Supporting Information

High Performance Multicolor Intelligent Supercapacitor and Its Quantitative Monitoring of Energy Storage Level by Electrochromic Parameters

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1. Experimental section

1.1 Materials and apparatus

Indole-5-carboxylic acid (5ICA, 98%), 3,4-ethylenedioxythiophene (EDOT, 98%), Tetrabutylammonium tetrafluoroborate (TBATFB, 98%) were bought from Aldrich. Sodium tungstate (98%) and polyvinyl alcohol (PVA, 98-99% hydrolyzed, medium molecular weight) were received from J&K chemical. Acetonitrile (ACN, AR) was purchased from Tianjin Guangcheng Chemical Reagent Co., Ltd. Hydrochloric acid (HCl, AR) and sulfuric acid (H_2SO_4, AR) were obtained from Yantai Sanhe Chemical Reagent Co., Ltd. Ethanol absolute (AR) was got from Tianjin Basifu Chemical Co., Ltd.

Electro-thermostatic blast oven (DHG-9623A Shanghai Jinghong) was used to control the preparation temperature of WO_3. CHI 660E electrochemical workstation (Shanghai Chenhua Ins., China) was used to carry out the cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and galvanostatic charge and discharge measurements of the P5ICA/WO_3 nanocomposites. Model 263 electrochemical workstation (EG&G Princeton Applied Research, USA) and Cary 500 UV-Vis-NIR spectrophotometer (Varian, USA) were used to study the spectroelectrochemical properties of the composites under computer control. The scanning electron microscope (SEM) measurement was performed using JEOL JSM-6700F scanning electron microscope (JEOL Ltd., Japan). Transmission electron microscope (TEM) measurements were taken by using JEM-2100 electron microscope (JEOL Ltd., Japan). Infrared spectra were recorded using Nicolet 510P

FTIR spectrometer (Nicolet Ltd., USA) with KBr pellets. X-ray diffraction (XRD) patterns were obtained by an XRD-6000 X-ray Diffractometer (Shimadzu, Japan). X-ray photoelectron spectroscopy (XPS) was recorded using an Omicron ESCA spectrometer (Omicron Ltd., Germany) using Al Kα irradiation as the excitation source. XPSPEAK41 software was used to analyze the XPS peaks. After analyzed by XPSPEAK41 software,

1.2 Preparation of P5ICA/WO_3 nanocomposites

WO_3 were grown on FTO substrate by a previously reported hydrothermal technique. Sodium tungstate was dissolved in deionized water and stirred for 30 min, then 1 M hydrochloric acid was added to the solution to adjust PH to 1.0. After that the precursor solution was obtained. The FTO substrate was placed in the Teflon-lined stainless steel autoclave. Then the prepared precursor solution was added to the autoclave. After the autoclave was sealed, it was kept at 200 ^oC for 45 min. After that, the prepared WO_3 were rinsed several times by deionized water and then annealed at 470 ^oC.

P5ICA was deposited directly on WO_3 surface by electrochemical polymerization in a one-compartment cell. The working electrode was FTO covered with WO_3 and counter electrode was stainless steel electrode. Ag/AgCl electrode was used as the reference electrode. The P5ICA layer was prepared in ACN solution containing 0.05 M 5ICA by potentiostatic method and 0.1 M TBATFB was added to the solution as supporting electrolyte. All the experimental steps were carried out in a dry argon flow, which was kept under a slight overpressure during the experiment.

The constant potential of 1.5 V was carried out in the polymerization process. After that, the working electrode was taken out from the electrolyte solution, subsequently washed by ultrapure water and ethanol, and finally dried under the air for further characterization.

In order to exert the synergistic effect of P5ICA and WO_3 to get the best performance of the composite material, the fabrication parameters of the P5ICA/WO_3 nanocomposites were optimized through the EIS. As can be seen from Fig. S5, the pure WO_3 showed the largest charge-transfer transfer resistance (R_{ct}) and the equivalent series resistance (R_s). As the polymerization charge of P5ICA gradually increased, the values of R_s and R_{ct} of the composite material gradually decreased. This may be attributed to the synergistic effect of P5ICA and WO_3. When the polymerization charge of P5ICA was 300 mC, the P5ICA/WO_3 nanocomposites showed the smallest R_s (8 Ω) and R_{ct} (6 Ω). At this state, the P5ICA/WO_3 nanocomposites also showed the best electrochemical properties. However, when the polymerization charge was higher than 300 mC, excessively thick P5ICA was covered on the surface of WO_3, which hindered the electron transfer between P5ICA and WO_3 and leaded to the increased resistance of the composite material. Hence, in the P5ICA/WO_3 nanocomposites, P5ICA with 300 mC polymerization charge was used in this study.

1.3 Preparation of H_2SO_4-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 H_2SO_4 was added to the PVA solution. The weight ratio between H_2SO_4 and PVA was about 1:1. After 5 minutes of continue heating, the H_2SO_4-PVA gel electrolyte was successfully prepared.

1.4 The construction of asymmetric solid-state ESD

The asymmetric solid-state ESD had a sandwich structure. P5ICA/WO_3 nanocomposites and PEDOT were coated separately on FTO electrodes. PEDOT had also gained special attention because it can be easily prepared with well defined polymer backbone structure and high electrochemical stability. In addition, it was found to be almost transparent or light blue in its oxidized (p-doped) state or dark blue in its dedoped state.[1] Thus, PEDOT was intensively used in the construction of electrochromic device. Furthermore, two different p-doped conducting polymers used as the positive and negative material respectively, 75% of the doping capacity of the polymer can be utilized to enhance the charge storage capacity of supercapacitor.[2] Hence, in this study, PEDOT was used as negative electrode material to construct the asymmetric solid-state ESD. The PEDOT was prepared in ACN containing 0.1 M TBATFB at a constant applied potential of 1.1 V *vs*. Ag/AgCl. In order to maintain the injected/ejected charge balance, the two electrodes need the same amount of electric quantity during the redox process. And the P5ICA/WO_3 electrode was in neutral state, while the PEDOT electrode was in oxidation state before the device was assembled. These two electrodes were separated by H_2SO_4-PVA gel electrolyte.

1.5 Capacitance and coloration efficiency calculation

The areal specific capacitance can be calculated by means of equation (1) when

used the charge-discharge method:

$$C=It/VS \qquad (1)$$

Where C stands for areal capacitance (F cm^{-2}), V is the potential window (V), I stands for discharge current (mA), t is the discharge time (s), and S represents the surface area of the active materials (cm^2).

Coloration efficiency (CE) can be calculated according to the following equation:

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

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

where Q_d refers to the injected/ejected charge during the redox process; T_b and T_c refer to the transmittances of the material in its bleached and colored states, respectively.

1.6 The detailed derivation of the linear relationship between ESL and electrochromic parameters of the device

According to the equation (2) and (3), the relationship between the optical density (ΔOD) and the charge consumed during the electrochromic process (Q_d) can be expressed as:

$$\log (T_b / T_c) = CE \times Q_d \qquad (4)$$

Since the electrochromic process also means the charging process for the electrochromic supercapacitors, we can regard T_b as the transmission at 0% ELS (T_0), and T_c as the transmission at different ELSs (T_{ELS}).

Moreover, Q_d can be expressed as:

$$Q_d = ELS \times Q_t \qquad (5)$$

where Q_t, is the total charge that can be stored in the electrochromic supercapacitors in a certain situation. Therefore, the color change at different ELSs can be quantifiably expressed using the equation:

$$log(T_0/T_{ESL}) = CE \times ESL \times Q_t \qquad (6)$$

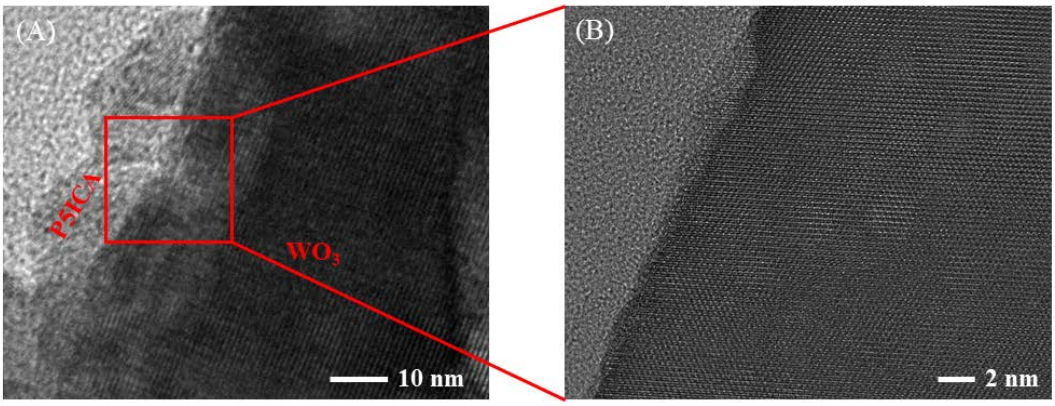

Fig. S1 HRTEM images of P5ICA/WO_3 nanocomposites.

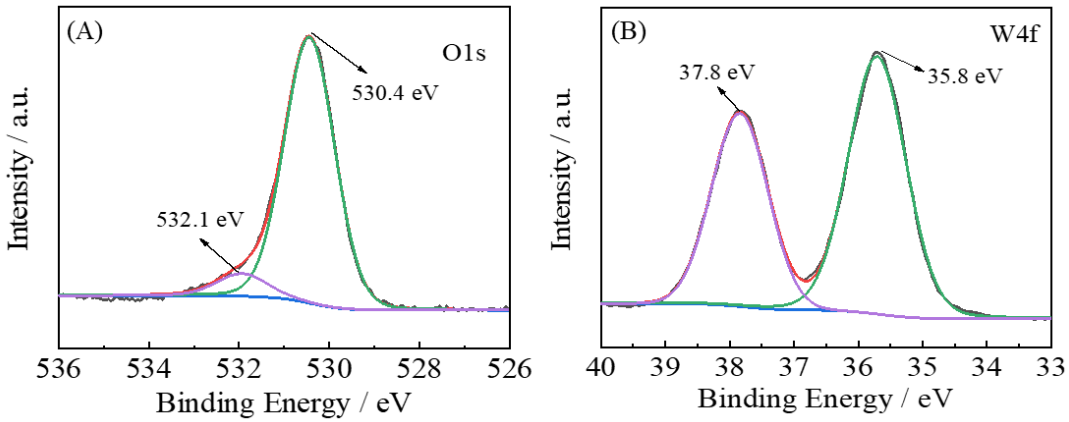

Fig. S2 High-resolution XPS spectra for (A) O1s and (B) W 4f of the WO_3.

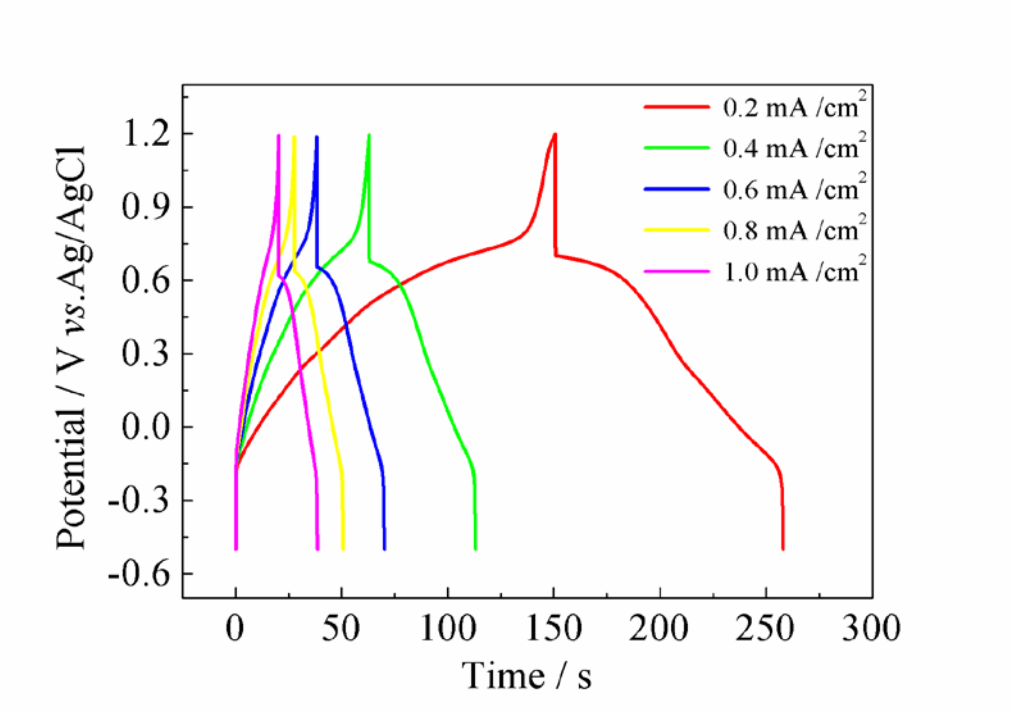

Fig. S3 The galvanostatic charge-discharge curves of the P5ICA under different current density.

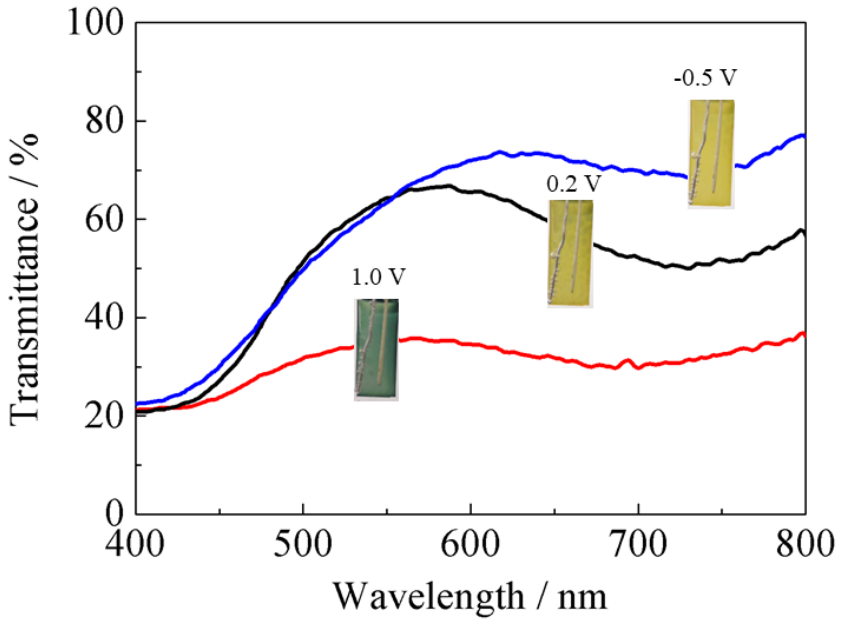

Fig. S4 Spectroelectrochemistry of the P5ICA under different voltages (inset: the photos of P5ICA under different voltage).

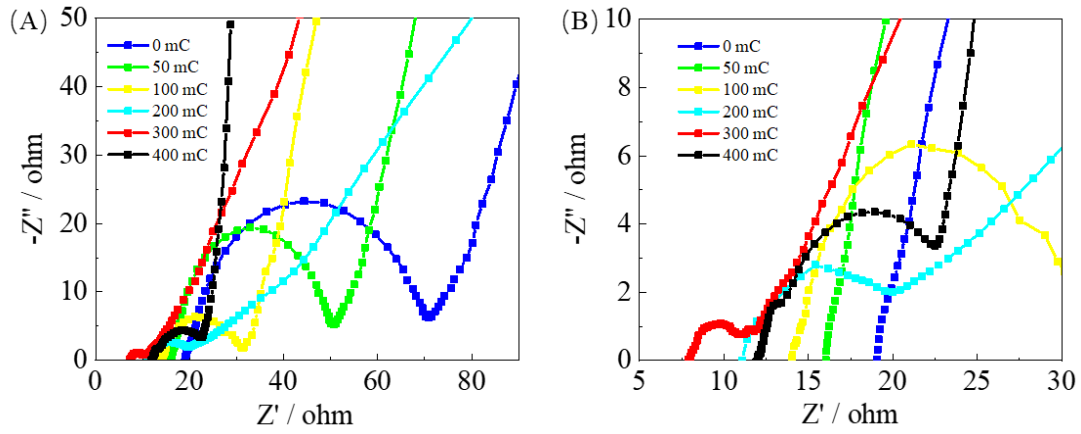

Fig. S5 EIS spectra (A) and its local magnification spectra (B) of P5ICA/WO_3 nanocomposites with different polymerization charge of P5ICA.

References

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(2) Guo Y. T.; Li W. S.; Yu H. T.; Perepichka D. F.; Meng H. Flexible Asymmetric Supercapacitors via Spray Coating of A New Electrochromic Donor-Acceptor Polymer. *Adv. Energy Mater.* **2016**, *7*, 1601623.