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Supporting Information

**Intelligent electrochromic-supercapacitor based on effective
energy level matching poly(indole-6-carboxylic acid)/WO₃
nanocomposites**

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Experimental Section

1.1 Chemicals

Unless otherwise noted, all chemicals were commercially available. FTO glasses ($\leq 7 \Omega$, South China Xiangcheng Technology Co., Ltd.), indole-6-carboxylic acid (6ICA, 98%, J&K Chemical), 3,4-ethylenedioxythiophene (EDOT, 98%, Sigma-Aldrich), tetrabutylammonium tetrafluoroborate (TBATFB, 95%, Sigma-Aldrich), polyvinyl alcohol (PVA, 98%, Medium Molecular Weight), $\text{NaWO}_4 \cdot 2\text{H}_2\text{O}$ (99.5%, Macklin), absolute ethanol (analytical grade, Yantai Institute of Chemical Industry), acetone (analytical grade, Jinan Reagent Plant), concentrated hydrochloric acid (chromatographically pure, Tianjin Bodi Chemical Plant), acetonitrile (chromatographically pure, Tianjin Bodi Chemical Plant), and concentrated sulfuric acid (chromatographically pure, Tianjin Bodi Chemical Plant) were used directly.

1.2 Characterization

The preparation temperature of WO_3 on FTO glasses (0.7 cm*5.0 cm) was controlled by an electric heating constant temperature blast furnace (Jinghong) on DHG-9623A. The CHI 660E Electrochemical Workstation (Shanghai, conducted by Chen Hua Instruments, China) measured cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and Galvanostatic charge and discharge (GCD) measurements. Cary500 UV-Vis-Near-infrared spectrophotometer (Varian, USA) and Model 263 Electrochemical Workstation (EG&G Princeton Applied Research, USA)

were used to study the spectral electrochemical properties. Scanning Electron Microscopy (SEM) measurements were taken by JEOL JSM-6700F scanning electron research microscope (JEOL Ltd., Japan). Transmission electron microscope (TEM) measurements were performed using JEM-2100 electron microscope (JEOL Ltd., Japan). Raman spectroscopy was obtained using a Renishaw Invia Raman microscope (Renishaw Ltd., UK). Infrared spectrometer (Nicolet Ltd., USA) was recorded using a Nicolet 510P FTIR containing KBr particles. The electrochemical, electrochromic and supercapacitive properties characterizations of P6ICA/WO₃ nanocomposites were evaluated with the three-electrode system in 1 M H₂SO₄ solution. During the test, FTO coated with active material was used as the working electrode, platinum wire was used as the counter electrode and Ag/AgCl electrode was used as the reference electrode.

1.3 Preparation of P6ICA/WO₃ with Core-shell Nanorod Structure

The WO₃ nanorods were prepared by a previously reported hydrothermal technique¹ and made minor changes. In a typical synthesis, NaWO₄•2H₂O (1.953 g) was mixed in deionized water (45 mL) while stirring for 30 min to form clear. Then, HCl (1 M) was added into the solution till pH value reached 0.5 as precursor solution. FTO glasses (0.7 × 5.0 cm) were washed with acetone, absolute ethanol and water for 10 min in sequence. The cleaned FTO glasses were placed conducting surface close to the inner wall of the Teflon-lined stainless steel autoclave (100 mL). Precursor solution was added in sealed Teflon-lined autoclave and maintained at 200 °C for 1 h. The autoclave was cooled to room temperature naturally. The FTO with WO₃

nanorods were rinsed several times with deionized water and annealed at 450 °C for 0.5 h.

P6ICA/WO₃ films were prepared by electrochemical method in a three-electrode system with WO₃ nanorods as working electrode, Ag/AgCl as reference electrode, and platinum wire as counter electrode. The acetonitrile solution containing 0.1 M tetrabutylammonium tetrafluoroborate (TBATFB) and 0.05 M indole-6-carboxylic acid (6ICA) was electrolyte system. The P6ICA was electrodeposited on WO₃ film under the applied potential of 1.5 V for 40 s. Finally, the prepared P6ICA/WO₃ film was washed with deionized water and natural drying.

1.4 Preparation of H₂SO₄-PVA Gel Electrolyte

Firstly, 2 g polyvinyl alcohol (PVA) powder was added into 20 ml deionized water with vigorous stirring and subsequent heating under stirring to ~85°C until the solution becomes clear. Then, a certain amount of H₂SO₄ was added to the PVA solution. The weight ratio between H₂SO₄ and PVA was about 1:1. After 5 minutes of continue heating, the H₂SO₄-PVA gel electrolyte was successfully prepared.

1.5 Capacitance and Coloring Efficiency (CE) Calculation

The specific capacitance of materials and devices was calculated by GCD following equation (1):

$$C = It / \Delta V S \quad (1)$$

Where C represents the specific capacitance of the material or device (mF cm⁻²); I is the discharge current (mA); t is the discharge time (s); ΔV is the different

potential windows (V); S is the effective area of the material or device (cm^2).

The CE can be calculated according to the following equation (2), (3):

$$CE = \Delta OD / Q_d \quad (2)$$

$$\Delta OD = \log (T_b / T_c) \quad (3)$$

Where Q_d is the amount of charge required in the redox process. ΔOD is the optical density. T_b and T_c refer to the transmittance of the material in the bleached and colored state, respectively.

1.6 Energy Level Calculation

In the calculation process, half of the sum of the oxidation potential (E_{ox}) and reduction potential (E_{red}) of ferrocene (Fc) is used as the reference potential (E_{ref}^{Fc})² by the following equation (4):

$$E_{ref}^{Fc} = (E_{ox} + E_{red}) / 2 \quad (4)$$

The calculation formula of HOMO energy level of PICA was as following by the following equation (5):

$$E_{HOMO} = -(4.8 \text{ eV} - E_{ref}^{Fc} + E_{ox}) \quad (5)$$

Where E_{ox} is the oxidation initiation potential of P6ICA.

The calculation formulas for the valence band (VB) and conduction band (CB) of inorganic materials were by the following equation (6) (7) (8) as follows:^{3,4}

$$CB = VB + E_g \quad (6)$$

$$VB = -(4.8 \text{ eV} - E_{ref}^{Fc} + E_{ox}) \quad (7)$$

$$E_g = 1240 / \lambda_{onset} \quad (8)$$

Where E_g is optical bandgap of materials. λ_{onset} is edge wavelength of the

ultraviolet absorption peak of materials. E_{ox} is the oxidation initiation potential of inorganic materials.

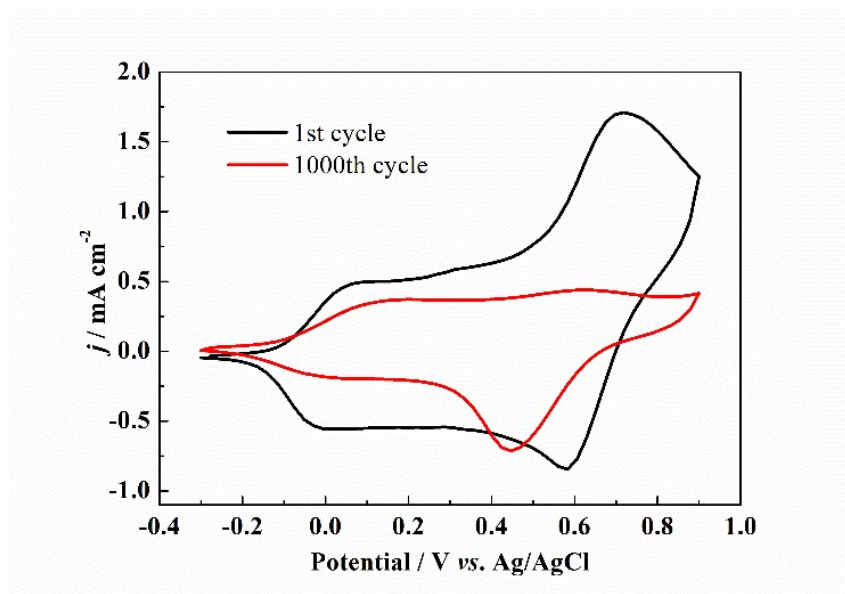


Fig. S1 CV stability of P6ICA film in 1 M H₂SO₄ with 100 mV s⁻¹

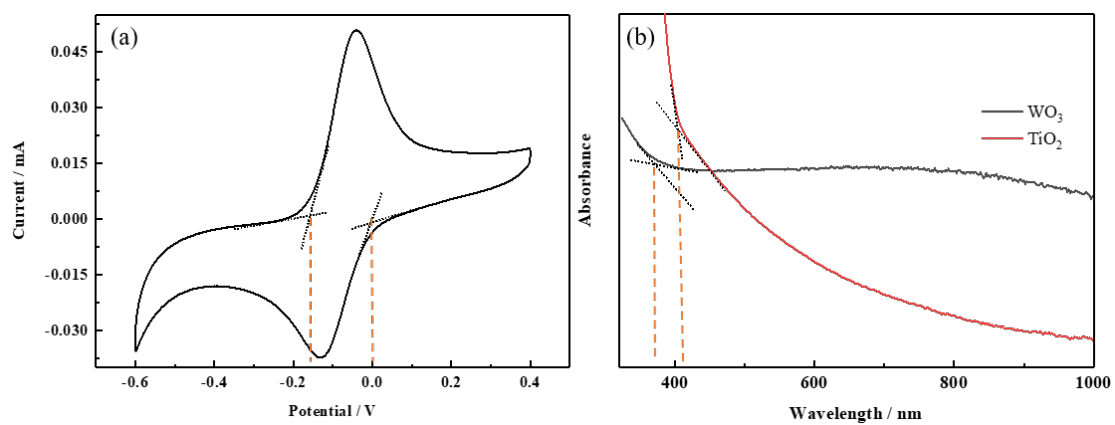


Fig. S2 (a) CV curves of Fc. (b) UV-vis absorption spectra of WO₃ and TiO₂

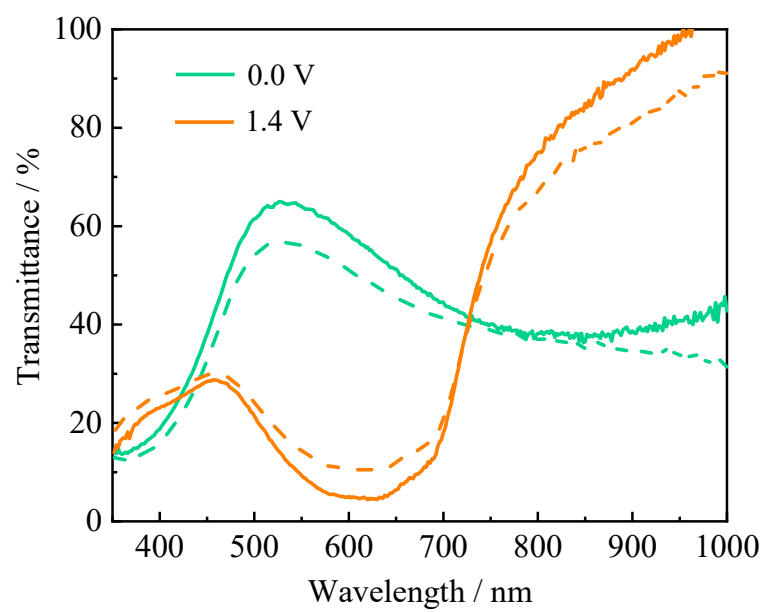


Fig. S3 Spectroelectrochemistry curves of the device under 0.0 V and 1.4 V initially (solid line) and after 3000 cycles (dashed).

Table S1 Comparison of specific capacitance values of other reported composite materials

Sample	Specific Capacitance	Reference
P5ICA/WO ₃ electrode	30.20 mF cm ⁻²	1
P6ICA/TiO ₂ electrode	23.34 mF cm ⁻²	5
P6ICA electrode	16.20 mF cm ⁻²	6
e-WO ₃ /PPy hybrid electrodes	11.38 mF cm ⁻²	7
PANI	23.20 mF cm ⁻²	8
W ₁₈ O ₄₉ /PANI	10.00 mF cm ⁻²	9
(PEDOT:PSS)/PANI	17.00 mF cm ⁻²	10
P6ICA/WO ₃ nanocomposite	33.80 mF cm ⁻²	This work

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