immersion of a silicon wafer into the LPEI polymer solution (1 $mg\ mL^{-1}$, pH 2) and the vanadium oxide dispersion (25 mM) for 20 min each. After each deposition, the silicon substrates were rinsed for 1 min in HCl solution (pH 2) for two times. This procedure was repeated several times to form multilayers of LPEI/vanadium oxide films.

30 Characterization

Contact Angle

Static water contact angle of the films was measured by a FTA-200 automated goniometer (First Ten Angstroms, Portsmouth, VA) equipped with FTA32 v2.1 software. The measurements were conducted with drops of 5 μL deionized water. For each sample, the final result shown was the average of more than 10 measurements.

35 Atomic Force Microscopy

Atomic force microscopy (AFM) was carried out with a DI 3100 (Veeco, Digital Instruments) under ambient conditions. AFM was operated in the tapping mode with an optical readout using Al-coated silicon cantilevers (Tap300Al-G, Budget Sensors).

Electrochemical properties

Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) of bare, LPEI- and PDDA-modified ITO electrodes were measured in a redox system consisting of 1 mM $K_3Fe(CN)_6$ (99%, Sigma-Aldrich) and 50 mM KCl (\geq 99.0%, Sigma-Aldrich). The electrode area was 0.2827 cm^2 . Ag/AgCl (Sat. KCl) was used as reference electrode and Pt foil was used as counter electrode. The

measurements were carried out on a Solartron 1470E electrochemical interface analyzer.

Electrochromic performance

Optical transmittance spectra were measured using a Shimadzu UV-3600 spectrophotometer. A three-electrode cell was used for controlling the potential of the Ti-doped vanadium oxide and WO₃ films. An Ag wire was used as reference electrode and a Pt wire served as counter electrode. 1 M lithium perchlorate (LiClO₄, 99.99%, Sigma-Aldrich) in propylene carbonate (PC, 99.7%, Sigma-Aldrich) was used as electrolyte. The potentiostatic and chronoamperometric measurements were performed on Solartron 1470E potentiostat. Continuous double potential steps of 0.7 V for 10 s and -0.6 V for 15 s vs. Ag wire were applied to the Ti-doped vanadium oxide films. It should be mentioned that for the Ti-doped vanadium oxide films prepared on the bare ITO and PDDA-modified ITO substrates, the biasing duration elongated to 0.7 V for 30 s and -0.6 V for 20 s in order to get to its platform in optical modulation. For tungsten oxide films, the double potential steps applied were 0.4 V for 15 s and -1.2 V for 20 s vs. Ag wire. A double potential step is denoted as one cycle.

Infrared Spectroscopy

Attenuated Total Reflectance (ATR) Fourier transform infrared (FT-IR) spectroscopy was performed on a Frontier™ FT-IR/NIR Spectrometer (PerkinElmer, Inc.) using the ATR Polarization accessory. The spectra were recorded between 4000 and 700 cm⁻¹ at a resolution of 4 cm⁻¹.

Figures and Tables

Table S1. Roughness, contact angle and electrochemical behavior (parameters obtained from CV and EIS) of bare, LPEI- and PDDA-modified ITO electrodes.

Electrodes	Physical Property		CV		EIS
	Roughness	Contact Angle	ΔE_p (mV)	I_p^a/I_p^c	R_{ct} ($\Omega \cdot \text{cm}^2$)
Bare ITO	2.92 nm	77.1 °	102.9	1.103	106.58
ITO/LPEI	3.42 nm	46.4 °	101.9	1.062	100.92
ITO/PDDA	3.70 nm	34.9 °	98.9	1.051	87.07

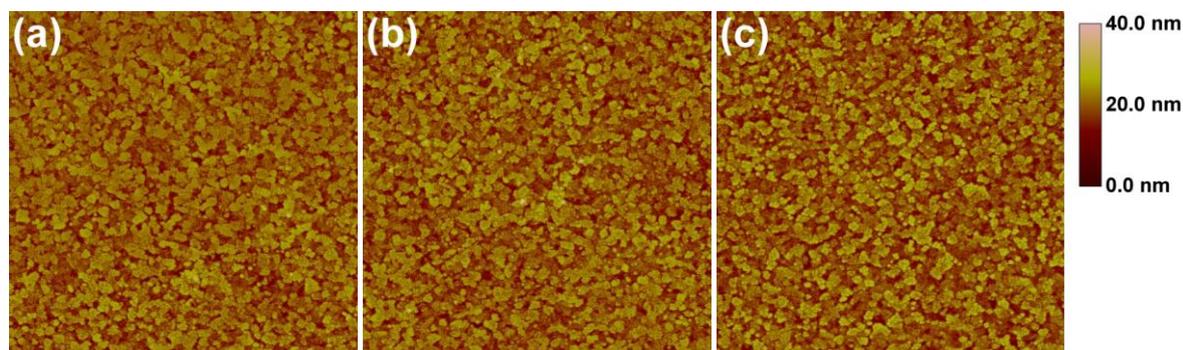


Figure S1. AFM images of bare, LPEI- and PDDA-modified ITO glasses. Scan size is 5×5 μm.

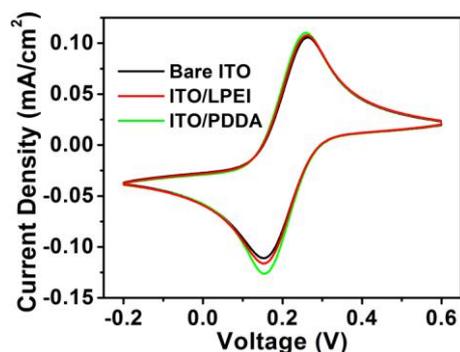


Figure S2. CV of bare, LPEI- and PDDA-modified ITO electrodes in 1 mM K₃Fe(CN)₆ redox solution with 50 mM KCl. Scan rate is 50 mV s⁻¹.

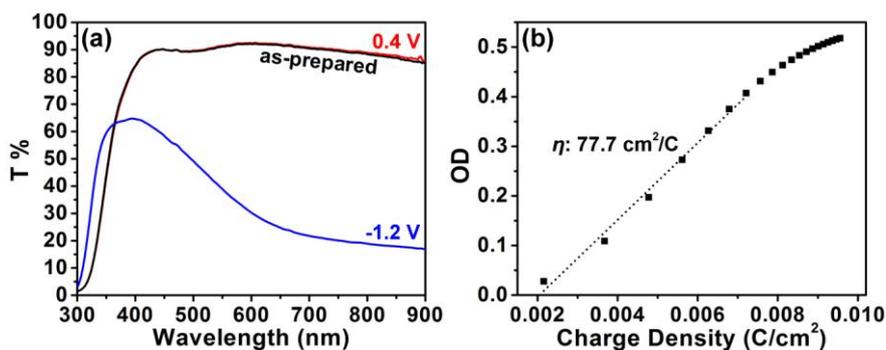


Figure S3. (a) Optical transmittance spectra at different potentials and (b) Optical density (OD) variation with respect to the charge density (measured at 633 nm) for the tungsten oxide film.

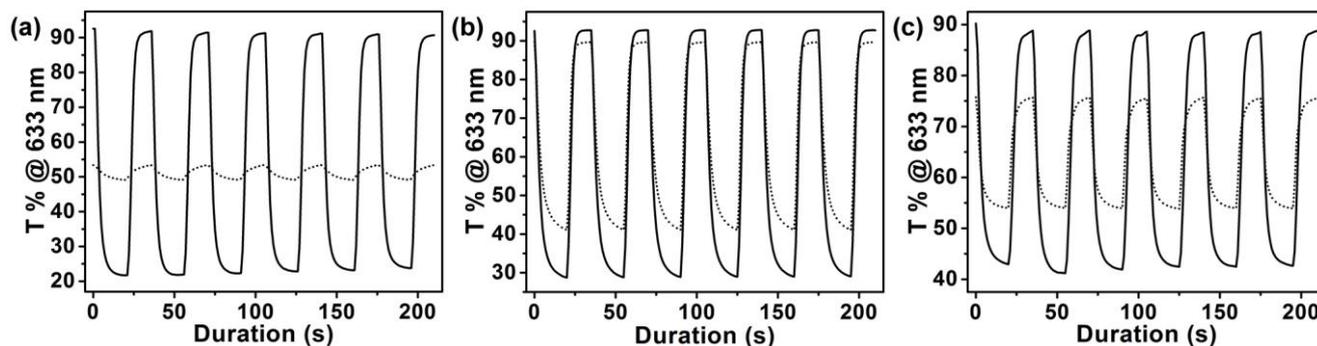


Figure S4. Transmittance variations of tungsten oxide films prepared on bare (a), LPEI- (b) and PDDA-modified ITO (c). The measurements were carried out in 1 M LiClO₄/PC solution with continuous double potential steps of 0.4 V and -1.2 V vs. Ag wire. (—) 1st-6th cycles; (···) 995th-1000th cycles.

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