Supporting information

A transparent 3D electrode with criss-crossed nanofibers network for solid electrochromic device

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Figure S17. (a) The table of BET surface area and surface area of FTO and FTO-3D with ITO nanofibers at different diameters. (b) The U-I curves of different FTO-3D devices with various surface areas. (c) The change of absorbance for FTO device and FTO-3D devices with various surface areas when added the same time (1-5 s) with the same voltage (-1.2 V).

1. Experimental details

Characterizations. X-ray diffraction (XRD) pattern was recorded using Empyrean xray diffractometer (Cu Ka radiation). Scanning electron microscopy (SEM) images were taken using field-emission scanning electronic microscopy (FE-SEM; SU8020, HITACHI) operated at an accelerating voltage of 3.0 kV. Elemental mapping of prepared nanofibers was evaluated using the SEM at 20 kV. XPS wide scan spectra was measured using a ESCALAB 250 X-Ray Photoelectron Spectroscopy (XPS). High-resolution transmission electron microscopy (HRTEM) images were taken using a JEM-2100F, operated at 200 kV. IR spectra studies were performed on Vertex 80/80V FT-IR spectrometer with LN-MCT Mid DC detector over the range of 4000-400cm-1 using a KBr plate. The thermal properties were measured using a Thermal Gravimetric Analyzer (Q500, TA.) at a heating rate of 10 K/min. The electrochemical data were obtained from Bio-logic electrochemical work station. Fluorescence spectra were obtained with a Shimadzu spectrofluorimeter RF-5301PC. UV-Vis absorption spectra and optical transmittance spectra were measured using a Shimadzu UV-2550 PC double-beam spectrophotometer. The sheet resistances were measured using a ST-2258C multifunction digital four-probe tester. The roughness of the FTO-3D was measured by Atomic Force Microscopy (SPA300, SEIKO).

Reagents. Polyvinyl pyrrolidone (PVP, Mw~1,300,000), Indium nitrate tetrahydrate (In(NO₃)₃·4H₂O), Polymethyl methacrylate (PMMA, Mw~100,000), conductive plasticizer and Hydroquinone (HQ) were purchased from Energy Chemicals, China. Stannous chloride dihydrate (SnCl₂·2H₂O), p-benzoquinone (BQ) and fluorescein (Flu) were purchased from Aladdin Chemicals, China. The nanofibers were produced by the ET-2535DC electrospinning equipment. The FTO was purchased from South China Xiang Science & Technology company (Sheet Resistance < 8 Ω ; Transmittance > 80%; the thickness of FTO is 500 nm). All the solvents were purchased in commercialized way and used without further purification.

Fabrication of FTO-3D. ITO nanofibers were synthesized by electrospinning. The precursor solution was prepared by dissolving $0.09 \text{ g} \text{ In}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$, $1.45 \text{ g} \text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in a mixture solvent of 7 mL DMF and 9 mL anhydrous $\text{C}_2\text{H}_5\text{OH}$ firstly. Then PVP was added into it and the concentration of PVP to the solvent was 8.4 %. The solution was stirred at 45 °C until a clear precursor solution was produced. After that, the precursor solution was loaded into a plastic syringe with a 21G needle and the electrospun nanofibers were collected onto a FTO on grounded stainless steel plate, which were placed 15 cm away from the spinneret. The applied voltage was +15 kV and the flow rate was 1 mL/h. The optimized deposition time was 3.0 min which was chosen by a comprehensive comparison of conductivity and transmittance. After the nanofibers completely deposited, the nanofibers-coated FTO were heated in air at 200 °C for 1 hour at a heating rate of 2 °C/min and then heated at 520 °C for 2 hours with a heating rate of 1 °C/min. After the above treatments, FTO modified with ITO nanofibers (FTO-3D) was fabricated.

Fabrication of FTO/FTO-3D all-solid-state device. FTO/FTO-3D all-solid-state device was fabricated by automatic film applicator (BEVS 1811/1). Devices contained three layers. The composition of three layers as below: Electrochromic layer: PMMA 3.5 g, conductive plasticizer 1.7 mL, Flu (5×10-3 mol/L), BQ (5×10-2 mol/L), CH₃CN 20 mL; Ion conductive layer: PMMA 3.5 g, conductive plasticizer 1.7 mL, CH₃COOCH₃ 20 mL; Ion storage layer: PMMA 3.5 g, conductive plasticizer 1.7 mL, BQ (5×10⁻² mol/L), HQ (1×10⁻¹ mol/L), CH₃CN 20 mL. The one electrode was a FTO/FTO-3D with an electrochromic layer. It was coated by a 200 µm wire rod for one time. Every layer was coated with a same coating rate of 50 mm/s. The other electrode was a FTO/FTO-3D with an ion storage layer and a conductive layer. The ion storage layer was coated by 200 µm wire rod for one time. After the solvent was volatiled completely, the conductive layer would be coated. It was coated by 200 µm wire rod for three times. Each time was dried completely before the next coating. electrodes contacted Finally, the two were with each other.

2. Characterization of FTO-3D



Figure S1. Schematic diagram of fabricating FTO-3D electrode.



Figure S2. TGA curves of PVP, PVP/SnCl₂ composite nanofibers and PVP/SnCl₂/In(NO₃)₃ composite nanofibers. (PVP/SnCl₂ composite nanofibers were produced by electrospinning. The precursor solution contained 1.2 g SnCl₂ $2H_2O$, 6 mL DMF, 8 mL anhydrous C₂H₅OH, 1.2 g PVP. And all the spinning condition was the same as PVP/SnCl₂/In(NO₃)₃ composite nanofibers.)



Figure S3. FT-IR spectra of $PVP/SnCl_2/In(NO_3)_3$ composite nanofibers and ITO nanofibers.



Figure S4. (a) Energy dispersed electron spectroscopy (EDS) spectra of ITO nanofibers; (b) EDS elemental mappings of ITO nanofibers.



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Roughness: 147 nm



Figure S7. The AFM pictures of FTO-3D with ITO nanofibers and its corresponding roughness.



Figure S8. The SEM pictures of the cross sections of glasses with ITO nanofibers at various deposition time (a) 1 min; (b) 2 min; (c) 3 min; (d) 4 min and (e) the thickness of the ITO nanofibers at various deposition time.



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Figure S11. The absorption and emission spectra (Ex-480 nm) of electrochromic layer after the fumigation of ethylenediamine with about three seconds.



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Figure S13. The comparison of the response time between FTO device and FTO-3D device.



 l_1 : diffusion distance of electron; l_2 : diffusion distance of ion; l_3 : the length of ITO nanofiber; l: the total distance from FTO electrode surface to the farthest molecules being oxidized/reduced

Figure S14. The schematic diagram of diffusion distance of electrons and ions in FTO (left) & FTO-3D (right) with electrochromic film.



Figure S15. The initial transmittance of FTO device and FTO-3D device with ITO nanofiber at various thickness (take the air as reference).



Figure S16. The intensity change of absorbance (505 nm) and emission (530 nm, slit 5,5) of FTO device and FTO-3D device with ITO nanofiber at various thickness when added the same time (1-5 s) with the same voltage (-1.2 V).



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