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In situ XRD and operando spectra-electrochemical investigation of tetragonal WO_{3-x} nanowire networks for electrochromic supercapacitors

Shen Wang¹, Hongbo Xu¹, Tingting Hao¹, Peiyuan Wang², Xiang Zhang³, Hongming Zhang¹, Junying Xue¹, Jiupeng Zhao¹ and Yao Li³

Abstract

Electrochromic supercapacitors (ESCs) are appealing for smart electronic device applications due to their advantages of dual-function integration. Unfortunately, the synchronous dual-function evaluation and the essential reaction mechanism are ambiguous. Herein, we constructed a 3D WO_{3-x} nanowire networks/fluorine-doped tin oxide (WO_{3-x} NWNs/FTO) bifunctional electrode for ESCs by a solvothermal self-crystal seeding method. The synchronous correspondence relationship between the optical and electrochemical performances of the WO_{3-x} NWNs/FTO electrode was explored using an operando spectra-electrochemical characterization method. It reveals an excellent areal capacity of 57.57 mF cm^{-2} with a high corresponding optical modulation (ΔT) of 85.05% and high optical-electrochemical cycling stability. Furthermore, the synergistic reaction mechanism between the Al^{3+} ion intercalation behavior and the surface pseudocapacitance reaction during electrochemical cycling is revealed utilizing in situ X-ray diffraction. Based on these results, an ESC device was constructed by pairing WO_{3-x} /FTO as the cathode with V_2O_5 nanoflowers/FTO (V_2O_5 NFs/FTO) as the anode, which simultaneously deliver high capacity and large optical modulation. Moreover, the energy storage level of the ESC device could be visually monitored by rapid and reversible color transitions in real time. This work provides a promising pathway to developing multi-functional integrated smart supercapacitors.

Introduction

As smart power systems, electrochromic supercapacitor (ESC) devices have attracted increasing attention. This is because they have the capability to monitor the energy storage level of the device in real time through color change, which makes the energy storage devices more advanced¹.

Much effort has been devoted to promoting the wide application of ESC devices. In general, the energy storage

and electrochromic performance of ESC devices are mainly influenced by the performance of bifunctional electrodes. Hence, high-performance bifunctional electrodes need to be constructed^{2–6}. For example, Kim et al.² presented WO_3 -embedded Au nanofilament array bifunctional electrodes, which exhibited a specific capacity of 202 F g^{-1} at 5 mV s^{-1} (-0.9 to 0.45 V vs. $\text{Hg}/\text{Hg}_2\text{Cl}_2$) and a high ΔT of 67.49% by applying potential steps of $\pm 0.75 \text{ V}$ (vs. $\text{Hg}/\text{Hg}_2\text{Cl}_2$). Shen et al.⁴ prepared tungsten oxide/titanium dioxide nanorod arrays on an FTO substrate, which showed a ΔT of 78% at pulse-type voltage ($\pm 3 \text{ V}$ vs. Ag/AgCl) and specific capacitance of 426.8 F g^{-1} at a current density of 1 A g^{-1} with a voltage window of -1.2 to 0 V (vs. Ag/AgCl). In addition, all ESC devices have also been developed^{3,4,7–12}. For instance, Yun et al. fabricated an ESC device using an indium tin oxide

Correspondence: Jiupeng Zhao (jzhaohit@hit.edu.cn) or Yao Li (yaoli@hit.edu.cn)

¹School of Chemistry and Chemical Engineering, Harbin Institute of Technology, 150001 Harbin, PR China

²Henan Provincial Key Laboratory of Surface and Interface Science, Department of Materials and Chemical Engineering, Zhengzhou University of Light Industry, 450002 Zhengzhou, PR China

Full list of author information is available at the end of the article

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(ITO) glass electrode and WO_3/ITO glass electrode, which exhibited a large ΔT ($\sim 91\%$) with a pulse-type voltage (between -1.5 and 0 V) and high areal capacitance ($\sim 13.6 \text{ mF cm}^{-2}$) at 0.4 mA cm^{-2} within a potential range of -1.5 to 0 V¹³. Subsequently, Guo et al.⁹ constructed a solid-state ESC device with poly(5-formylindole)/ WO_3/ITO and poly(3,4-ethylenedioxythiophene)/ITO. The device showed a ΔT of 55% under square-wave potentials from 0 V to $+1.0$ V with step times of 5 s and an areal specific capacitance of 10.38 mF cm^{-2} at a current density of 0.025 mA cm^{-2} under a voltage range of 0.0 – 1.0 V.

Despite the above achievements, to the best of our knowledge, the capacitance and optical modulation of the bifunctional electrodes or ESC devices reported in many papers have not been measured synchronously. In other words, the electrochromic performances were normally tested by stepping between a positive and negative voltage, while the energy storage performances were carried out under continuous voltage or current conditions. Thus, it is difficult to accurately determine the correspondence between the energy storage capacity and optical modulation due to their separated measurements^{7,8}. Moreover, the crystal evolution and ion storage mechanism of the dual-functional electrode is ambiguous. This is because the structural evolution of the bifunctional electrode is not continuously monitored in the optical-electrochemical change process; thus, it is impossible to determine how ions embed or adsorb on the lattice or surface of the electrode material. However, the well-defined reaction mechanism is helpful for selecting the best counter electrode and electrolyte when constructing high-performance ESC devices and optimizing or designing electrode materials of this crystal type. To address these challenges, in situ/operando characterization techniques, including in situ X-ray diffraction and operando spectra-electrochemical characterizations, need to be introduced. These tools can provide valuable information on bifunctional electrodes in charge/discharge processes, such as the evolution of the crystalline structure and the relationship between energy storage capability and optical modulation.

Herein, 3D WO_{3-x} nanowire networks self-assembled on FTO by a solvothermal reaction and annealing treatment. This self-seeded growth strategy can significantly accelerate the charge transfer between the WO_{3-x} layer and FTO layer. To determine the corresponding relationship between the optical and electrochemical performances of the electrode, we employ operando spectra-electrochemical characterization techniques, which exhibit high areal capacities (57.57 mF cm^{-2}) with a corresponding ΔT of 85.05% due to the material's unique 3D crosslinked nanowire network and hierarchical pore structure. In addition, to probe the opto-electrochemical mechanism of the aluminum ions embedded into the

tetragonal WO_{3-x} electrode, in situ X-ray diffraction characterization techniques were employed, which revealed that the synergistic mechanism between the Al^{3+} ion intercalation behavior and the surface pseudocapacitance reaction occurred during the electrochemical process. As a proof of concept, a superior ESC device, which comprises a 3D WO_{3-x} NWNs/FTO cathode and V_2O_5 NFs/FTO anode, has been achieved. The V_2O_5 NF/FTO electrode not only has a high transmittance but also matches well with the WO_{3-x} NWN electrode in terms of the capacity, reaction mechanism and voltage window. The device is equipped with a high capacity and homologous optical modulation. Specifically, the visualization of the energy storage level for the ESC is achieved by reversible color changes from dark blue to transparent during the electrochemical cycle process. Our work paves the way for the development of an intelligent transparent capacitor.

Results and discussion

As shown in Scheme 1, the 3D WO_{3-x} NWN/FTO dual-functional electrode was prepared by combining a solvothermal method and subsequent thermal treatment. At the beginning of the solvothermal reaction, glucose acted as a bridge to link the tungsten trioxide crystal nucleus with FTO. Under the influence of hydrogen bonding forces and other physical adsorption, the tungsten trioxide crystal seed layer spontaneously formed on the FTO. In the subsequent solvothermal process, WO_{3-x} precursor nanowires grew along the $[110]$ direction of the seed layer of the FTO. Additionally, a crosslinking nanowire network of the WO_{3-x} precursor self-assembly progressively occurred on FTO to reduce the surface energy¹⁴. Then, the prepared WO_{3-x} /FTO was heat-treated at 400°C for 2 h, and thermal gravimetric analysis (TGA) was performed on the WO_{3-x} precursor in an air atmosphere

Fig. 1 Characterization of 3D WO_{3-x} NWNs/FTO. **a** SEM image, Insets: cross-sectional SEM image of 3D WO_{3-x} NWNs/FTO, **b** TEM image, **c** XRD patterns, **d** Raman spectra, **e** Nitrogen adsorption/desorption isotherms, and **f** Aperture distribution curve of 3D WO_{3-x} NWNs.

(Supplementary Fig. S1) to remove the excess carbon and impurities, eliminating the color effect of carbon and forming crystalline WO_{3-x} . As shown in a typical field emission scanning electron microscope (FESEM) image of the 3D WO_{3-x} NWNs/FTO (Fig. 1a), the interconnected WO_{3-x} nanowires are uniformly anchored on the FTO substrate, forming 3D disordered crosslinking networks with randomly distributed pores. This unique structure can provide numerous active sites and shorten the diffusion path of the ions and electrons. Additionally, it can alleviate the mechanical stress of ion insertion/extraction in the charging/discharging process. From the cross-sectional SEM image in the inset of Fig. 1a, the cross-linking WO_{3-x} nanowire networks with a thickness of 730 ± 20 nm self-assembled on FTO.

Microcosmic information about the WO_{3-x} NWNs/FTO was obtained from transmission electron microscopy (TEM) and high-resolution TEM (HRTEM). Figure 1b and Supplementary Fig. S2 also confirm that the WO_{3-x} NWNs show a crosslinked nanowire network structure, and a single WO_{3-x} nanowire is $\sim 4\text{--}10$ nm in diameter and $\sim 1\text{--}2$ μm in length. In addition, the HRTEM image shows the high crystallinity of the single nanowire, and the 0.36 nm lattice spacing corresponds to the (110) crystal plane of tetragonal WO_{3-x} (Supplementary Fig. S3).

The crystal structure of the prepared samples was investigated by XRD analysis, and the results are shown in Fig. 1c. For the WO_{3-x} powders, all the peaks in the XRD pattern are well matched with the tetragonal structure

(P4/nmm) phase of nonstoichiometric WO_3 (with lattice constants of $a = b = 5.31 \text{ \AA}$, $c = 3.93 \text{ \AA}$, JCPDS card no. 89-8052), which confirms the successful preparation of WO_{3-x} . The obvious diffraction peaks at $\sim 23.7^\circ$, 27.8° , 35.3° , 48.1° , and 55.7° correspond well to the (110), (101), (200), (220), and (310) crystal planes of WO_{3-x} , respectively, and no impurity peaks can be observed. Moreover, the peak intensity of the (110) crystal plane is significantly stronger, which indicates that WO_{3-x} nanowires are preferentially grown along the [110] crystal plane orientation¹⁵. This observation is in accordance with the results of HRTEM. The diffraction peaks of WO_{3-x} NWNs/FTO glass are consistent with those of the WO_{3-x} powders when several FTO diffraction peaks are deducted (JCPDS card no. 46-1088). To further evaluate the structure of the prepared samples, Raman spectroscopy was applied to reveal the various variations in crystalline symmetry and microstructure (Fig. 1d). In the Raman spectrum of WO_3 NWN powders, two peaks at 696.56 and 801.63 cm^{-1} represent the stretching modes of $\text{O}-\text{W}^{6+}-\text{O}$. The peak at 258.12 cm^{-1} is attributed to the bending vibration mode of the bridging oxygen, while the peak at 59.31 cm^{-1} arises due to the vibration of the lattice^{16,17}. A broadened Raman peak at $\sim 989.11 \text{ cm}^{-1}$ belonging to the terminal $\text{W}=\text{O}$ bond on the surface is observed. The integrated intensity ratio of $\text{W}=\text{O}/\text{O}-\text{W}^{6+}-\text{O}$ for WO_{3-x} NWNs is 0.53, indicating its high crystallinity¹⁸. Moreover, two absorption bands at 1374.64 and 1596.88 cm^{-1} belong to the D and G bands of carbon, respectively, where the carbon is derived primarily from the carbonation of glucose. The presence of a small amount of carbon is expected to increase the conductivity of WO_{3-x} without affecting the transparency of the electrode. In addition, a weak Raman peak at 327.75 cm^{-1} belongs to the bending mode $\text{O}-\text{W}^{5+}-\text{O}$ ^{16,17}. In the spectrum of the WO_{3-x} NWNs/FTO, similar Raman vibrations could be observed at 65.36 , 262.22 , 705.93 , and 814.81 cm^{-1} , along with two additional features at 1386.73 and 1614.43 cm^{-1} that were due to the remaining carbon. The estimated intensity ratio of $\text{W}=\text{O}/\text{O}-\text{W}^{6+}-\text{O}$ for 3D WO_{3-x} NWNs/FTO is 0.68, also revealing the high crystallinity of WO_{3-x} nanowires. Moreover, a weak Raman peak at 326.92 cm^{-1} is attributed to the bending mode $\text{O}-\text{W}^{5+}-\text{O}$, affirming the presence of a small amount of W^{5+} in WO_{3-x} NWNs/FTO. These results strongly suggest the successful preparation of tetragonal WO_{3-x} NWNs on FTO glass.

To evaluate the constitutive properties of the WO_{3-x} NWNs in depth, Brunauer-Emmett-Teller (BET) measurements were carried out. As seen from Fig. 1(e and f), the isotherm of WO_{3-x} NWNs reveals a distinct hysteresis loop in the relative pressure (P/P_0) range of 0.4–0.85, which is attributed to a typical Langmuir type IV adsorption isotherm. This isotherm clearly illustrates that the WO_{3-x} NWNs possess a mesoporous structure. The

pore size distribution of the WO_{3-x} NWNs according to the Barrett-Joyner-Halenda (BJH) analysis is within a very narrow range of 3–5 nm, which is derived from the nanowire network structure of tungsten trioxide. Nano-hierarchical porous frameworks are formed through integration with the macroporous structure that is shaped by the crosslinking nanowire networks. These networks are propitious to the diffusion of ions, improving the dynamic behaviors of the electrode, achieving rapid redox energy storage and color transformation, and easing volume expansion. According to the multipoint BET formula, the specific surface area of WO_{3-x} NWNs is $109.8 \text{ m}^2\text{-g}^{-1}$, which is superior to that of many other WO_3 -based materials^{19–22}. The higher specific surface area of the 3D WO_{3-x} NWNs/FTO electrode allows for enough electroactive sites for the electrochemical reaction to occur, improving the energy storage and the corresponding optical performance.

X-ray photoelectron spectroscopy (XPS) was used to analyze the elemental composition and valence state of WO_{3-x} NWNs/FTO. The offset of the binding energy of the spectrum was calibrated with the C 1s peak (284.8 eV) as a reference. The full survey spectrum (Supplementary Fig. S4a) indicates the coexistence of W, O, C, F, and Sn, among which Sn and F originate from the FTO substrate²³. In the W 4f spectrum (Supplementary Fig. S4b), the binding energy peaks at 35.88 and 38.08 eV are indexed to W^{6+} , and those at 34.78 and 36.88 eV originate from W^{5+} ^{16,17}. The relative percentages of W^{6+} and W^{5+} in the WO_{3-x} NWNs on FTO are calculated to be $\sim 92.07\%$ and 7.93% , respectively. Hence, the O/W atomic ratio is ~ 2.92 , indicating that the WO_{3-x} NWNs are multivalent and nonstoichiometric; this result is aligned with the XRD results. In addition, the binding energy peak at 41.61 eV belongs to the W $5p_{3/2}$ level, which confirms the growth of WO_{3-x} NWNs. As shown in Supplementary Fig. S4c, the O 1s binding energy peak can be resolved into three components at ~ 530.7 , 531.3 , and 532.8 eV , belonging to W–O bonds derived from WO_{3-x} , W–O–C bonds, and –OH and/or C–O–C bonds stemming from the doped carbon and absorbed H_2O , respectively²⁴. Therefore, the W–O–C bond reveals that the covalent bond between the WO_3 nanowires and glucose is built, which can increase the conductivity of WO_3 , resulting in rapid electron transport and an excellent rate performance. The XPS results further confirm that WO_3 NWNs grow directly on the FTO substrate.

To monitor the charge storage state of the WO_{3-x} NWNs/FTO electrode by color, we employed the operando spectra-electrochemical characterization method. The synchronous operando test could show the correlation between the quantity of stored charge and the optical property of the charging/discharging process. Hence, cyclic voltammetry (CV) curves and optical profiles of the

Fig. 2 CV and corresponding electrochromic performance of the WO_{3-x} NWNs/FTO electrode. **a** CV curves of the WO_{3-x} NWNs/FTO electrode at different scan rates from 5 to 100 mV s^{-1} (inset: digital photographs of the electrode during the charge/discharge process), **b** The full transmittance spectra of the WO_{3-x} NWNs/FTO electrode during the positive scan of 5 mV s^{-1} , **c** In situ transmittance at 750 nm of the WO_{3-x} NWNs/FTO electrode at a scan rate of 5 mV s^{-1} , **d** The areal specific capacitance and corresponding optical modulation at different scan rates and at 750 nm, **e** The black closed CV curve (total charge capacity) with a red shadowed area corresponding to the surface capacitive section at a scan rate of 100 mV s^{-1} , **f** Separations of ion diffusion-controlled processes and surface capacitance-controlled Al^{3+} storage at different scan rates.

WO_{3-x} NWNs/FTO electrode are obtained synchronously at different scan rates, and the results are shown in Fig. 2(a, b, and c), Supplementary Fig. S5 and Fig. S6. All CV curves (Fig. 2a) show the nonrectangular form, which indicates the typical pseudocapacitive behavior of the reversible redox reaction. With increasing scan rate, the shape of the curves is almost unchanged compared with those at low scan rates, indicating good dynamic reversibility of the WO_{3-x} NWNs/FTO electrode. In Fig. 2b, each point along

the CV curve has a corresponding full transmittance curve, which shows that the electrode simultaneously exhibits the phenomena of energy storage and discoloration on the macro level during the microscopic electrochemical reaction. It is further confirmed that the energy storage and discoloration are synchronous; that is, the energy storage state can be monitored by color visualization. In Fig. 2c and Fig. S5a, the ΔT of the WO_{3-x} NWNs/FTO electrode is $\sim 85.05\%$ at 750 nm and $\sim 70.68\%$ at 550 nm at a voltage

of 0.8 V, respectively, and the electrode becomes colorless and transparent due to double extraction of aluminum ions and electrons. During the negative scan, the transmittance of the electrode gradually decreases, and the color of the electrode gradually turns dark blue. In addition, this result also confirms that the transmittance of the electrode is different and can be controlled by voltage in the visible or near infrared ranges of light. As seen in Supplementary Figs. S5, S6, and S7 and Table S1, under the same scanning speed, the ΔT of the electrode is different at different wavelengths, but the change trend is consistent. At different scanning speeds, the time required to reach the same ΔT at the same wavelength is different. This observation is consistent with the change in the CV curve under different scanning speeds, further proving that it is feasible to monitor the energy storage level by color. Additionally, it can be found that the modulation ability of the electrode in the visible light region is better than that in the near infrared light region at high scanning speed. The areal capacitance and corresponding optical modulation of the WO_{3-x} NWNs/FTO electrode based on the discharging processes of different scan rates were calculated according to Supplementary Equation 1, and the results are shown in Fig. 2d. The WO_{3-x} NWNs/FTO electrode shows a specific capacitance of 57.57 mF cm^{-2} and a corresponding ΔT of 85.05% at 750 nm at a scan rate of 5 mV s^{-1} . Even when the sweep speed increases to 100 mV s^{-1} , the electrodes can still display a specific capacitance of 20.53 mF cm^{-2} and a corresponding ΔT of 62.34% at 750 nm. These results indicate that the WO_{3-x} NWNs/FTO electrode can maintain a high optical-electrochemical performance throughout the electrochemical process due to the crosslinked nanowire network structure of WO_{3-x} , ensuring the fast and effective delivery of Al^{3+} ions.

Moreover, CV curves also offer wider insight into the difference in charge storage kinetics. The capacitive effect and the diffusion-controlled process can be characterized by CV data analysis according to $i = a\nu^b$ ²⁵. In the formula, I and ν represent the current and scan rate, respectively, and a and b are adjustable parameters. When the b value approaches 0.5, the charge storage process is controlled by diffusion, and when the b value equals 1.0, a surface capacitive electrochemical reaction occurs. To calculate the b value of the WO_{3-x} NWNs/FTO electrode, the linear correlation between $\log(i)$ and $\log(\nu)$ at different potentials was fitted in Supplementary Fig. S8. The b -values for the WO_{3-x} NWNs/FTO electrode at different potentials are shown in Supplementary Fig. S9 and are 0.46, 0.68, 0.98, and 0.9. The synergistic reactions controlled by diffusion and surface redox are involved with the Al^{3+} ion storage behavior; these reactions affect the capacitance and optical modulation of the electrodes. Furthermore, the ratio of the surface capacity ($k_1\nu$) to diffusion-

controlled intercalation ($k_2\nu^{0.5}$) in the total capacity can be calculated based on the following equation: $i = k_1\nu + k_2\nu^{0.5}$ ²⁶. Fig. 2e displays a high capacitance contribution of 89.98% at a scan rate of 100 mV s^{-1} . Generally, the surface process capacity can be divided into electrical-double-layer capacitance and surface redox capacitance, in which the electrical-double-layer type needs an ultrahigh specific surface area (such as carbon material of over $2000 \text{ m}^2 \text{ g}^{-1}$) because its specific capacitance is mainly affected by the specific surface area²⁷. Since the specific surface area of the WO_{3-x} NWNs/FTO electrode is $109.8 \text{ m}^2 \text{ g}^{-1}$, the surface capacitance of the electrode is mainly attributed to the pseudocapacitive reaction. Moreover, the capacitance contributions for the total Al^{3+} storage capacity at different scan rates could be calculated, and the results are presented in Fig. 2f. It is obvious that with increasing scan rate, the contribution from diffusion-controlled capacitance gradually decreases; this trend indicates that a long relaxation time impedes Al^{3+} intercalation at higher scan rates. The surface reaction contribution capacitance remains stable owing to the good conductivity, high specific area, and crosslinking porous structure of the electrode. The 3D nanowire structure can supply abundant electrochemical active sites on the surface of WO_{3-x} to promote the adsorption of Al^{3+} , accelerate the surface redox reactions, and reinforce the energy collection efficiency²⁸. Hence, we can affirm that the synergistic effects between the surface pseudocapacitance reaction and Al^{3+} intercalation reaction play a crucial role in the energy storage and electrochromic behaviors of the WO_{3-x} NWNs/FTO electrode.

To further probe the reaction mechanism of energy storage and the corresponding optical behaviors of the WO_{3-x} NWN/FTO electrode caused by Al^{3+} ions, we studied the crystal structure evolution of the WO_{3-x} NWN/FTO electrode during the actual electrochemical process using in situ XRD measurements. A schematic diagram of the in situ XRD measurement using a three-electrode polytetrafluoroethylene (PTFE) electrochemical cell is shown in Fig. 3a. The CV experiment and the corresponding structural evolution of the electrode were monitored synchronously at a scan rate of 0.5 mV s^{-1} , and the results are shown in Fig. 3b–d and Supplementary Fig. S10. In the full-scale in situ XRD patterns of the WO_{3-x} NWNs/FTO electrode, no other peaks are observed, except for the FTO and (110) of WO_{3-x} NWN peaks, revealing that no other phases are formed during the electrochemical cycling process. In stage I (0.8–0.0 V), the WO_{3-x} NWNs/FTO electrode starts to discharge, and the transmittance of the electrode decreases gradually. From the in situ XRD patterns, the 2θ degree and the peak intensity of the (110) crystal plane of WO_{3-x} NWNs remain unchanged, which indicates that the charge storage and optical modulation of the electrode are mainly

Fig. 3 In-situ XRD patterns for WO_{3-x} NWNs/FTO. **a** Schematic diagram of the in situ XRD under a three-electrode mode, **b** Typical CV curve of the WO_{3-x} NWNs/FTO electrode at a scan rate of 0.5 mV s⁻¹, **c** In situ XRD results based on the cycling process in Fig. 3b, **d** Enlarged in situ XRD patterns of the WO_{3-x} NWNs/FTO electrode at 2θ from 15° to 30°, **e** Interlayer distance of the WO_{3-x} NWNs calculated from the XRD patterns during the CV processes.

ascribed to the pseudocapacitive reaction due to the large surface area and nanohierarchical pore structure of WO_{3-x} NWNs^{29,30}. In stage II (0.0 to -0.6 V), the color of the WO_{3-x} NWNs/FTO electrode transforms to dark blue with increasing electrode discharge depth. In terms of the microstructure, the (110) peak gradually shifts toward the lower 2θ degree (23.61°), which indicates that the lattice expands along the [110] direction, suggesting the insertion of Al³⁺ ions^{31,32}. The increased interlayer distance can be attributed to the incremental interlayer electrostatic repulsion caused by the intercalation of aluminum ions. Moreover, the intensity of the peak decreases, revealing the conversion of WO_{3-x} NWNs into an amorphous phase during the discharge process. In the stage III (-0.6 to 0.15 V), the transmittance of the WO_{3-x} NWNs/FTO electrode gradually increases as electrode charging proceeds. Additionally, we found that the (110) peak located

at 23.61° gradually shifts toward 23.77° and that the interlayer space gradually decreases, demonstrating the extraction of the Al³⁺ ions. When the voltage is fully recharged back to 0.8 V (in stage IV), the tungsten trioxide electrode becomes transparent. From the in situ XRD pattern, the 2θ and intensity of the (110) peak of WO_{3-x} NWNs are restored to the original state. The interlayer distance (*d*₁₁₀) values at the charging/discharging process were calculated and are shown in Fig. 3(e), which shows that the interlayered lattice variation of *d*₁₁₀ is highly reversible. The largest expansion of *d*₁₁₀ is ~0.02 Å, indicating that the lattice change of the WO_{3-x} NWNs can be considered negligible during the Al³⁺ ion insertion/extraction process, implying high cycling durability. Based on the electrochemical testing results, in situ XRD analysis and Supplementary Fig. S11, the mechanism of the charge storage and electrochromic behavior of the

Fig. 4 Electrochemical and corresponding electrochromic performance of the WO_{3-x} NWNs/FTO. **a** Chronopotentiometry curves of the WO_{3-x} NWNs/FTO electrode at current densities from 2 to 6 mA cm^{-2} , **b** The relationship between transmittance change profile at 750 nm and charge/discharge curve at 2 mA cm^{-2} (inset: digital photographs of the electrode during charge/discharge process), **c** Influence of different current densities on the areal specific capacitance and the transmittance change of the WO_{3-x} NWNs/FTO electrode, **d** Cycle performance of the WO_{3-x} NWNs/FTO electrode.

WO_{3-x} NWNs/FTO electrode can be attributed to the combined effect of the surface pseudocapacitive reaction and insertion/extraction process, which may be described as follows:

Al^{3+} adsorption : surface pseudo capacitance (1)

Al^{3+} intercalation : $\text{WO}_{3-x} + y\text{Al}^{3+} + 3ye^- \rightarrow \text{Al}_y\text{WO}_{3-x}$ (2)

Al^{3+} extraction : $\text{Al}_y\text{WO}_{3-x} \rightarrow \text{WO}_{3-x} + y\text{Al}^{3+} + 3ye^-$ (3)

Al^{3+} desorption : surface pseudo capacitance (4)

Benefitting from the surface pseudocapacitive and insertion/extraction behaviors, the WO_{3-x} NWNs/FTO electrode can display excellent charge storage and electrochromic performances. To further verify this result, chronopotentiometry (CP) and in situ spectroscopy measurements were conducted at different current densities. Furthermore, the feasibility of monitoring the charge storage level of the WO_{3-x} NWNs/FTO electrode

by visual contrast was verified. All the CP curves (Fig. 4a) exhibit deformed triangular shapes, revealing the occurrence of a Faradaic reaction between the WO_{3-x} NWNs and the Al^{3+} ions. The corresponding optical performance of the electrode at different current densities was recorded, and the results are shown in Supplementary Fig. S12. It is obvious that the time for the charge/discharge process and the response time for bleaching/coloring process of the electrode are reduced synchronously with the increase of the current density, which is because Al^{3+} ions cannot participate completely in the redox reaction of WO_{3-x} NWNs at high current density. In Fig. 4b, the color of the WO_{3-x} NWNs/FTO electrode gradually turns dark blue when it is discharged to -0.6 V. While in the reverse charging process, the electrode returns to transparent, and the charge storage state can be effectively revealed by a broad range of optical modulations. In other words, the energy storage level of the electrode can be visually monitored by its color. At a current density of 2 mA cm^{-2} , the areal specific capacitance of the WO_{3-x} NWNs obtained from the CP performance is calculated to be 60.02 mF cm^{-2} , and the corresponding ΔT reaches ~64.98% (Supplementary Fig. S12). A diagram (Fig. 4c) of

the areal specific capacitance of the WO_{3-x} NWNs/FTO electrode determined from the CP curves and the corresponding transmittance change as a function of the current density were drawn according to Supplementary Equation 2 and the results of Supplementary Fig. S12. With increasing current density, the areal specific capacitance and ΔT of the WO_{3-x} NWNs/FTO electrode gradually decrease and finally reach relatively stable values of $\sim 15.78 \text{ mF cm}^{-2}$ and 38.48%, respectively.

To evaluate the stability of the WO_{3-x} NWNs/FTO electrode, cycling tests were examined. As shown in Fig. 4d, the electrode retains 87.53% of its initial specific capacitance and 75.42% of its initial optical modulation (Supplementary Fig. S13a-c) after 10,000 consecutive CV cycles, indicating excellent electrochemical and optical stability. The excellent optical-electrochemical stability of the WO_{3-x} NWNs/FTO electrode can lay a foundation for real-world application as an electrode for an ESC device. Electrochemical impedance spectroscopy (EIS) was used to further reveal the cycle performance of the WO_{3-x} NWNs/FTO electrode at the open circuit potential. The resultant EIS spectra of the electrode after 1 cycle and after 10,000 cycles are shown in Supplementary Fig. S13d. The values of $R1$ and $R2$ after 10,000 cycles increase slightly compared with those after the 1st cycle. This result is in accordance with Fig. 4d, indicating the excellent cycling stability of the WO_{3-x} NWNs/FTO electrode. In addition, the increased slope after 10,000 cycles at low frequency shows a low Warburg resistance, indicating high Al^{3+} ion diffusion in the structure of the WO_{3-x} NWNs/FTO electrode.

Based on the above results, an ESC device was constructed using WO_{3-x} NWNs/FTO and V_2O_5 nanoflowers/FTO (V_2O_5 NFs/FTO) as the cathode and anode, respectively, and $1 \text{ mol L}^{-1} \text{ AlCl}_3$ as the electrolyte. A schematic illustration of the device is shown in Fig. 5a. Information on the physicochemical and electrochemical properties of V_2O_5 NFs/FTO is presented in Supplementary Fig. S14. The relevant evaluation of ESC device construction is also shown in Supplementary Fig. S15. Figure 5b shows the CV curves of the ESC device at different scan rates of $5\text{--}100 \text{ mV s}^{-1}$. The CV curves have a nonrectangular shape with broad redox peaks, which indicates a faradaic redox process. Furthermore, in Fig. 5c, the CP curves of the device at various current densities show asymmetrical triangular shapes, which are in accordance with the results of the CV measurement. According to the discharge curves of the ESC device, the calculated specific areal capacitances range from 18.46 to 5.44 mF cm^{-2} as the current density increases from 1 to 4 mA cm^{-2} based on the total area of the device (Fig. 5d). To evaluate the charge storage characteristics of the ESC device, the energy density (E) and corresponding power density (P) were computed from Supplementary Equations 4 and 5, and the results are shown in Fig. 5e. The device delivers a high energy density

of $39.34 \text{ mWh cm}^{-3}$ at a power density of 4.26 W cm^{-3} , and can still maintain $11.61 \text{ mWh cm}^{-3}$ at a power density of 17.05 W cm^{-3} , which is comparable to or higher than those of previously reported thin film-based asymmetric supercapacitors (ASCs), including $\text{WO}_3/\text{V}_2\text{O}_5$ hybrid thin film devices ($19 \text{ mWh cm}^{-3}/1.42 \text{ W cm}^{-3}$)³³, $\text{WO}_3/\text{WO}_3/\text{MnO}_2$ ASCs ($1.2 \text{ mWh cm}^{-3}/0.411 \text{ W cm}^{-3}$)³⁴, PANI// $\text{WO}_{3-x}/\text{MoO}_{3-x}$ ASCs ($1.1 \text{ mWh cm}^{-3}/0.73 \text{ W cm}^{-3}$)³⁵, and SCNT/PANI//SCNT/ $\text{W}_{18}\text{O}_{49}$ ASCs ($19 \text{ mWh cm}^{-3}/295 \text{ mW cm}^{-3}$)³⁶.

To verify the ability of in situ visual monitoring of the charge storage state of the transparent capacitors, the energy storage state and the corresponding optical state of the device are studied synchronously. Figure 5f shows that the color of the ESC device gradually turns dark blue, and the transmittance decreases during the charging process, while the color of the device reversibly fades during the discharging process. The ESC device delivers an areal specific capacitance of 12.40 mF cm^{-2} with a corresponding ΔT (at 750 nm) of 26.85% at 1 mA cm^{-2} . In addition, the specific capacity and color of the device in the discharge process are also studied in detail in Supplementary Fig. S16. It is found that each energy status of the device is monitored by the corresponding visual color. In the charging process, Al^{3+} ions are released from the V_2O_5 NFs/FTO electrode and then embedded in the WO_{3-x} NWNs/FTO electrode, accompanied by the device color turning dark blue. When the devices are completely discharged, the color of the ESC device changes from dark blue to transparent. The above results evidently prove the possibility of quantitatively monitoring the energy storage level by the optical performance, which is a convenient and effective indicator for the energy level of an energy storage device³⁷.

The superior dual-function integrated performance of the ESC might be attributed to the following reasons: (1) The crosslinked nanowire networks of the 3D WO_{3-x} NWN/FTO electrode with a hierarchical pore structure can provide a large number of active sites, shorten the ion diffusion paths, enhance redox reactions and alleviate the expansion of WO_{3-x} NWNs caused by the Al^{3+} ion reaction, resulting in high capacitance and a large corresponding ΔT . (2) The direct growth of WO_{3-x} NWNs on FTO glass can increase the adhesion force and reduce the extra contact impedance, benefitting the rapid transfer of electrons. (3) The synergistic electrochemical reactions between the Al^{3+} ion intercalation behavior and the surface pseudocapacitance reaction contribute to the electrochemical and optical properties of the electrode. (4) The V_2O_5 NF/FTO electrode, which matches well with the 3D WO_{3-x} NWN/FTO electrode, provides high optical transmittance and good electrochemical performance, beneficial to achieving ESC devices with high optical-electrochemical performance.

Fig. 5 Electrochromic energy storage performance of the ESC device. **a** Schematic illustration of the assembly of an ESC device, **b** CV curves of the device at different scan rates; **c** Chronopotentiometry curves of the device at current densities from 1 to 4 mA cm^{-2} , **d** The areal capacitance of the ESC at different current densities, **e** Ragone plots of the ESC device, **f** Chronopotentiometry curves and the corresponding optical transmittance (at 750 nm) tested at 1 mA cm^{-2} (inset: digital photographs of the device during charge/discharge process).

Conclusions

In this work, we successfully prepared a 3D WO_{3-x} NWNs/FTO electrode through a solvothermal method combined with a calcination process. Based on the results of an operando spectra-electrochemical synchronous test, the WO_{3-x} NWNs/FTO cathode exhibits a high areal specific capacitance (57.57 mF cm^{-2}) with a corresponding large ΔT (85.05%) and excellent cycling stability (specific capacitance retention of 87.53% and homologous optical modulation range retention of 75.42% after 10,000 cycles) owing to the 3D crosslinked nanowire network structure, hierarchical porous channel, large specific area and strong adhesion with the FTO substrate. In addition, the reaction mechanism was further revealed and verified by in situ XRD, which demonstrated the behavior of surface pseudocapacitance and the inserted reaction that occurred at

different voltage intervals. Furthermore, an ESC device based on the WO_{3-x} NWNs/FTO cathode and V_2O_5 NFs/FTO anode shows high capacity and large optical modulation. Remarkably, the charge storage state of the ESC can be intelligently quantified by the corresponding color of the device during the charging/discharging process, thus realizing the color-to-energy monitoring of the ESC. This study offers new insights for developing integrated intelligent supercapacitors.

Experimental section

Information regarding the raw materials and solvents used in this experiment, the construction of 3D WO_{3-x} NWNs/FTO, V_2O_5 NFs/FTO, and asymmetric ESC devices, in situ XRD methods, area capacitance, energy density and power density calculations are all offered in the Supporting Information.

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Author details

¹School of Chemistry and Chemical Engineering, Harbin Institute of Technology, 150001 Harbin, PR China. ²Henan Provincial Key Laboratory of Surface and Interface Science, Department of Materials and Chemical Engineering, Zhengzhou University of Light Industry, 450002 Zhengzhou, PR China. ³Center for Composite Materials and Structure, Harbin Institute of Technology, 150001 Harbin, PR China

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