Triggering Superior Sodium Ion Adsorption on (200) Facet of Mesoporous WO₃ Nanosheet Arrays for Enhanced Supercapacitance

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Abstract

Tungsten trioxide (WO_3) is believed to be a promising electrode candidate for supercapacitors, due to its reversible surface redox reaction resulted from the almost same W-O bond lengths with different oxidation states. However, the specific capacitance of WO_3 electrode is very low ($< 250 \text{ mF cm}^{-2}$) because of its low conductivity and slow surface redox reaction kinetics. Herein, to address these issues, mesoporous WO_3 nanosheets with exposed (200) facets were anchored on activated carbon cloth (ACC) *via* a simple two-step process including heat treatment and alcohol-thermal process. The ACC was coated on WO_3 seeds and proceed a heat treatment at 500°C and the time of alcohol-thermal process were 7 h, 8 h, and 9 h labeled as $\text{WO}_3@\text{ACC}-n$ ($n = 7, 8, 9$). SEM and TEM images confirmed the WO_3 nanosheets were successful anchored on the ACC. The $\text{WO}_3@\text{ACC}-8$ electrode showed the best specific areal capacitance which could reach as high as 659 mF cm^{-2} at a current density of 5 mA cm^{-2} and superior stability with almost no decrease in 10,000 cycles in the presence of Na_2SO_4 as the neutral electrolyte. The capacitance is encouragingly much higher than the previously reported values in a three-electrode system in the neutral aqueous condition. DFT calculations reveal that, in comparison to the (002) and (020) facets, the exposed (200) facets of the mesoporous WO_3 nanosheets triggers the superior Na^+ adsorption, which accelerates the Na^+ -involved surface redox reaction for the boosted supercapacitor performance. A flexible asymmetric supercapacitor (FASC) was fabricated from the $\text{WO}_3@\text{ACC}$ electrode, which exhibits high energy density (0.5 mWh cm^{-3}) and power density (62 mW cm^{-3}) without any attenuation during $\pm 180^\circ$ wide-angle bending.

Keywords: sodium ion adsorption, mesoporous WO₃ nanosheets, exposed facet, flexible asymmetric supercapacitor

1. Introduction

Supercapacitors (SCs), regarding as the most prospective energy storage devices, can provide high power density with great charge/discharge rates, electrochemical reversibility and long cycle life [1-4]. Nanostructured materials have attracted much attention due to the large surface area which can provide plenty of atoms to involve in the reactions. Therefore, the characterization and synthesis of nanostructured semiconductor have been extensively investigated [5,6]. Tungsten oxide (WO₃), owing to its inherent characteristics such as high theoretical specific capacitance, reversible electrochemical redox reaction, low cost, and environmental friendliness, is considered to be a promising candidate for SC materials [7,8]. WO₃ always generates higher pseudocapacitance than common double-layer capacitors by transferring electrons through the electrode/electrolyte interface *via* redox reactions [9]. Given the shortened ion diffusion length and increased specific surface area in nanostructured electrodes, various WO₃ nanostructures such as quantum dots [10], nanoribbons [11,12], and nanorods [13,14], *etc.*, have been developed for fast charge/discharge rates and thus much improved capacitances [15]. For example, Cong et al. reported that WO₃ quantum dots (QDs) with high volume-to-surface ratio, synthesized *via* a colloid process, could facilitate the intimate contact between electrolyte and electrode materials, and thus provide fast charge-transport kinetics for the improved pseudocapacitance [10]. However, the pseudocapacitances of these WO₃ nanostructures were still lower than 100 mF cm⁻², which is too far from practical application. Such low capacity of WO₃ has been generally ascribed to two reasons: (i) the poor electrical conductivity inhibiting the

ion transport in WO_3 ; (ii) the hardly formed porous structures of WO_3 electrodes due to the condensation and hydrolysis of the tungsten alkoxides [16], resulting in the poor surface redox reaction kinetics. To enhance electrical conductivity, carbon nanotubes [17] and carbon cloth [18] have been coupled with WO_3 nanostructures, giving rise to enhanced specific capacitance reaching as high as 250 mF cm^{-2} at a current density of 0.67 mA cm^{-2} in the 3 M NaOH electrolyte. It has been also evidenced that the mesoporous structures introduced into WO_3 electrodes could increase the electroactive sites thus facilitate the Faradaic redox reactions [19]. For example, an ordered mesoporous WO_{3-x} /carbon electrode demonstrated a 60% improvement in pseudocapacitance as compared to the WO_3 electrode without mesoporous structure [20]. However, the capacitance of these hybrid WO_3 electrodes are still lower than 250 mF cm^{-2} . Thus, some unraveled underlying processes or properties could also contribute to or even determine the specific capacitance of WO_3 electrodes.

It is well recognized that in a neutral aqueous solution of Na_2SO_4 electrolyte, WO_3 conducts the redox reactions with Na^+ intercalation/deintercalation and the Faradic redox reactions at the surface of WO_3 electrodes exhibits the high reversible kinetics which could enhance the specific capacitance. Therefore, the sufficient Na^+ adsorption on the surface of the WO_3 electrode is crucial to accelerate the redox reaction kinetics and then to improve the specific capacitance. This thus inspires us to investigate the Na^+ adsorption properties of WO_3 electrodes and their contribution to the supercapacitor performance. Actually, it has been demonstrated that the BiOCl single-crystalline nanosheets with exposed $\{010\}$ facets exhibited higher activity for photocatalytic pollutant degradation, due to the stronger absorption capacity of organic molecules on the exposed $\{010\}$ facets, as compared to the counterpart with exposed $\{001\}$ facets

[21]. Similarly, Liu et al. reported that ZnO nanosheets with exposed {0001} facets could selectively adsorb cationic organic molecules rather than neutral and anionic organic molecules, giving rise to the selective photodegradation of contaminant with cationic organic molecules on the {0001} facets [22]. As motivated by these observation, it could be thus meaningful to trigger superior Na^+ adsorption on specific exposed facets of WO_3 to improve the redox kinetics for the unexpectedly high specific capacitances.

Herein, mesoporous WO_3 nanosheets with exposed (200) facets were successfully anchored on activated carbon cloth (ACC) *via* a simple alcohol-thermal method, for the superior Na^+ adsorption and then the excellent supercapacitance in the neutral Na_2SO_4 aqueous solution, as boosted by the accelerated redox reaction kinetics. These two-dimensional (2D) nanosheets ensure sufficient contact between the electrode and the electrolyte, and the well-developed mesoporous structure is able to accommodate a large amount of superficial electroactive sites for Faradaic redox reactions [23]. It was also revealed by density functional theory (DFT) calculations that the exposed (200) facets can ensure plentiful adsorption sites for Na^+ in electrolytes in comparison with (002) and (020) facets, benefiting more efficient Faradaic redox reactions on (200) facets for the remarkable enhancement in pseudocapacitance. Additionally, the flexible ACC substrate with excellent electrical conductivity for fast electron transport, can serve as an electron collector for the design of flexible energy-storage devices. The obtained $\text{WO}_3@\text{ACC}$ exhibits a high specific areal capacitance of 659 mF cm^{-2} at a current density of 5 mA cm^{-2} , which is the highest specific capacitance among all the previously reported values in neutral condition. In addition, an asymmetric supercapacitor, which was assembled by using $\text{WO}_3@\text{ACC}$ and activated carbon (AC)

coated ACC (AC@ACC) as the positive and negative electrodes, respectively, also exhibits encouraging energy density (0.5 mWh cm^{-3}) and power density (62 mW cm^{-3}) as well as good flexibility.

2. Experimental

2.1 Materials

Carbon cloth (WOS1002) was purchased from CeTech Co., Ltd (Taiwan, China). Ethanol, Polyvinyl Alcohol (CH_2CHOH)_n and hydrogen peroxide (H_2O_2) was purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Tungsten Chloride (WCl_6) and Tungstic acid (H_2WO_4) was purchased from Aladdin Chemistry Co., Ltd (Shanghai, China).

2.2 Preparation of WO_3 nanosheets as negative electrodes

Carbon cloth was soaked into 12 M HCl for 12 h to obtain activated carbon cloth (ACC). Mesoporous WO_3 nanosheets on ACC substrates were synthesized by a simple alcohol-thermal method. Typically, 6.25 g of tungstic acid (H_2WO_4) and 5 g of polyvinyl alcohol (CH_2CHOH)_n were dissolved in 100 mL of hydrogen peroxide (H_2O_2). After sonicated for 10 min and stirring for 3 h, the color of the solution turned to cream yellow, a piece of ACC was soaked into this cream yellow solution for 20 min and then dried at 60 °C for 2 h. The dried ACC was transferred to muffle furnace and heated at 500 °C for 2 h to obtain the WO_3 seeds. This WO_3 seeded ACC was immersed in 70 mL of ethanol solution with 0.6 g of tungsten chloride (WCl_6) and transferred into a Teflon vessel (100 cm^3) and maintained at 100 °C for 7 h, 8h and 9 h, respectively, with the obtained samples labeled as $\text{WO}_3\text{@ACC-}n$ ($n = 7, 8, 9$). Pure WO_3 was synthesized by the same alcohol-thermal method as $\text{WO}_3\text{@ACC-8}$ without carbon cloth. For

preparation of the mechanical mixture, 6 mg of WO_3 (*i.e.*, pure WO_3 nanosheets without mesoporous structure) was mixed with 1 mg poly vinylidene fluoride and 1 mg acetylene black in N-methyl-2-pyrrolidone (NMP) solvent to form slurry. Then, the mixture was coated onto a $1\text{ cm} \times 1\text{ cm}$ piece of ACC. The prepared electrode was dried in a vacuum oven at $100\text{ }^\circ\text{C}$ overnight to remove all the organic reagent.

2.3 Preparation of positive electrode

The AC@ACC positive electrode of activated carbon (AC) on ACC was fabricated by a simple mixture method. Typically, 32 mg activated carbon (AC) was mixed with 4 mg poly vinylidene fluoride and 4 mg acetylene black in N-methyl-2-pyrrolidone (NMP) solvent to form slurry. Then, the mixture was coated on a piece of ACC uniformly. The prepared electrode was dried in a vacuum oven at $100\text{ }^\circ\text{C}$ overnight [24-28].

2.4 Fabrication of flexible asymmetric supercapacitor (FASC) device

A piece of WO_3 @ACC negative electrode (8.25 cm^2) and a piece of AC@ACC positive electrode (3 cm^2) were separated with PVA/ H_2SO_4 solid electrolyte. Then, the FASC device packaged by thin PET (ethylene terephthalate) films.

2.5 Characterization

The structure of as-prepared samples were characterized by XRD (DX2700, China) at a scan rate (2θ) of 2° min^{-1} ranging from 5 to 90° , operating with Cu K α radiation ($\lambda = 1.5418\text{ \AA}$) with an accelerating voltage of 40 kV and an applied current of 30 mA. The morphology of the samples were investigated with SEM (Hitachi, S-4800), FESEM (JSM-7001F) with EDS, and TEM (HRTEM) using JEOL-2100F. The XPS (Thermo Scientific Corporation) was used to investigate the chemical compositions. The TGA

(HTG-1, Beijing HengjiuScientific Instruments) measurement was carried out for analyzing the weight of loaded sample, with samples heated to 900 °C in air.

2.6 Electrochemical measurements

The supercapacitor performances of as-prepared active materials including cyclic voltammetry (CV), galvanostatic charge/discharge (GCD), Electrochemical Impedance Spectroscopy (EIS) and rate capabilities were measured under ambient conditions in using the cell testing instrument (LANDCT2001A) and CHI 760E work station with three-electrode system using 0.5 M Na₂SO₄ as the neutral aqueous electrolyte. In this study, the Pt sheet served as counter electrodes while Ag/AgCl served as reference electrodes. The final electrodes were prepared by putting the active materials between two nickel foams (current collector), which were then pressed to 10 MPa. For quantitative considerations, the areal capacitance of the active electrode is given according to the equation as follows:

$$C = \frac{I\Delta t}{\Delta E} \quad (1)$$

$$C_a = \frac{C}{S} = \frac{I\Delta t}{S\Delta E} \quad (2)$$

Where C (mF) is the total capacitance, I (A) is the discharge current, Δt (s) is the discharge time, ΔE (V) is the potential window during the discharge process after IR drop (R is resistance), C_a (mF cm⁻²) is the areal capacitance, and S (cm²) is the working area of the electrodes. The energy density values (E) and the power density (P) were calculated based on the following equations:

$$E = \frac{1}{2} C_a \Delta V^2 \quad (3)$$

$$P = \frac{E}{\Delta t} \quad (4)$$

Where E (mWh cm⁻³) is the energy density, C_a (mF cm⁻²) is the areal capacitance of the WO₃@ACC-8 calculated, ΔV (V) is the potential window; Δt (s) is the discharge time and P (mW cm⁻³) is the power density.

2.7 Computation detail

All Density Functional Theory (DFT) computations were performed using the Vienna ab initio Simulation Package (VASP) [29-31]. The ion–electron interaction is described with the Projector Augmented Wave (PAW) method, and the exchange–correlation energy is described by the functional of the Perdew–Burke–Ernzerhof (PBE) form of the generalized gradient approximation (GGA) [32-34]. An energy cut-off of 450 eV is used for the plane-wave basis set. The geometry optimizations are performed using the conjugated gradient method, and the convergence threshold is set to be 10⁻⁵ eV in energy and 10⁻² eV Å⁻¹ in force. The Brillouin zone is sampled using a Monkhorst-Pack special k-point mesh of 2×2×1 for geometry optimizations. A 2×2×1 super-cell is used to investigate single Na adsorption on the (200), (020), and (002) surfaces. In order to improve the description of the electronic structure of WO₃ systems, we adopt a DFT+U method with U values of 4.5 eV for W atom. In addition, to obtain the work function of three surfaces respectively, the Fermi energies are aligned to the electron energies in vacuum by calculating the electrostatic potential. While calculating the electrostatic potentials of three surfaces, the c-axis is set to be 40 Å to get convergence vacuum level. The work function is evaluated by the energy differences between Fermi level and corresponding vacuum level.

2.8 Open circuit voltage calculation

Generally, the charging and discharging process would accompany the change of the open circuit voltage (OCV) which would determine the adsorption capability of Na⁺ in WO₃. So the capacities of Na⁺ and structural changes are investigated to systematically evaluate the performance of WO₃ surfaces as Na⁺-ion hybrid capacitor electrode materials. Generally, once the OCV goes to 0 V, the WO₃ surfaces could not accommodate more Na⁺. Typically, the charge/discharge process assumes the following half-cell reaction *vs.* Na/Na⁺ redox potential:

The OCV for an intercalation reaction involving xNa^+ could be computed from the energy difference if volume and entropy effects are neglected:

$$OCV \approx [E(\text{substrate}) + xE(Na)] - E(Na_x / \text{substrate}) / xe \quad (6)$$

Where $E(\text{substrate})$, $E(Na_x/\text{substrate})$, and $E(Na)$ are the total energies of substrates (that is (200), (020), and (002) of WO₃), Na_x/substrate, and metallic Na, respectively. To compute the OCVs, a 2×2×1 unit cell, which is essential to simulate the intercalation of Na-ions, is used. At each step, two Na-ions are added to the stoichiometric supercell of WO₃ to mimic the dynamic charging process where the Na-ions are randomly inserted into the host.

3. Results and discussion

A two-step process of seed treatment and alcohol-thermal growth was developed to anchor mesoporous WO₃ nanosheets on ACC substrate, as presented in **Scheme 1**. Typically, a piece of ACC was firstly soaked into a WO₃ seed solution for seed treatment. To fix the WO₃ seeds firmly onto the surface, the soaked ACC was subsequently annealed at 500 °C in air for 2 h, monoclinic WO₃ seeds were formed (**Fig. S1**) and uniformly distributed on the ACC fibers (**Fig. S2a and S2b**). Then, the WO₃

seeded ACC substrate was immersed into a WCl_6 /ethanol solution for the growth of WO_3 nanosheets *via* alcohol-thermal process at 100 °C for 7 h (WO_3 @ACC-7), 8 h (WO_3 @ACC-8), and 9 h (WO_3 @ACC-9), respectively. The weight ratios of WO_3 nanosheets in the obtained WO_3 @ACC- n ($n = 7, 8, 9$) samples were determined to be 29.6%, 31.8%, and 34.5%, respectively, for WO_3 @ACC-7, WO_3 @ACC-8, and WO_3 @ACC-9, by TGA technique (**Fig. S3**).

3.1 Morphology and Structural Characterization of WO_3 @ACC- n .

Fig. 1a presents the XRD patterns of WO_3 @ACC- n ($n = 7, 8, 9$). The diffraction peaks are located at 24.4° , 26.6° , 28.9° , 34.2° , 41.9° , 50.0° , and 55.9° , which correspond to the (200), (0-21), (1-12), (202), (-2-22), (-400), and (-420) planes of monoclinic WO_3 , respectively [35,36]. Obviously, the (200) peak is most intensive, indicating the predominant exposure of the (200) facets for the WO_3 nanosheets grown on ACC substrate. The successful growth of WO_3 on ACC could be also confirmed by XPS analysis (**Fig. S4, 1b and 1c**). The full scan spectrum of WO_3 @ACC-8 was provided in **Fig. S4**, in which WO_3 @ACC-8 contains all the C, O, and W elements. As shown in **Fig. 1b-d**, the full survey scan spectrum exhibits the existence of C, O, W elements in sample WO_3 @ACC-8. **Fig. 1b** presents the high-resolution spectrum of W 4f. All the peaks located at 41.8 eV (W $5p_{3/2}$), 38.0 eV (W $4f_{5/2}$) and 36.0 eV (W $4f_{7/2}$) arise from the W^{6+} state. The peak located at 34.6 eV corresponds to W^{5+} . Apparently, the intensity of W^{5+} is much weaker than that of W^{6+} , indicating that the nanosheets mostly consists of WO_3 [37-40]. O 1s signal can be deconvoluted into three oxygen contributions located at 532.8 eV, 531.6 eV, and 530.8 eV (**Fig. 1c**), which are assigned to the characteristic peaks of O-H, C=O and W-O bonds, respectively [40,41]. The C 1s XPS peaks are located at 288.4 eV, 284.6 eV, and 285.6 eV, attributed to sp^2 -hybridized

carbon, C=O and C-C (**Fig. 1d**), respectively [40,42,43], which stem from exposed carbon cloth.

As observed from SEM images (**Fig. 2a and 2b**), WO₃ nanosheets were perpendicularly and uniformly grown on the ACC substrate without visible aggregation. **Fig. S5** presents the morphology change of WO₃@ACC-*n* (*n* = 7, 8, 9) depending on the various alcohol-thermal times. With the alcohol-thermal times extended from 7 h to 9 h, these vertically grown WO₃ nanosheets show gradual increase in height and thickness, with 35 nm in thickness and 580 nm in height for WO₃@ACC-7, in comparison to 60 nm and 820 nm for WO₃@ACC-9, respectively. Additionally, homogeneously distributed C, O, and W elements are observed from a single carbon fiber according to the elemental mapping analysis (**Fig. 2c**). The nanosheet structure can be further confirmed by TEM image, with the width and length of ~500 nm for a single piece of nanosheet (**Fig. 2d**). From the high resolution TEM image (**Fig. 2e**), one set of lattice fringes with a spacing of 0.365 nm can be observed for the WO₃ nanosheet, which corresponds to the d-spacing value of the (200) plane of monoclinic WO₃, as further evidenced by the Fast Fourier Transform (FFT) image (inset of **Fig. 2e**). More interestingly, abundant mesopores with the diameter of ~5 nm are observed to be evenly distributed on the nanosheets (**Fig. 2f**), such mesoporous structure is believed to provide more electroactive sites to conduct the interfacial charge-transfer reaction. Moreover, The N₂ adsorption/desorption isotherms were measured to investigate the specific surface area of all the electrodes. As shown in **Fig. S6a-c**, all the samples displays hysteresis loop which indicates the existence of mesopores. From **Fig. S6**, WO₃@ACC-8 has the largest specific surface area (53.40 m² g⁻¹) compared to WO₃@ACC-7 (41.14 m² g⁻¹) and WO₃@ACC-9 (44.25 m² g⁻¹), which indicates the best specific capacitance

of all the electrodes.

3.2 The Three-Electrode System Performances of WO₃@ACC-*n*.

The electrochemical performances of the WO₃@ACC-*n* (*n* = 7, 8, 9) samples were investigated as the working electrodes immersed into 0.5 M Na₂SO₄, in a three-electrode system, with Ag/AgCl as the reference electrode and Pt counter electrode. Obviously, the WO₃@ACC-*n* samples, especially the WO₃@ACC-8, exhibit much higher specific areal capacitance (**Fig. 3a** and **Fig. S7**), in comparison to ACC, pure WO₃ nanosheets without mesoporous structure (**Fig. S8**) as well as the mechanical mixture of WO₃ and ACC. These results are explainable for the WO₃@ACC-*n* samples, as the 2D mesoporous structure and the excellent electrical conductivity of ACC could provide plentiful electroactive sites and facilitate electron transport. The CV curves were collected for WO₃@ACC-*n* at a scan rate of 5 mV s⁻¹ as shown in **Fig. 3a**. Similar redox peaks could be observed in the CV curves of all the WO₃@ACC-*n* samples, due to the reaction between Na⁺ and WO₃, *i.e.*, $\text{WO}_3 + x\text{Na}^+ + xe^- = \text{Na}_x\text{WO}_3$. Obviously, WO₃@ACC-8 has the largest area in the CV curve, indicating the best supercapacitor performance among the three samples. **Fig. S9** presents the galvanostatic charge/discharge (GCD) performances of the three samples at a current density of 5 mA cm⁻², and WO₃@ACC-8 shows the longest discharge time, corresponding to the highest supercapacitance as noted from CV curves. For all the three samples, a weak platform appeared at -0.83 V in the discharge curves, corresponding well with the cathode peaks at the CV curves (**Fig. 3a**), which means that these WO₃@ACC-*n* samples exhibit the typical pseudocapacitive performances [44-46]. In addition, the discharge curves are not straight and flat, demonstrating that the specific capacitance follows the Faradaic process [47]. **Fig. 3b** shows the electrochemical impedance spectroscopy of

WO₃@ACC-*n* (*n* = 7, 8, 9). At the low frequency, the line of WO₃@ACC-8 is more vertical compared with the other samples, indicating a more ideal capacitive behavior [48,49]. The smallest semicircle obtained at the middle-frequency (inset of **Fig. 3b**) for WO₃@ACC-8 suggests the lowest charge-transfer resistance between the electrode/electrolyte interface and the accelerated surface redox reaction kinetics, contributing to the improved specific capacitance [48-52]. Furthermore, WO₃@ACC-8 exhibits larger specific capacitances at the current densities of 5-10 mA cm⁻² and thus better rate performance, in comparison to WO₃@ACC-7 and WO₃@ACC-9 (**Fig. 3c**). Even at a high current density of 10 mA cm⁻², the specific areal capacitance of WO₃@ACC-8 can reach as high as 450 mF cm⁻².

To further determine the capacitive performance of WO₃@ACC-8, the CV, GCD and long-term stability were investigated in detail. **Fig. 3d** shows the CV curves at different scan rates. With the scan rate increasing, the corresponding current response expanded, implying the excellent rate properties [53]. At the scan rate of 5 mV s⁻¹, the anodic and cathodic peaks are located at -0.71 V and -0.83 V, which indicates that W⁵⁺ and W⁶⁺ are involved in the oxidation and reduction reactions, respectively. In addition, the small voltage difference of only ~120 mV between the anodic and cathodic peaks signifies the fast reversible redox reaction kinetics, contributing to the excellent specific capacitance of WO₃@ACC-8 [54]. **Fig. S10a** and **S10b** represent the CV curves of WO₃@ACC-7 and WO₃@ACC-9 at the scan rates of 5 - 50 mV s⁻¹, respectively. The redox peaks appear on all the CV curves indicating the pseudocapacitance of all the electrodes. The GCD curves at different current densities were collected in **Fig. 3e**. The WO₃@ACC-8 electrode exhibits a specific areal capacitance of 659 mF cm⁻² at a current density of 5 mA cm⁻², which is significantly higher than the previously reported values in neutral

aqueous condition (**Table S1**). Remarkably, the specific capacitance of WO₃@ACC-8 has almost no decrease after 10,000 continuous cycles at a current density of 5 mA cm⁻² (**Fig. 3f**), which indicates the outstanding stability of the as-prepared electrode as supercapacitor. The 3D-CV curves at a scan rate of 50 mV s⁻¹ and all the CV curves after 10000 cycles were presented in **Fig. S11**. It's found there is almost no change of all this CV curves which corresponds with the ones in **Fig. 3f**, indicating excellent stability of WO₃@ACC-8. [55,56].

3.3 Na⁺ Adsorption Mechanism on Different Facets.

As discussed above, the excellent specific capacitance should be attributed to the mesoporous 2D nanostructure of WO₃ nanosheets grown on ACC substrates, which provide enough electroactive sites and excellent electrical conductivity. Moreover, as evidenced by the excellent rate properties in **Fig. 3d**, it is believed that the exposed (200) faces of WO₃ nanosheets could contribute to the superior Na⁺ adsorption, which would enhance the redox reaction kinetics for the greatly boosted pseudocapacitance. From the viewpoint of the facets dependent ion adsorption and redox reaction kinetics, DFT calculations were conducted to disclose the adsorption property of Na⁺ on different exposed facets. **Fig. 4a** and **4b** represent the relaxed unit cell and the model of Na⁺ adsorption on the (200) facet, and **Fig. S12** presents the models of Na⁺ adsorption on (002), and (020) facets, respectively. Given the Na₂SO₄ aqueous solution as electrolyte, Na⁺ were used as adsorbate in the adsorption models. It is well accepted that the charging and discharging process would accompany the change in the open circuit voltage (OCV), which determines the capability of Na⁺ absorbed on the surface of WO₃ in the present study. Generally, once the OCV goes to 0 V, the WO₃ surfaces could not accommodate Na⁺ for further. Herein, three typical crystal facets of monoclinic WO₃,

i.e., (002), (020), and (200), were chosen to investigate their Na^+ adsorption properties by DFT calculation, with calculated OCVs shown in **Fig. 4c** (see OCV calculation details in Supporting Information). The x-axis of **Fig. 4c** can be defined as the Na^+ adsorption concentration, *i.e.*, the number of Na^+ adsorbed on the super-cell divided by the area of super-cell which is 4. It can be easily observed that at different Na^+ adsorbed concentrations varying from $x = 1 \sim 4$, the (200) facet shows much higher OCV than (020) and (002) facets, implying (200) facet possesses higher capacity of Na^+ accommodation. Remarkably, with the Na^+ adsorption concentration increasing up to $x = 4$, the OCV of the (200) facet maintains at 85%, whereas those of the (002) and (020) facets can only keep 16% and 26%, respectively. These calculation results indicate that the (200) facet is more energy favorable for the Na^+ adsorption and can adsorb more Na^+ than (002) and (020) facets. More efficient Na^+ adsorption leads to higher redox kinetics, giving rise to the facilitated transition between Na_xWO_3 and WO_3 and thus greatly enhanced pseudocapacitance.

The pseudocapacitive stability and capacitance of the (002), (020), and (200) facets in the aqueous electrolyte were further simulated and evaluated using DFT calculations, with the integral density of states (IDOS) and the partial density of states (PDOS) of the (002), (020), and (200) facets shown in **Fig. 4d-f**. The light blue regions stand for the aqueous electrolyte potential window which lies at 0 ~ 1.23 V *vs.* SHE (Standard Hydrogen Electrode). It is clearly schemed that the Fermi level of (002) and (020) facets are beyond the electrode potential window (**Fig. 4d and 4e**), while the Fermi level of (200) facet lies inside the electrolyte potential window (**Fig. 4f**), which indicates that (200) facet is more stable than (002) and (020) facets for Na^+ adsorption thermodynamics [57]. Moreover, in the electrolyte potential window, a peak at the

IDOS curve corresponding to the pseudocapacitive characteristics, appears at -4.2 eV with respect to the vacuum scale, which means that abundant charges would be stored on the (200) facets of WO_3 (**Fig. 4f**). In comparison, no peaks can be observed in the IDOS curves of (002) and (020) facets (**Fig. 4d and 4e**), indicating that the pseudocapacitive characteristics is not clear. These results are in good agreement with superior Na^+ adsorption on the (200) facet of WO_3 as evidenced by the OCV calculation in **Fig. 4c**, and as a result, the higher pseudocapacitive performance can be reasonably expected for the (200) facet as compared to the (002) and (020) facets.

3.4 The Electrochemical Performance of Flexible Asymmetric Supercapacitor.

It has been well recognized that flexibility is important for extensive application of the energy-storage devices. Given the good flexibility and conductivity of ACC as substrate, a flexible asymmetric supercapacitor (FASC) device was fabricated in the PVA/ H_2SO_4 gel electrolyte using WO_3 @ACC-8 and activated carbon (AC) coated ACC (AC@ACC) as the negative and positive electrodes, respectively, as schemed in **Fig. 5a**. In the obtained FASC device, the solid electrolyte can be directly used as separator without any other solid substitute (**Fig. 5b**). As shown in **Fig. S13**, the CV curves of AC@ACC exhibit rectangle shape and keep well in higher scan rates (**Fig. S13a**), indicating ideal electrochemical double-layer capacitance. From the GCD curves at different current densities shown in **Fig. S13b**, the specific capacitance of AC@ACC is determined to be 240 mF cm^{-2} at the current density of 5 mA cm^{-2} . Given the specific capacitances of WO_3 @ACC-8 (659 mF cm^{-2}) and AC@ACC (240 mF cm^{-2}), the area ratio of negative and positive electrodes was confirmed at 1:2.75, and meanwhile the amount of the AC coated on ACC was determined the same as that of the WO_3 nanosheets grown on ACC, to equilibrate the capacitance for the fabrication of FASC

device. Considering that the working voltage of WO₃@ACC-8 and AC@ACC is 0.72 V and 0.8 V, respectively (**Fig. 3a and S13a**), the theoretically maximum working voltage of the FASC device should reach as high as 1.5 V. As expected, CV curves of the FASC device at different scan rates confirm that the device can be operated with a working voltage of 1.5 V (**Fig. 5c**). In addition, obvious redox peaks appear in the CV curves and the shapes of redox peaks keep almost unchanged, which demonstrates the excellent capacitance triggered by the Faradic redox reaction. The non-triangle shape of GCD curves at different current densities as shown in **Fig. 5d** further confirms the redox process (*i.e.*, $\text{WO}_3 + x\text{Na}^+ + xe^- = \text{Na}_x\text{WO}_3$) is involved in the operation of the device, with the specific capacitance calculated to be as high as 96 mF cm⁻² at a current density of 5 mA cm⁻². Encouragingly, based on the Ragone plots shown in **Fig. 5e**, the FASC device exhibits a good power performance, with an excellent power density of 62 mW cm⁻³ and an energy density of 0.5 mWh cm⁻³ obtained at 5 mA cm⁻². Furthermore, two FASC devices were connected in series to light LEDs as shown in **Fig. 5f**, which indicates the great potential of practical application.

The flexibility of the FASC device was demonstrated by bending at different angles as shown in **Fig. 6**. Clearly, the FASC device presents fantastic structural flexibility with no break at bending angles of 180° and -180° during bending process (**Fig. 6a-c**). The area of the CV curves remain unchanged when the device was bent by ±180° as shown in **Fig. 6d**, indicating the outstanding stability of the device for flexible application.

4. Conclusions

In summary, the mesoporous WO₃ nanosheets exposed with (200) facets were deposited on ACCs *via* a simple alcohol-thermal process. The hybrid electrode showed excellent

supercapacitor performance in neutral aqueous condition, with specific areal capacitance reaching as high as 659 mF cm^{-2} at the current density of 5 mA cm^{-2} and almost no capacitance decrease after 10,000 cycles. The 2D mesoporous structure and the excellent electrical conductivity of ACC substrates can provide plentiful electroactive sites and facilitate the fast electron transport. More importantly, the exposed (200) facet of the WO_3 nanosheets is evidenced to trigger the superior Na^+ adsorption and then accelerate the surface redox reaction kinetics to facilitate the process of $\text{WO}_3 + x\text{Na}^+ + xe^- = \text{Na}_x\text{WO}_3$, which essentially boosts the supercapacitor performance of the hybrid WO_3/ACC electrodes. With the highest specific capacitance in neutral aqueous conditions achieved so far, this study demonstrates an alternative opportunity to improve the capacity and stability of the transition metal oxide electrodes for supercapacitors.

Acknowledgements

We are grateful for the financial support by the National Natural Science Foundation of China (Nos. 51473081, 51672143, 51672210 and 51323011), Outstanding Youth of Natural Science in Shandong Province (JQ201713), Taishan Scholars Program, and ARC Discovery Project (No. 170103317).

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Scheme and Figure captions

Scheme 1 Schematic illustration of the synthesis process of WO₃@ACCs.

Fig. 1 (a) XRD patterns of WO₃@ACC-*n* (*n* = 7, 8, 9) and pure activated carbon cloth. (b-d) XPS spectra of W 4f, O 1s, C 1s of WO₃@ACC-8, respectively.

Fig. 2 (a) SEM image of WO₃@ACC-8. The inset shows the low magnification picture. (b) High resolution SEM image of WO₃@ACC-8, (c) EDS elemental mapping images of WO₃@ACC-8. (d) TEM image of individual WO₃@ACC-8 nanosheets. (e) HRTEM and FFT (inset) images of WO₃@ACC-8 nanosheets. (f) High-magnification TEM image of WO₃@ACC-8 nanosheets.

Fig. 3 (a) CV curves of WO₃@ACC-*n* (*n* = 7, 8, 9) at the scan rate of 5 mV s⁻¹. (b) The Nyquist plots of WO₃@ACC-*n*. (c) Rate capabilities of WO₃@ACC-*n*. (d) CV curves of WO₃@ACC-8 at the scan rates of 5-50 mV s⁻¹. (e) Galvanostatic charge/discharge curves of WO₃@ACC-8 at the current densities of 5-30 mA cm⁻². (f) Cycling stability of WO₃@ACC-8.

Fig. 4 (a) The relaxed unit cell of WO₃. (b) The Na⁺ adsorption models of (200) facet. Red balls represent the O atoms; blue balls represent the W atoms; purple balls represent the Na atoms. (c) OCV as a function of Na concentration at different facets of WO₃. (d-f) PDOS (green region) and IDOS (yellow line) of (002), (020), and (200) crystal facets of WO₃. The dashed pink lines indicate the Fermi level positions of WO₃ crystal facets. The light blue regions indicate the electrolyte potential window.

Fig. 5 (a) Schematic diagram of the FASC device. (b) Photograph of the assembled FASC device. (c) CV curves of the FASC device at the scan rates of 5-50 mV s⁻¹. (d) Galvanostatic charge/discharge curves of the FASC device at the current

densities of 5-30 mA cm⁻². (e) Ragone plots obtained from galvanostatic charge/discharge curves of the FASC device. (f) Photograph of the FASC device lightening up a LED set.

Fig. 6 (a-c) Photograph of FASC in bending angles of 180°, -180°, and 0°, respectively.

(d) CV curves of the FASC device at different bending angles.

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(d) CV curves of the FASC device at different bending angles.

Highlights

- Mesoporous WO₃ nanosheets with exposed (200) facets were anchored on carbon cloth.
- The superior Na⁺ adsorption on (200) facet of WO₃ nanosheets was evidenced by DFT.
- The WO₃@ACC electrode exhibits a very high and stable specific areal capacitance.
- A flexible supercapacitor was fabricated with high energy and power density.

Graphical Abstract

Mesoporous WO_3 nanosheets with exposed (200) facets were anchored on activated carbon cloth ($\text{WO}_3@ \text{ACC}$) *via* a simple alcohol-thermal process. The exposed (200) facets triggered superior Na^+ adsorption and thus greatly improved pseudocapacitance was achieved over $\text{WO}_3@ \text{ACC}$ electrodes, which exceeded most of the previous values reported for WO_3 in the Na_2SO_4 neutral aqueous electrolyte.

Accepted Manuscript

Triggering Superior Sodium Ion Adsorption on (200) Facet of Mesoporous WO₃ Nanosheet Arrays for Enhanced Supercapacitance

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PII: S1385-8947(18)30456-X
DOI: <https://doi.org/10.1016/j.cej.2018.03.100>
Reference: CEJ 18707

To appear in: *Chemical Engineering Journal*

Received Date: 12 February 2018
Revised Date: 15 March 2018
Accepted Date: 19 March 2018

Please cite this article as: Z. Yin, Y. Bu, J. Ren, S. Chen, D. Zhao, Y. Zou, S. Shen, D. Yang, Triggering Superior Sodium Ion Adsorption on (200) Facet of Mesoporous WO₃ Nanosheet Arrays for Enhanced Supercapacitance, *Chemical Engineering Journal* (2018), doi: <https://doi.org/10.1016/j.cej.2018.03.100>

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